

# Authors' response to referee 1

We would like to thank the anonymous Referee #1 who gave his/her time to provide the comments. First of all, the manuscript is a “measurement report” which presents substantial new results on atmospheric VOCs observed in one of the most important industrial areas in China. It is not a “Research articles” type manuscript. Secondly, the objective of the study/manuscript was not to report the process-specific/industry-specific VOC emissions, the objective was to present the characteristics of VOCs in an industry affected area. There have been many process-specific/industry-specific VOC emissions studies already performed (e.g. Mo et al., 2015; Zhang et al., 2017; Yan et al., 2016; Shi et al., 2015).

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# Authors' response to referee 2

The authors are grateful to the anonymous referee #2 who gave his/her time to provide helpful comments and suggestions that improved our manuscript. Here, we present the answers for each of the comments. The manuscript and supplement with tracked changes can be found at the end of the document.

- 5       ▪ **The writing of the paper obscured the fact that the observations were not continuous. The dataset includes ~ 1 month in winter, spring, and summer and 3 months in autumn. Some of the differences in comparison to other studies may be due to the comparison of 1 month data to a season.**

Authors' response: The information about the investigation period is now clearly mentioned in the abstract, introduction, and methods sections. Besides, the time series plot (Figure 1) also shows the observation period clearly and it is mentioned in section 3.1. Comparison with other studies is now done carefully. The observation periods of the previous studies are also mentioned in the text. Most of the previous studies we presented in our comparison discussion did not present any time series plot for the whole observation period and also did not mention clearly that the measurement was continuously performed for a season or a year. So, it is not certain that we are comparing our 1-3 months data to a season.

- 15
- 20       ▪ **I do not suggest including halocarbons in TVOC comparison. Halocarbons are not reactive and do not contribute significantly to OH reactive or the productions of ozone and SOA. There are good reasons for not including halocarbons in TVOC data in previous studies. In the discussion of Line 250-260, it is unclear if and what halocarbons and OVOCs were included in TVOCs in previous studies. Not knowing that, the comparison results can be misleading.**

Authors' response: Many previous studies also included halocarbons in TVOC estimation and we already included those reported TVOC concentrations in our comparison discussion (e.g. Li et al., 2015; Zhang et al., 2018; Zeng et al., 2018; Sun et al., 2019). We still want to compare our observation with these studies. That is why we are now reporting TVOC concentration with halocarbons and without halocarbons. Now we have rewritten the TVOC comparison part. We checked carefully each previous study to find out what kind of VOCs they included in their TVOC estimation and the comparison with our observation is done accordingly. Moreover, OVOCs are also not included in TVOC estimation in several studies (e.g. Zhang et al., 2018; Jia

et al., 2016; Hui et al., 2018; Liu et al., 2016a; Mo et al., 2017; Song et al., 2018). That is why we also estimated TVOC without OVOCs and compare it with those studies.

- 35
- **The discussion of section 3.3.1 can be removed. T/B ratio is meaningful only if they are from a single source. The PMF results show that T and B are from multiple sources and T/B ratio is not meaning. The same argument applies to the ratios of alkanes or aromatics to acetylene.**

Authors' response: Section 3.3.1 is removed.

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- **The PMF results are confusing. In summer, for example, ethane is from vehicle, isopentane is from biogenic sources, ethane and propane are from vehicles, and propane is from solvent use. None of these make much sense. It's more or less the same for other seasons. In autumn, biomass burning has ethane but not acetylene. In winter, vehicle 1 and 2 are similar. Spring and autumn have gasoline**
- 45
- **evaporation, but summer and winter do not. Gasoline evaporation should be largest in summer. LPG/NP does not have ethylene in spring but has most of ethylene in winter.**

Authors' response: PMF model analysis is carried out again using typical tracers of various emission sources and the text has been modified accordingly.

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- **PSFC analysis is applicable only to VOCs that are short lived because the backtrajectories are only 24 hours.**

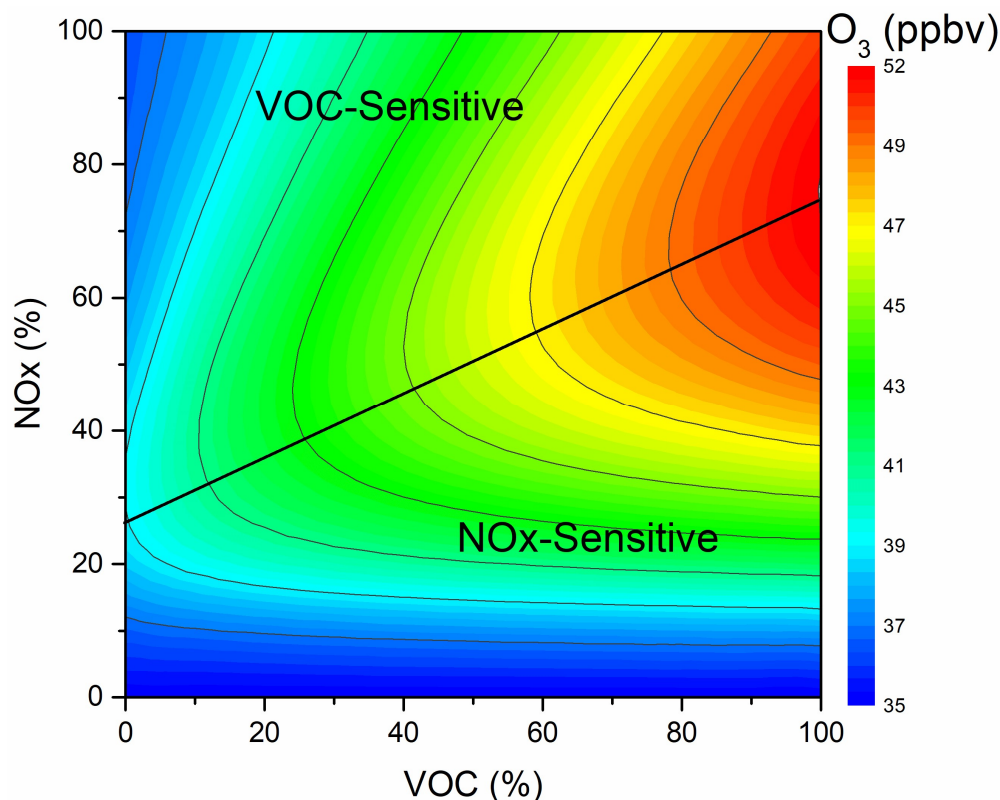
Authors' response: New PSCF analysis based on 72 hours backward air mass trajectories is now added. The text has been modified according to the new PSCF analysis.

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- **I do not feel OFP and SOAP analyses are useful (although they are often included in VOC papers). Figures 7 and 8 show that VOCs have much higher OFP and SOAP in winter than summer, which is technically true but we know the contributions of VOCs to ozone and SOA are much larger in summer than winter.**

60 Authors' response: The OFP and SOAP analyses are removed.

- 65 ▪ The EKMA diagrams of Figure 10 show ozone at ~50 ppbv for 100% NO<sub>x</sub> and VOCs in summer. Ozone here is daily 1 hour maximum, I think. 50 ppbv seems low for daily 1 hour maximum in summer. One possible reason is that the Thermo chemiluminescence instrument can severely overestimate NO<sub>2</sub> because of the conversion of NO<sub>y</sub> to NO<sub>x</sub>.

Response: Yes, the Thermo chemiluminescence instrument can overestimate NO<sub>2</sub> concentrations (Dunlea et al., 2007). However, there is also evidence that it does not significantly overestimate NO<sub>2</sub> concentrations (Chate et al., 2014). Anyway, following Dunlea et al. (2007), we ran the box model using NO<sub>2</sub> concentrations reduced by 22% and made the summertime EKMA diagram (Figure R1 below). However, the 1-hour maximum O<sub>3</sub> concentration for 100% NO<sub>x</sub> and VOCs did not increase.



75 Figure R1: O<sub>3</sub> isopleth diagram for summer based on percentage changes in VOCs and NO<sub>x</sub> concentrations in Nanjing and corresponding modelled O<sub>3</sub> production. In the model input, the NO<sub>2</sub> concentrations were reduced by 22%.

- **“Halocarbons” was mis-spelled in several places.**

Authors’ response: Amended. The term “halocarbon” is used everywhere instead of “halohydrocarbon”.

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## Measurement report: High Contributions of Halocarbon and Aromatic Compounds to Emissions and Chemistry of Atmospheric VOCs in Industrial Area

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**Abstract.** Volatile organic compounds (VOCs) are key components for tropospheric chemistry and air quality. We investigated ambient VOCs in an industrial area in Nanjing, China for about 1 month in winter, spring, and summer and 3 months in autumn from-between July 2018 ~~to and~~ May 2020. The total VOCs (TVOCs) concentration was  $59.8 \pm 28.6$  ppbv during the investigation period. About twice TVOCs concentrations were observed in autumn ( $83 \pm 20$  ppbv) and winter ( $77.5 \pm 16.8$  ppbv) seasons compared to those in spring ( $39.6 \pm 13.1$  ppbv) and summer ( $38.8 \pm 10.2$  ppbv). Unlike-In previous studies in Nanjing, oxygenated-VOCs (OVOCs) and halocarbons were not measured, the observed TVOCs was about 1.5 and 3 times higher than those previously reported in the same study area and a nonindustrial suburban area in Nanjing, respectively the current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2 folds higher than the one reported in the nonindustrial suburban area in Nanjing. Observed TVOCs concentrations ~~were was~~ similar to ~~those the one in the~~ metropolitan city Beijing, ~~and but,~~ 1.3 fold smaller than the one reported in Shanghai.; Observed TVOCs concentration was similar to those in Lanzhou, Chengdu, Tokyo, and Xi'an, however, it was about 1.5-~~3~~-1.7 folds higher than those in ~~Lanzhou,~~ Wuhan, Tianjin, ~~and~~ Ningbo, ~~Chengdu, London, Los Angeles, and Tokyo.~~ Due to the industrial influence,

165 halocarbons ( $14.3 \pm 7.3$  ppbv, 24%) VOC-group was the second largest contributor to the TVOCs  
after alkanes ( $21 \pm 7$  ppbv, 35%), which is in contrast with the previous studies in Nanjing and  
also in almost other regions in China. Relatively high proportions of haloalkanes and  
aromatics were observed in autumn (25.7 and 19.3%, respectively) and winter (25.8 and 17.6%,  
170 13.6%, respectively). According to the potential source contribution function (PSCF), short-  
distance transports from the surrounding industrial areas and cities were the main reason for high  
VOC concentration in the study area. According to positive matrix factorization (PMF) model  
results, ~~industry-related sources (23–47%) followed by~~ vehicle-related emissions (24.3–34.4%)  
175 contributed the major portion to the ambient VOC concentrations. ~~Whereas aromatics~~ Aromatics  
followed by alkenes were the top contributors to the loss rate of OH radicals ( $L^{OH}$ ) (37 and 32%,  
respectively), ~~alkenes followed by aromatics contributed most to the ozone formation potential~~  
~~(OFP) (39 and 28%, respectively). Besides, the aromatics VOC group was also the major~~  
~~contributor to the secondary organic aerosol potential (SOAP) (97%).~~ According to the empirical  
kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis in  
180 assistance with a photochemical box model, the study area was in the VOC-sensitive regime for  
ozone ( $O_3$ ) formation during all the measurements seasons. Therefore, mainly alkenes and  
aromatics emissions chiefly from ~~industries and~~ automobiles should be reduced to decrease the  
secondary air pollution formation in the study area.

## 1 Introduction

185 Air pollution characterized by severe ozone ( $O_3$ ) and haze pollution is a big problem in urban  
and industrial areas in China (He et al., 2019; Hui et al., 2018; Tan et al., 2018; Jia et al., 2016;  
Feng et al., 2016; Hui et al., 2019). In recent years,  $O_3$  concentration above the national standard,  
and severe haze events are frequently reported (He et al., 2019; Hui et al., 2019; Sheng et al.,  
2018; Feng et al., 2016; Tan et al., 2018; Jia et al., 2016). As a precursor of  $O_3$  and secondary  
190 organic aerosol (SOA), volatile organic compounds (VOCs) are largely responsible for the  
severe air pollution in China (Song et al., 2018; Hui et al., 2019; Hui et al., 2018; He et al.,  
2019). Unfortunately, anthropogenic VOC emissions have been increasing over the last 2  
decades in China and it is expected to do so in the future (Mozaffar & Zhang, 2020, and  
references therein).

195 Atmospheric VOC has plenty of sources; it can be emitted from various anthropogenic and biogenic sources. Besides, it can also be formed in the atmosphere. Anthropogenic VOC sources mainly include industrial emission, vehicle exhaust, solvent usages, biomass burning, and fuel evaporation. On the other hand, vegetation is the main biogenic sources of VOC. In developed areas in China, vehicle exhaust and industrial emission are the 2 major VOC sources (He et al., 2002; Hui et al., 2018; Hui et al., 2019; Mo et al., 2017; Song et al., 2018; An et al., 2014; Mozaffar & Zhang, 2020). Whereas vehicle-related sources are more dominant in the North China Plain (NCP), Central China (CC), and Pearl River Delta region (PRD), industry-related sources are more influential in the Yangtze River Delta (YRD) area (Zhang et al., 2017; Meng et al., 2015; Sun et al., 2019; He et al., 2019; Zhang et al., 2018; An et al., 2017; Mozaffar & Zhang, 2020; Shao et al., 2016). Alkanes, Alkenes, aromatics, oxygenated-VOCs (OVOCs), and halocarbons are the most common VOC-groups in the atmosphere (Hui et al., 2019; Hung-Lung et al., 2007; Song et al., 2018; Tiwari et al., 2010; He et al., 2019; Na et al., 2001; Hui et al., 2018). VOC concentration and composition changes depending on seasons, for example, the contribution from biogenic and solvent utilization increases in summer, and contribution from combustion sources increases in winter (Mo et al., 2017; Song et al., 2018; An et al., 2014). The chemical reactivity of VOC depends on its chemical composition, for instance, alkenes and aromatics are generally more reactive than alkanes (Carter, 2010). To understand the chemical reactivity ~~and secondary product formation ability~~ of VOCs, analysis of OH radical loss rate ( $L^{OH}$ ), ~~ozone formation potential (OFP), and secondary organic aerosol potential (SOAP) are~~ is commonly used (Song et al., 2018; He et al., 2019; Hui et al., 2018); ~~Hui et al., 2019~~. Industries are an important source of VOC, and different reactive and hazardous VOCs emissions from industries are already reported in different areas on earth (Zhang et al., 2018; Na et al., 2001; Hung-Lung et al., 2007; Yan et al. 2016; Tiwari et al., 2010; Shi et al., 2015; Zhang et al., 2018b). For instance, Zhang et al. (2018) reported a high concentration of alkanes (82%) and lifetime cancer risk of different aromatics and halocarbons in a petroleum refinery in Guangzhou, China. A high concentration of OVOCs (63%) was observed in an industrial area in Ulsan, Korea (Na et al., 2001). Hung-Lung et al.(2007) mentioned a high concentration of aromatics in an industrial area in Taiwan. A high concentration of halocarbons (49%) was observed in an iron smelt plant in Liaoning, China (Shi et al., 2015). Zhang et al. (2018) mentioned a high concentration of alkanes (42%) and aromatics (20%) in a petrochemical and

other industries affected area in Shanghai, China. High concentrations of aliphatic and aromatics were observed in a petrochemical industrial area in Yokohama, Japan (Tiwari et al., 2010). Therefore, VOC composition varied among the industries/industrial areas in different regions. Mostly short-term investigations were performed to characterize the VOCs in industry-affected areas. In the current study, we carried out a comprehensive investigation on VOC in an industrial area in Nanjing for about 1 month in winter, spring, and summer and 3 months in autumn between July 2018 and May 2020. Nanjing is located in the YRD region which is mainly affected by industrial emissions. Several VOC investigations have already been performed in the Nanjing industrial area but OVOCs and halocarbons were not measured in those studies (An et al., 2017; An et al., 2014). However, OVOCs and halocarbons are already mentioned as one of the highest concentrated VOC-groups in other industrial regions (Na et al., 2001; Shi et al., 2015). In the current study area, a high concentration of alkanes (45%) and alkenes (25%) were observed in a previous investigation (An et al., 2014). Besides the incomplete VOC measurements, O<sub>3</sub> formation sensitivity to its precursors was not investigated properly using a photochemical box model in Nanjing. Moreover, source apportionment of VOCs was not conducted for different seasons of a year.

In the current study, we report the variations in concentrations and compositions of VOC during the observation period. We present the possible source areas and potential sources of VOC based on potential source contribution function (PSCF) and positive matrix factorization (PMF) model analysis. We also present the contributions of different sources to ambient VOC during the measurement period. We report the chemical reactivity and secondary product formation capacity of the VOC using L<sup>OH</sup>, OPF, and SOAP analysis. We also present the sensitivity analysis of O<sub>3</sub> formation using empirical kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis. Therefore, this study provides valuable information to the scientific community and policymakers.

## 2 Material and Methods

### 2.1 Sampling Site Description, Gases Analysis, and Meteorology Data

255 | Field measurements were carried out ~~for about 1 month in winter, spring, and summer and 3~~  
~~months in autumn from-between~~ July 2018 ~~to-and~~ May 2020 at Nanjing University of  
Information Science and Technology (32.1°N, 118.4°E), which is located in an industrial area in  
Nanjing, China. The sampling site was on the rooftop of a building (~20 m). The sampling site  
is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high  
traffic roads, and residential areas. A detailed description of the sampling site can be found  
260 | elsewhere (Mozaffar et al., 2020).

We analysed ambient air VOCs using an online GC-FID/MS instrument (AC-GCMS 1000,  
Guangzhou Hexin Instrument Co., Ltd., China). FID detector analysed C2-C5 VOCs and MS  
analysed C6-C12 VOCs. The instrument analysed one sample at every hour. During the  
investigation period, we inspected and calibrated the instrument regularly to ensure the accuracy  
265 | of the data. We monitored the O<sub>3</sub> concentrations using a 49i O<sub>3</sub> analyser (Thermo Fisher  
Scientific Inc., USA), NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations were measured using a 42i NO-NO<sub>2</sub>-  
NO<sub>x</sub> analyser (Thermo Fisher Scientific Inc., USA), SO<sub>2</sub> concentrations were followed using a  
43i SO<sub>2</sub> analyser (Thermo Fisher Scientific Inc., USA), and CO concentrations were measured  
using a 48i CO analyser (Thermo Fisher Scientific Inc., USA). We also measured temperature  
270 | and relative humidity, wind speed, wind direction, and solar radiation by HMP155 (Vaisala,  
Finland), 010C (Met One Instruments, Inc., USA), 020CC (Met One Instruments, Inc., USA),  
and CNR4 (Kipp & Zonen, The Netherlands) analysers, respectively. A detailed description of  
the instrumentation, sampling procedure, analysis, quality control, and calibration procedure can  
be found elsewhere (Mozaffar et al., 2020).

### 275 | 2.2 Positive Matrix Factorization (PMF) model and Potential Source Contribution Function (PSCF)

We used the positive matrix factorization (PMF) model (US Environmental Protection Agency,  
USEPA, version 5.0) for the source apportionments of VOCs. A detailed description of the  
model can be found elsewhere (Hui et al., 2019; Song, ~~Tan, Feng, Qu, Liu,~~ et al., 2018). In this  
280 | study, we used 620 potential VOC tracers (Fig. S1 - S4) in the PMF model to analyse the VOC  
sources for different seasons. The error fraction was set to 20% for the sample data uncertainty

estimation. We explored the PMF factor number from 4-8 to determine the optimal number of sources. Finally, we decided to choose an 7 to 8-factor solution ( $Q_{\text{true}}/Q_{\text{robust}} = \sim 1.0$ ) for different seasons.

285 We used the potential source contribution function (PSCF) to locate possible source areas of VOCs for different seasons during the investigation period. We used Zefir analysis software to do the PSCF analysis and the Hysplit4 model to cluster the backward trajectories (Petit et al., 2017). Backward trajectories in the sampling site were estimated using the data provided by the National Centers for Environmental Prediction (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1>).  
290 We estimated 24-72 hr backward trajectories 24 times a day arriving at 500 m above the ground surface using the hysplit4 model. For the PSCF analysis, we divided the geographic region covered by the back trajectories into an array of  $0.1^\circ \times 0.1^\circ$  grid cells and used the mean TVOCs concentration as the VOC reference value. More details about the PSCF analysis can be found in previous studies (Chen et al., 2018).

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### **2.3 OH radical loss rate ( $L^{\text{OH}}$ ), ~~Ozone formation potential (OFP), and Secondary organic aerosol potential (SOAP)~~**

To evaluate the daytime photochemistry of VOCs, we estimated their OH radical loss rate ( $L^{\text{OH}}$ ). The following equation was used to estimate the  $L^{\text{OH}}$  ( $\text{s}^{-1}$ ) (Zhang et al., 2020).

$$300 \quad L^{\text{OH}} = [\text{VOC}]_i \times K_i^{\text{OH}} \quad (1)$$

Where  $[\text{VOC}]_i$  is the concentration of VOC species  $i$  ( $\text{molecule cm}^{-3}$ ),  $K_i^{\text{OH}}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is the reaction rate constant of  $i$  VOC with OH radical. The  $K^{\text{OH}}$  values for the VOCs are collected from Carter (2010) (Table S1).

305 ~~The Ozone formation potential (OFP) of the VOCs is their maximum contribution to the  $\text{O}_3$  formation (Hui et al., 2018a). The OFP (ppbv) of the VOCs was estimated using the following equation:~~

$$\text{OFP} = [\text{VOC}]_i \times \text{MIR}_i \quad (2)$$

310 ~~Where  $\text{MIR}_i$  is the maximum incremental reactivity of the  $i$  VOC. The MIR values for the VOCs are also collected from Carter (2010) (Table S1).~~

~~The contribution of VOCs to the formation of secondary organic aerosol is estimated by secondary organic aerosol potential (SOAP) (Song et al., 2018). We estimated the SOAP (ppbv) of VOCs using the following equation.~~

$$SOAP = [VOC]_i \times SOAP_i^P$$

(3)

~~Where  $SOAP_i^P$  is the SOA formation potential of the  $i$  VOC on a mass basis relative to toluene (Derwent et al., 2010). In this study, the  $SOAP^P$  factors of the VOCs are collected from Derwent et al. (2010) (Table S1).~~

#### 2.4 Empirical Kinetic Modelling Approach (EKMA) and Relative Incremental Reactivity (RIR)

The empirical kinetic modelling approach (EKMA) is a well-known procedure to develop the O<sub>3</sub> formation reduction strategy by testing the relationship between ambient O<sub>3</sub> and its precursors (He et al., 2019; Hui et al., 2018; Vermeuel et al., 2019; Tan et al., 2018). In this study, we used the Framework for 0-D Atmospheric Model (FOAM v 3.2, Wolfe et al., 2016), a photochemical box model run by Master Chemical Mechanism (MCM) v3.2 chemistry (Jenkin et al., 1997; 2003, 2015; Saunders et al., 2003), to get the data for the EKMA isopleth. The FOAM-MCM box model can simulate 16940 reactions of 5733 chemical species. The box model was run using the VOCs and gas concentrations and the meteorological data as input. To generate the O<sub>3</sub> isopleth from the model simulated data, a total of 121 reduction scenarios (11 NO<sub>x</sub> × 11 VOC) were simulated and the maximum O<sub>3</sub> produced in each scenario was saved.

The O<sub>3</sub> formation sensitivity to its precursors' concentrations can also be assessed by the relative incremental reactivity (RIR, Cardelino & Chameides, 1995). We also utilized the FOAM-MCM box model data to estimate the RIR. The RIR is simply defined as the percentage change in O<sub>3</sub> formation per percentage change in precursor's concentration. In this study, we reduced the precursor's concentration by 10% for the RIR estimation. The RIR was estimated using the following equation.

$$RIR(X) = \frac{[P_{O_3}(X) - P_{O_3}(X - \Delta X)] / P_{O_3}(X)}{[\Delta X] / [X]}$$

(4)

Where  $[X]$  is the observed concentration of a precursor  $X$ ,  $[\Delta X]$  is the changes in the concentration of  $X$ .  $P_{O_3}(X)$  and  $P_{O_3}(X - \Delta X)$  are the simulated net  $O_3$  production with the observed and the reduced concentration of the precursor  $X$ , respectively.

### 3 Results and discussion

#### 3.1 Overview of the metrological conditions and air pollutants concentrations

The time series of the hourly inorganic air pollutants, meteorological parameters, and TVOC concentrations estimated with all the measured VOCs and without halocarbons are shown in Fig. 1. The discontinuity of the time series data is due to the failure of the instruments. The measured data from July to August 2018, September to November 2018, December 2018 to January 2019, and April to May 2020 are termed as summer, autumn, winter, and springtime data, respectively. Overall, the observed temperature and solar radiation gradually decreased from summer to winter and increased back to the summertime level in spring. The temperature ranged between -5.7 and 41.4 °C during the measurement period. The relative humidity values varied from 18 to 100% and high values were generally observed in winter and autumn. During the observation period, wind speed ranged between 0.1 and 7.5  $ms^{-1}$ . Wind prevailed at the sampling site from many directions during the measurement periods; more details about the wind direction will be discussed in Sect.3.3.2. The  $O_3$  and  $NO_x$  concentrations varied from 2 to 160 ppbv and 0.4 to 90 ppbv, respectively. Whereas high  $O_3$  concentrations (>80 ppbv) were observed in summer and spring, high  $NO_x$  concentrations were measured in winter and at the end of autumn. The CO and  $SO_2$  concentrations ranged from 83 to 3398 ppbv and 0.5 to 21 ppbv, respectively. Generally, high concentrations of CO and  $SO_2$  were observed in winter and spring. The measured NO and  $NO_2$  concentrations varied from 0.4 to 51 ppbv and 1 to 79 ppbv, respectively. In general, the high NO and  $NO_2$  concentrations were observed in autumn and winter. The TVOCs concentrations estimated with all the measured VOCs varied between 9 and 393 ppbv during the observation period and the high values were measured in autumn and winter. More details about the abovementioned parameters will be discussed in the following section.

#### 3.2 Concentration and composition of VOCs

In total 100 VOCs were observed in Nanjing industrial area, including 27 alkanes, 11 alkenes, 1 alkyne, 17 aromatics, 31 halocarbons, 12 OVOCs, and 1 other (carbon disulfide) (Table S2).



370 Ethane ( $5.8 \pm 2.5$  ppbv), propane ( $4.2 \pm 1.5$  ppbv), and ethylene ( $3 \pm 1.6$  ppbv) were the most abundant VOCs in the study area during the observation period. However, we observed season-wise variations in the order of abundant VOC species (Table S2). For instance, acetone was the 3<sup>rd</sup> highest concentrated VOC in spring. The abovementioned 4 VOC species are also frequently mentioned as the most abundant VOCs in different regions in China (Deng et al., 2019; He et al., 375 2019; J. Li et al., 2018; Ma et al., 2019). We compared the individual VOC concentrations with the available data presented in recent investigations. The individual VOC concentrations in the current observation were similar to those in the previous investigations in the same study area, however, they were almost twice of those found in a nonindustrial suburban area in Nanjing (Table S2). Some of the differences in comparison to the study performed in the nonindustrial suburban area in Nanjing (Wu et al., 2020) may be due to the differences in the observation period. The yearly concentrations reported in the study performed in the nonindustrial suburban area in Nanjing were probably estimated over continuous measurement data for a year. However, the yearly concentrations in the current observation were estimated using the data which were not continuously measured during all the days of a year. The autumntime individual VOC concentrations in the current observation were about 1.4 fold lower than those measured in Beijing during October-November (Li et al., 2015). The winter time individual VOC concentrations in the current observation were also about 1.4 fold lower than those measured in and Shanghai during November-January (Zhang et al., 2018), ~~but~~ But, the yearly individual VOC concentrations in the current observation were similar to those measured in Guangzhou during June-May (Zou et al., 2015). During the observation period, the concentrations of different VOC-groups were in the order of alkanes ( $21 \pm 7$  ppbv, 35%)> halocarbons ( $14.3 \pm 7.3$  ppbv, 24%)> aromatics ( $9.9 \pm 5.8$  ppbv, 17%)> OVOCs ( $7.5 \pm 1.9$  ppbv, 13%)> alkenes ( $5 \pm 1.9$  ppbv, 8%)> alkynes ( $1.4 \pm 0.3$  ppbv, 2%)> others ( $0.5 \pm 0.2$  ppbv, 1%). However, we noticed relatively higher proportions of OVOCs (14% and 18%) than the aromatics (12% and 14%) in summer and spring (Fig. 2c & f). The relatively higher contribution of OVOCs in summer and spring 395 could be related to the biogenic emissions (e.g. acetone, MEK from trees). Indeed, the relative contribution of acetone and MEK to the TVOCs were higher in summer and spring than those in autumn and winter (Table S2). Huang et al. (2019) reported that the industries, biogenic emissions, and secondary formation are the main source of OVOCs in southern China. Relatively 400 high proportions of ~~heal~~ hydrocarbons and aromatics were observed in autumn (25.7 and 19.3%,

respectively) and winter (25.8 and 17.6%, respectively) compared to those measured in summer (20.4 and 11.8%, respectively) and spring (20.3 and 13.6%, respectively) (Fig. 2f). The high proportions of ~~halo~~hydrocarbons and aromatics in autumn and winter could be related to the burning of biomass and fossil fuel for additional heating. Similar to the observation in the current study, the alkane is generally the most abundant VOC group in China (Mozaffar & Zhang, 2020). The relatively high contribution from halocarbons to the TVOCs could be related to the industrial emissions in the study area. In previous studies in an iron smelt plant in Liaoning, China, a high concentration of halocarbons (49%) was observed (Shi et al., 2015). However, halocarbons and OVOCs were not measured in previous investigations in the same study area (An et al., 2014; An et al., 2017; Shao et al., 2016) and also in another suburban area in Nanjing (Wu et al., 2020). Either aromatics or alkenes was mentioned as the second most abundant VOC-group in those studies in Nanjing, which is the 3<sup>rd</sup> and 5<sup>th</sup> most abundant VOC group in the current investigation. In Shanghai, a nearby city, alkanes (42%) and alkenes (26%) were two major VOC-groups and halocarbons and OVOCs were not reported (Zhang et al., 2018). The TVOCs concentration including halocarbons was 59.8±28.6 ppbv over the whole observation period, and relatively higher TVOCs concentrations were measured in autumn (83±20 ppbv) and winter (77.5±16.8 ppbv) compared to those in spring (39.6±13.1 ppbv) and summer (38.8±10.2 ppbv). The TVOCs concentration without halocarbons were 45.4±20.4, 61.7±14.6, 57.4±11.8, 31.6±10.9, and 30.9±8.2 ppbv during the whole observation period, autumn, winter, spring and summer, respectively. About 1.5 times higher TVOCs concentration was observed relative to the previous investigation in the same study area (An et al., 2014; An et al., 2017). Besides, we also found 3 times higher TVOCs concentration compared to the one in a nonindustrial suburban area in Nanjing (Wu et al., 2020). As mentioned before, Hhalocarbons and OVOCs were not measured-reported in the previous investigation in the same study area (An et al., 2014; An et al., 2017) and in a nonindustrial suburban area in Nanjing (Wu et al., 2020). The current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2 folds higher than the one reported in the nonindustrial suburban area in Nanjing-those previous studies in Nanjing, it could be one of the reasons for the relatively high TVOCs concentration in the current study. Observed autumn-time and wintertime TVOCs concentrations including halocarbons were was similar to ~~those the one~~ measured in urban Beijing (86.2 ppbv ~~in autumn~~ during 17-31 October) (Li et al., 2015). and Wintertime TVOCs

435 ~~concentrations without OVOCs in Shanghai (94.1 ppbv during in winter Nov-Jan) was higher than~~  
~~the current observation (70±15.1 ppbv) (Li et al., 2015; (Zhang et al., 2018). Similarly,~~  
~~Observed summertime TVOCs concentration was similar to those found in urban Xi'an (42.6~~  
440 ~~ppbv, estimation includes halocarbons and OVOCs), Wuhan (43.9 ppbv estimation includes~~  
~~halocarbons and OVOCs) (Zeng et al., 2018; Sun et al., 2019). Yearly TVOCs concentration~~  
~~including halocarbons and OVOCs was 1.7 folds higher than the one found in Wuhan (Hui et~~  
~~al., 2018b). Besides, yearly TVOCs concentration without halocarbons and OVOCs (37.9 ppbv)~~  
~~was similar to Lanzhou, Chengdu, and Tokyo, however, 1.5 times higher than those reported for~~  
445 ~~Tianjin and Ningbo (Jia et al., 2016;(Hui et al., 2018b; B. Liu et al., 2016a; Hoshi et al., 2008;~~  
~~Mo et al., 2017; Song et al., 2018). However, yearly TVOCs concentration was 1.5-3 folds~~  
~~higher than those in Lanzhou, Wuhan, Tianjin, Ningbo, Chengdu, London, Los Angeles, and~~  
~~Tokyo (Jia et al., 2016; Hui et al., 2018; B. Liu et al., 2016a; Mo et al., 2017; Song et al., 2018;~~  
~~von Schneidmesser et al., 2010; Warneke et al., 2012; Hoshi et al., 2008). The diurnal variation~~  
450 of the TVOCs, alkenes, aromatics, halocarbons, OVOCs, and alkanes concentrations showed a  
double-hump structure (Fig. 2a, b, d, & e). This double-hump pattern indicates the contribution  
of traffic emission during the rush-hours in the morning and evening. The lowest concentration  
of the TVOCs and different VOC-groups reached 12:00-16:00. Oppositely, the highest  
concentration of O<sub>3</sub> reached at that period (Fig. 3). The lowest O<sub>3</sub> concentrations were observed  
in winter which was consistent with the solar radiations.

### 3.3 Sources of VOCs

#### 3.3.1 Specific Ratios

455 ~~The use of the toluene/benzene (T/B) ratio is one of the simplest ways to preliminary analyse the~~  
~~VOC sources. If the T/B ratio is < 2, the study area is mainly affected by vehicle emissions (Hui~~  
~~et al., 2018, 2019). If the T/B ratio is > 2, the study area is influenced by other sources (e.g.~~  
~~industry, solvent utilization) beside vehicle emissions (Kumar et al., 2018; Niu et al., 2012; Li et~~  
~~al., 2019). Moreover, the T/B ratios are ranged between 0.2-0.6 in coal and biomass burning~~  
~~affected areas (Wang et al., 2009; Akagi et al., 2011). The diurnal variations in T/B ratios during~~  
~~different seasons are depicted in Fig. 4 (a, b, c, & d). The mean values of T/B ratios were ranged~~  
460 ~~between 0.9-2 (1.4±0.3), 1.3-2 (1.7±0.2), 1.1-1.6 (1.4±0.1), and 1.4-2.7 (1.9±0.3) during~~  
~~summer, autumn, winter, and spring, respectively. As the mean values of T/B ratios were around~~

2, the study area could be mainly affected by vehicle emissions. The double-hump pattern in the diurnal variations in T/B ratios also indicates that the rush-hour traffic had a significant influence on the VOCs concentrations in the study area. Besides, the 75<sup>th</sup> percentiles of T/B ratios were above 2 most of the investigation periods, therefore, the study area could also be influenced by industrial emissions.

Figure 4 (e, f, g, & h) shows the ratios of different alkanes and aromatics to acetylene. Acetylene is a tracer of combustion sources, the ratios of different alkanes and aromatics to acetylene are used to comprehend the contribution of other sources to combustion sources. The mean ratios of propane, n-butane, and i-butane to acetylene were around 2.0-4.0, 0.7-1.6, and 0.4-0.8, respectively during all the seasons, which were smaller than those (11.5, 1.8, and 2.6, respectively) observed in Guangzhou city centre, which was affected by liquefied petroleum gas (LPG) emissions (Zhang et al., 2013). Therefore, LPG usages probably contributed a little fraction to the alkanes in the study area. The mean ratios of benzene, toluene, C8-aromatics, and C9-aromatics to acetylene were around 0.3-1.0, 0.4-1.1, 0.2-0.6, and 0.1, respectively during all the seasons. The observed ratios of benzene and toluene to acetylene were much higher than those found in Jianfeng Mountains in Hainan (0.2 and 0.1, respectively) but comparable to those measured in urban Guangzhou (0.4 and 0.4-1, respectively) (Tang et al., 2007). Besides, the observed ratios of C8-aromatics and C9-aromatics to acetylene were comparable to traffic emission influenced urban Guangzhou (0.68 and 0.2, respectively) and Wuhan (0.5 and 0.2, respectively) (Zhang et al., 2013; Hui et al., 2018). Therefore, vehicle exhaust probably contributed significantly to the aromatics in the study area.

### 3.3.2 Potential Source Contribution Function (PSCF)

Besides the local sources, both the long and short distance transport of air mass could bring VOCs to the study area. Figure 5 shows the wind cluster and PSCF analysis results for different seasons. During summer, the major air masses were was short-distance transports from the southwest (4044%) direction and two long distance transports from southeast (3931 and 25%) directions. A minor air mass (21%) was transported from the east direction. High PSCF values were in the nearby southwest, and southeast, and east directions; therefore, VOC pollution in the study area was mainly affected by the short-distance transport from the south and southeast directions. During autumn, the dominant air masses were short-distance transport from the

~~northeast-northwest (5935%) and long distance transport from the northwest (3034%) directions.~~  
However, according to the PSCF analysis, VOC pollution was mainly influenced by the short distance transport from the south ~~and east~~ directions. During winter, short-distance transports from the ~~northeast (46%) and~~ northwest (~~3752%~~) directions ~~were was~~ the major incoming air masses to the study area. According to the PSCF values, the short-distance air masses from the south and ~~east-north~~ directions were mainly transported VOC to the receptor site. During spring, air mass was mainly transported from the ~~southwestern-north (4950%) and eastern-southwest (3032%)~~ directions. ~~A minor long distance air mass transported from the northwest (18%) direction.~~ Atmospheric VOCs to the study area were mainly transported by these ~~two~~ air masses mostly from the nearby areas. Overall, the high PSCF values were concentrated around the measurement site, therefore, short distance transports from the surrounding areas and cities were the main reason for the high VOC concentration. The above conclusion perfectly makes sense as the sampling site is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high traffic roads, and residential areas.

### 3.3.3 PMF Model Analysis

~~Differences were observed among the source profiles of VOCs obtained for different seasons (Sect. S1). For instance, the biogenic source was identified in summer, biomass burning source was distinguished in autumn, and LPG/NG usage source was found in winter and spring. However, industry and vehicle-related VOC sources were identified during all the measurement seasons. According to PMF model results, aromatics were emitted from solvent usages, vehicle, and industry related sources. Besides, industry and combustion processes were the main sources of halocarbons and OVOCs. Moreover, alkanes and alkenes were emitted from vehicle exhaust and fuel usage sources.~~

~~Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, industry-related sources contributed to the major portion of the ambient VOC concentrations followed by vehicle emission. Industrial emission accounted for about 32%, 47%, 45%, and 23% in summer, autumn, winter, and spring, respectively. The contributions of vehicle emission were about 34%, 26%, 24%, and 27% in summer, autumn, winter, and spring, respectively. The contribution of vehicle emission remained similar during the 4 seasons,~~

525 however, the contribution of the industrial emission increased in autumn and winter. Previous investigations performed in Beijing, Tianjin, Wuhan, Chengdu, and Shuo Zhou also found that the industry and vehicle are the two most important VOC sources (Zhang et al. 2017; Liu et al. 2016; Hui et al. 2018; Song et al. 2018) Jia et al., 2016). Besides these two sources, solvent usage (11%, 10%, 10%, and 4%, respectively) and gasoline evaporation (17%, 10%, NA, 6%, respectively) were two important VOC sources during those 4 seasons. Moreover, source contribution from the biogenic source in summer (7%), biomass burning in autumn (7%), LPG/NG usage in winter (11%) and spring (18%), and multiple sources in winter (10%) and spring (23%) was observed.

530 According to the PMF model analysis, five VOC sources were common during all the measurement seasons. They were biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, and paint solvent usage (Sect. S1). The biogenic source was distinguished only in summer. Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, vehicle-related sources contributed to the major portion of the ambient VOC concentrations. The total contributions of vehicle-related emission were about 39%, 33%, 48%, and 42% in summer, autumn, winter, and spring, respectively. The contributions of biomass/biofuel burning were about 19%, 21%, 17%, and 16.4% in summer, autumn, winter, and spring, respectively. Besides these two sources, LPG/NG usage (18%, 21%, 16%, and 18%, respectively) and paint solvent usage (8%, 12%, 11%, 5%, respectively) were two important VOC sources during those 4 seasons.

### 3.4 Chemical reactivity ( $L^{OH}$ ) and contribution to $O_3$ - and SOA formation

545 The estimated loss rates of OH radical ( $L^{OH}$ ) with VOCs were about 2-fold high in autumn ( $13.7 s^{-1}$ ) and winter ( $13.5 s^{-1}$ ) compared to those in summer ( $7 s^{-1}$ ) and spring ( $7.5 s^{-1}$ ) (Fig. 7 a). The relatively high  $L^{OH}$  values in autumn and winter were due to the relatively high VOC concentrations in those seasons (Fig.2). The average  $L^{OH}$  value was  $10.4 \pm 3.6 s^{-1}$  over the four seasons. It was in a similar range with the values determined in Guangzhou ( $10.9 s^{-1}$ ), Chongqing ( $10 s^{-1}$ ), Xian ( $1.6-16.2 s^{-1}$ ), and Tokyo ( $7.7-13.4 s^{-1}$ ), however, higher than the values estimated in Shanghai ( $2.9-5 s^{-1}$ ,  $6.2 s^{-1}$ ) and Beijing ( $7 s^{-1}$ ) (Tan et al., 2019; Zhu et al., 2019; Yoshino et al., 2012; Song et al., 2020). While alkene was the highest contributor to the  $L^{OH}$  in summer ( $3 s^{-1}$ , 43%) and spring ( $2.6 s^{-1}$ , 35%), aromatic was the maximum contributor in autumn ( $6.9 s^{-1}$ ,

50%) and winter ( $5.9 \text{ s}^{-1}$ , 44%) (Fig. 11 a & d). An increase in the OH loss rate by OVOCs was observed in spring (17%) compared to the other seasons (10, 8, and 9% in summer, autumn, and winter, respectively). Over the four seasons, the contribution of VOC-groups to  $L^{\text{OH}}$  exhibited the following trend: aromatics > alkenes > alkanes > OVOCs > halocarbons. Similar to the current study, aromatic is also mentioned as the maximum contributors to  $L^{\text{OH}}$  in different regions in China, however, the alkene is generally reported as the top contributor to  $L^{\text{OH}}$  (Zhang et al., 2020; Zhao et al., 2020; Hui et al., 2018; Song et al., 2020). Figure 7 also shows the top 10 VOCs contributing to  $L^{\text{OH}}$  for different seasons. Whereas isoprene was the highest contributor to  $L^{\text{OH}}$  in summer, styrene was the largest contributor in autumn and winter. On the other hand, naphthalene was the main contributor to  $L^{\text{OH}}$  in spring. Overall, styrene, naphthalene, ethylene, and isoprene were the main contributor to  $L^{\text{OH}}$  in the study area. In previous studies in China, these compounds are also mentioned as one of the highest contributors to  $L^{\text{OH}}$  (Zhao et al., 2020; Hui et al., 2018; Song et al., 2020).

~~The estimated  $\text{O}_3$ -formation potential (OFP) of VOCs were about 2-times high in autumn (170.8 ppbv) and winter (175.4 ppbv) relative to those in summer (86.2 ppbv) and spring (82.8 ppbv) (Fig. 8 a). The average OFP value was  $128.8 \pm 51.2$  ppbv during the measurement period. The springtime OFP was similar to the one estimated in Beijing (80 ppbv) (Li et al., 2015). The summertime OFP was about 1.5 times higher than the one in Xi'an (Song et al., 2020), but, about 1.4-2 folds lower than those found in Shanghai (Liu et al., 2019). The average OFP was about 1.5 times higher than the one in Wuhan (Hui et al., 2018). Whereas alkene was the major contributor to OFP in summer (37.4 ppbv, 43%), winter (72.8 ppbv, 41%), and spring (31.6 ppbv, 38%), aromatics contributed the most to OFP in autumn (62.7 ppbv, 37%) (Fig. 12 a & d). During the measurement period, the contribution of VOC groups to OFP showed the following trend: alkenes > aromatics > alkanes > OVOCs > halocarbons. The alkene is also mentioned as the top contributor to OFP in Nanjing and the same observation is commonly found in China (An et al., 2014; Hui et al., 2018; Song et al., 2018; Song et al., 2020). The top 10 VOCs contributing to OFP for different seasons are also shown in Fig. 8 (b, c, e, & f). Ethylene was the major contributor to OFP during all the season. Followed by ethylene, cis-1,3-dichloropropene was the main contributor to OFP from summer to winter. In spring, propylene was the second most contributors to OFP. Overall, different alkenes were the highest contributor to OFP in the study area. Alkenes are also mentioned as the top contributor to OFP in the previous investigations in~~

Nanjing (An et al., 2014). Therefore, the reduction of these alkenes emissions in the study area could be one of the ways to reduce ambient O<sub>3</sub> concentration.

The secondary organic aerosol potentials (SOAP) were about 3 times higher in autumn (1422 ppbv) and winter (1269 ppbv) than those in summer (466 ppbv) and spring (398 ppbv) (Fig. 9a). The average SOAP was 889±531 ppbv during the measurement period. The average SOAP was about 2-3 times higher than those estimated in Wuhan and Beijing (Hui et al., 2019; Li et al., 2020). Aromatics was the main contributor to SOAP during all the seasons (95-97%) (Fig. 9 a & d) which was consistent with the observations in Chengdu (Song et al., 2018), Beijing (Li et al., 2020), and Wuhan (Hui et al., 2019). During the measurement period, the contribution of VOC-groups to SOAP exhibited the following trend: aromatics > alkanes > alkenes > OVOCs. Styrene, cumene, toluene, benzene, and o-xylene were the major contributor to SOAP during all the season (Fig. 9 b, c, e, & f). Therefore, the reduction of these aromatics emissions in the study area could be one of the ways to reduce ambient SOA concentration.

### 3.5 Sensitivity analysis of O<sub>3</sub> formation

Figure 10 shows the EKMA isopleth diagrams of O<sub>3</sub> for different seasons. In all the diagrams, VOC and NO<sub>x</sub> = 100 % is the base case. The ridgeline divided the diagrams into two regimes, VOC-sensitive (above) and NO<sub>x</sub>-sensitive (below) regimes. For all the seasons, the study area fell above the ridgeline. Moreover, a decrease in O<sub>3</sub> production was noticed with the decrease in VOC concentration. Therefore, the study area was in the VOC-sensitive regime for O<sub>3</sub> formation during all the seasons. As a case study, O<sub>3</sub> formation sensitivity to its precursors was tested on a high O<sub>3</sub> concentration day (July 29 2018, maximum 126 ppbv). During the high O<sub>3</sub> episode, the study area was also in the VOC-sensitive regime for O<sub>3</sub> formation (Fig. S5). We also employed the RIR analysis to evaluate the O<sub>3</sub> production sensitivity to VOC, NO<sub>x</sub>, and CO concentrations (Fig. 11). The RIR value of VOC was the highest during all the seasons. It indicates that the O<sub>3</sub> production was more sensitive to the reduction of VOC concentration. This finding is consistent with the above results in the EKMA isopleth (Fig. 10). Except for the spring, the RIR values of CO were very small relative to those for the VOC. It indicates that the CO concentrations were relatively less important for the O<sub>3</sub> formation during those seasons. The RIR values for NO<sub>x</sub> were negative during all the seasons, implying that the O<sub>3</sub> formation was in the NO<sub>x</sub>-titration regime in the study area. From the above analysis, it is evident that a reduction of VOC



concentration in the study area will be the most efficient way to reduce the O<sub>3</sub> formation. The previous two studies performed in Nanjing also concluded the same finding based on VOC/NO<sub>x</sub> ratios and RIR analysis (An et al., 2015; Xu et al., 2017). Our findings are also consistent with the previous studies performed in other regions in China (Tan et al., 2018a; He et al., 2019; Feng et al., 2019; Ma et al., 2019). However, NO<sub>x</sub>-sensitive regions for O<sub>3</sub> formation are also found in China (Tan et al., 2018; Jia et al., 2016).

#### 4 Conclusions

Industries are an important anthropogenic source of VOCs. VOC plays a major role in tropospheric chemistry and air quality. Nanjing is one of the biggest industrial cities in China. We performed a long term investigation of ambient VOCs in an industrial area in Nanjing. ~~About 1.5~~ Similar and ~~32~~-folds high TVOCs concentrations were observed compared to those previously reported in the same study area and a nonindustrial suburban area in Nanjing, respectively. ~~The relatively high TVOCs was due to halocarbons and OVOCs concentrations were not measured in those previous studies in Nanjing. Therefore, halocarbons and OVOCs were an important part of the TVOCs in Nanjing, and industrial emissions had a large influence on VOC concentration in the study area.~~ Observed TVOCs concentration was also ~~about 1.5 similar~~ ~~3-1.7~~ folds higher than those reported in other cities in China and the world, but, ~~similar 1.3 times smaller to than those the one~~ measured in urban ~~Beijing and~~ Shanghai. ~~This~~ The high VOC concentration in the study area needs to be reduced to decrease O<sub>3</sub> concentration and improve the local air quality. TVOCs concentrations were about 2-times high in autumn and winter compared to those in summer and spring. Generally, haze pollutions frequently happen in autumn and winter, therefore, VOC concentration reduction in these seasons is an important step to reduce haze pollutions in the study area. After alkane, halocarbon was the 2<sup>nd</sup> largest contributor to the TVOCs, indicating a high influence of industrial emissions. Generally, alkenes/aromatics/OVOCs are the 2<sup>nd</sup> largest contributor to the TVOCs in China, therefore, industries in Nanjing emitted a high amount of halocarbons into the atmosphere. As halocarbons are carcinogenic, their emissions should be reduced. PSCF analysis indicated that the short distance transports from the surrounding areas and cities were the main reason for high VOC concentration in the study area. Hence, local emissions should be reduced to decrease the haze and O<sub>3</sub> pollution in the study area. ~~Industries~~ Vehicle-related emissions were the major VOC

sources in the study area ~~followed by vehicles~~, thus, emission reduction from these ~~two~~-sources should get more priority. Aromatics and alkenes accounted for most of the  $L^{OH}$ , ~~OFP, and SOAP~~, thus, these 2 kinds of VOCs should get more priority in emission reduction policies and strategies. During all the seasons, the study area was in the VOC-sensitive regime for  $O_3$  formation. Therefore, VOCs especially aromatics and alkenes emission reduction is the most effective way to decrease the local  $O_3$  formation.

#### 650 **Data availability**

All the data presented in this article can be accessed through <https://osf.io/bm6cs/>.

#### **Author contribution**

YLZ designed and supervised the project; MYF, FX, YCL, FC, and AM conducted the measurements; AM analysed the data and prepared the manuscript. All authors contributed in discussion to improve the article.

#### **Competing interests**

The authors declare that they have no conflict of interest.

660

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665

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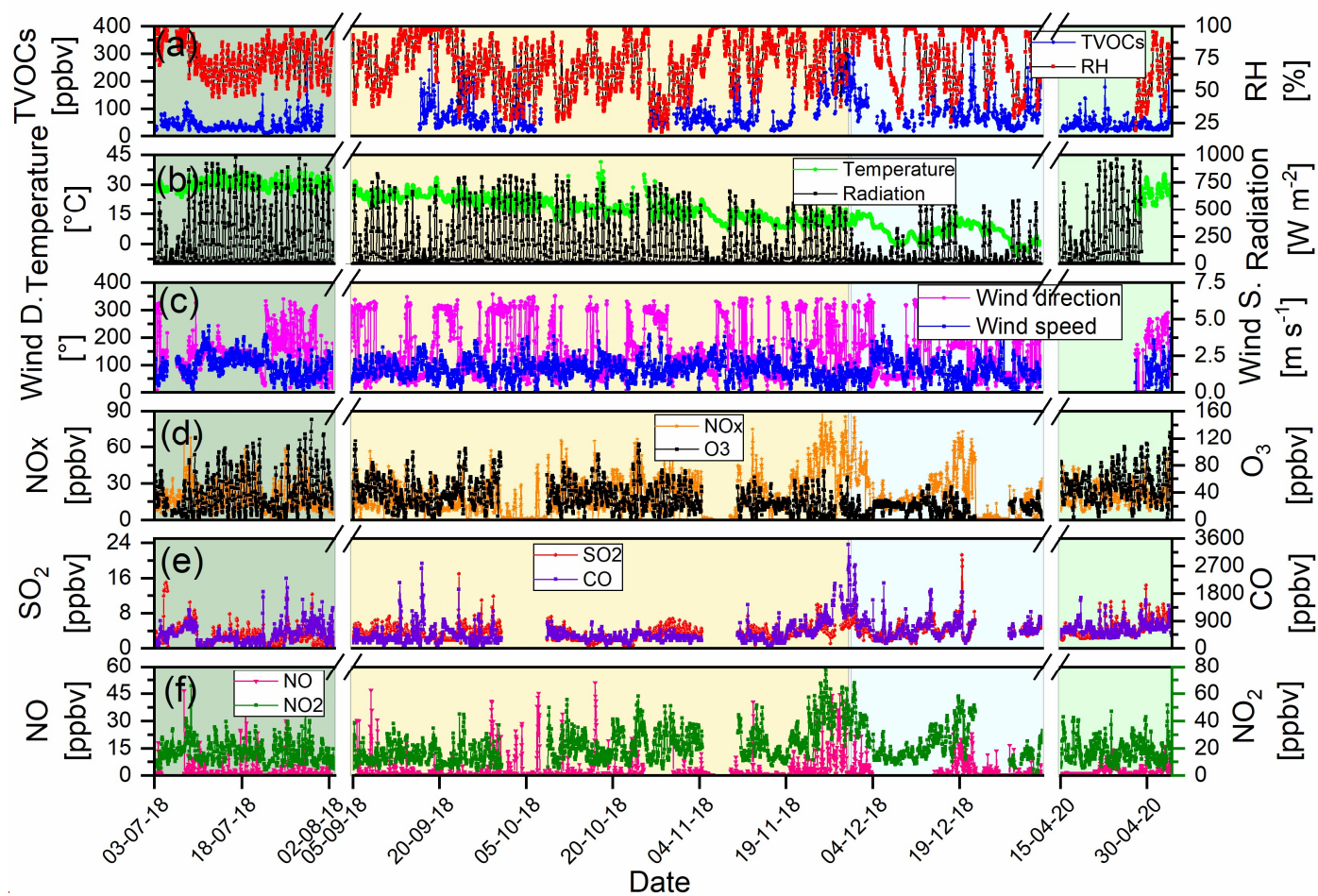
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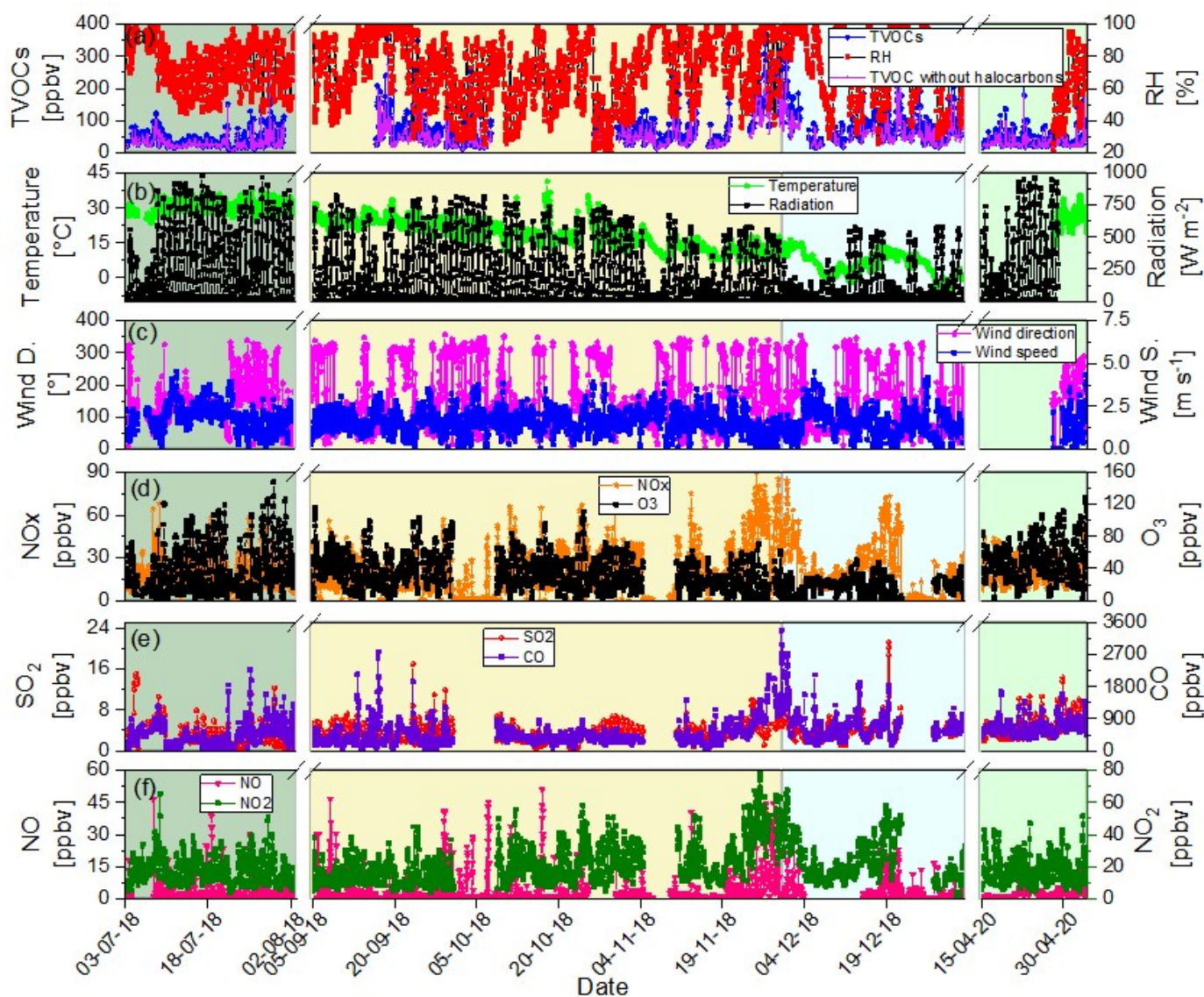


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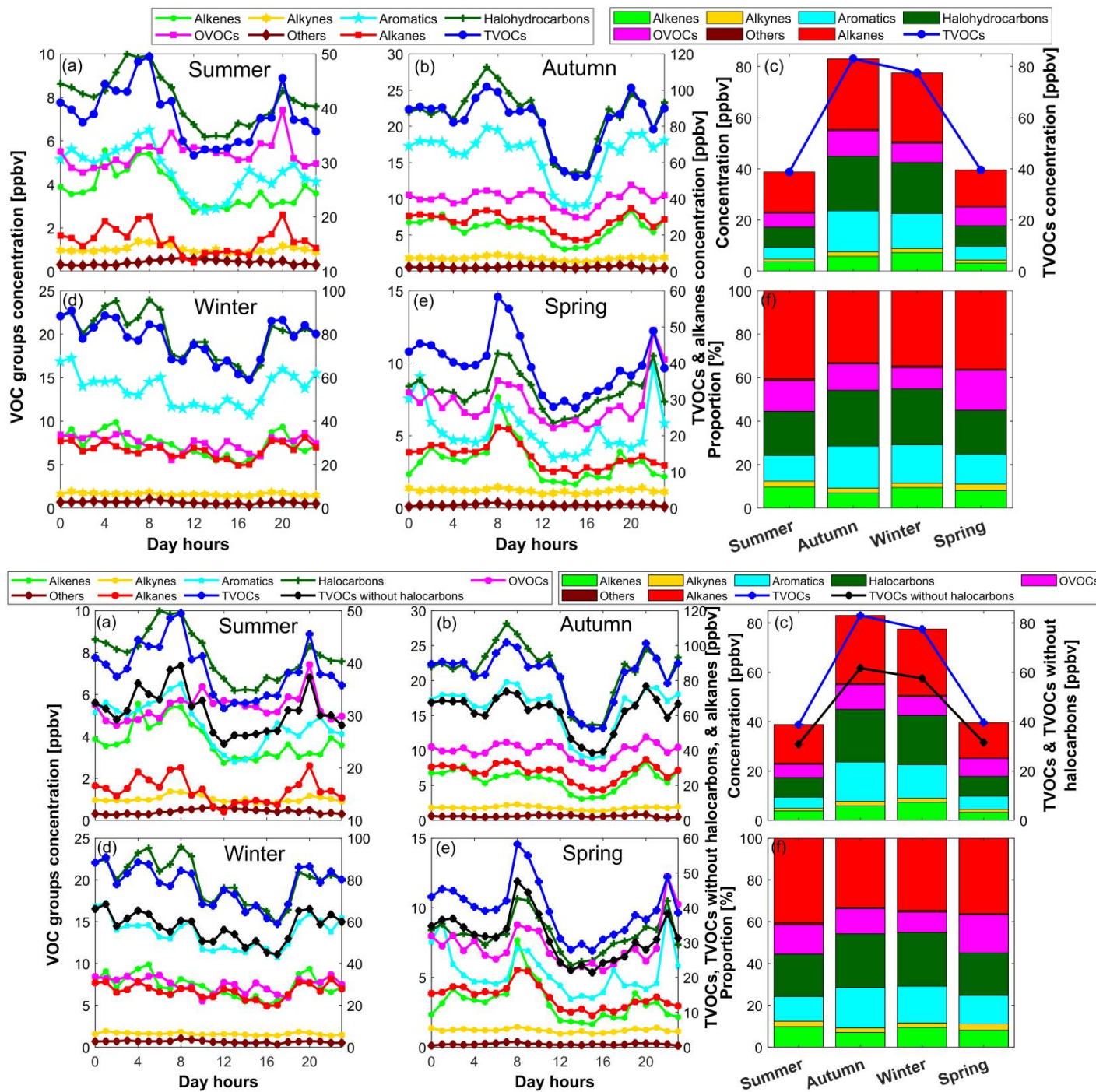
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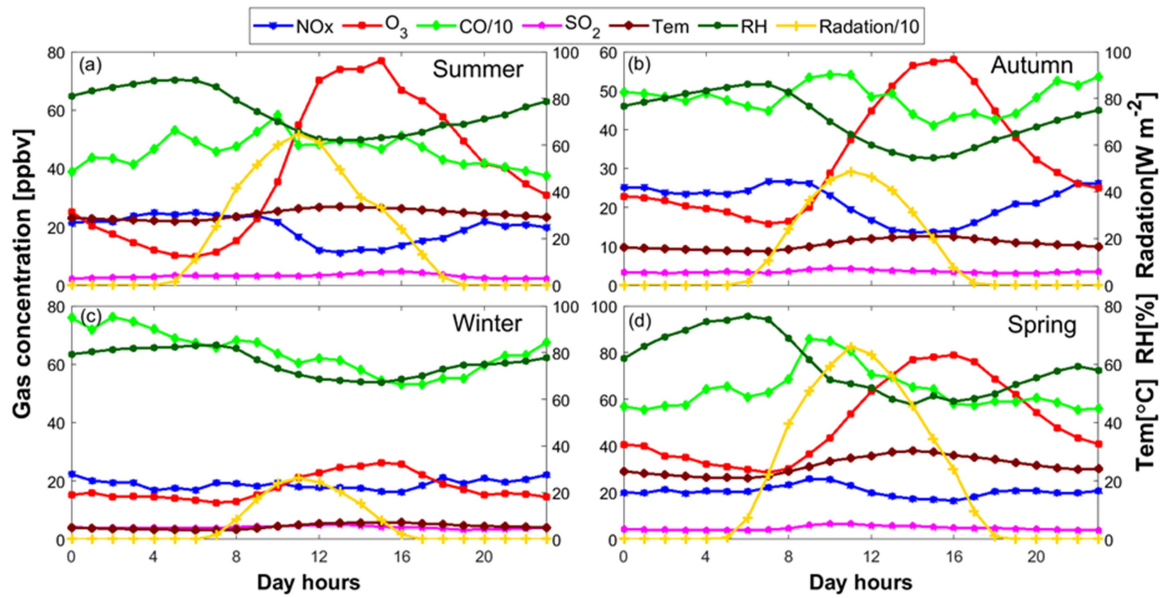
**Figure 1: Time series of hourly meteorological parameters, inorganic air pollutants, and TVOCs, and TVOCs without halocarbons concentrations during the observation period at Nanjing. The green, yellow, cyan, and light-green shaded areas indicate summer, autumn, winter, and spring seasons, respectively. The discontinuity of the measured data is due to the instruments failure.**

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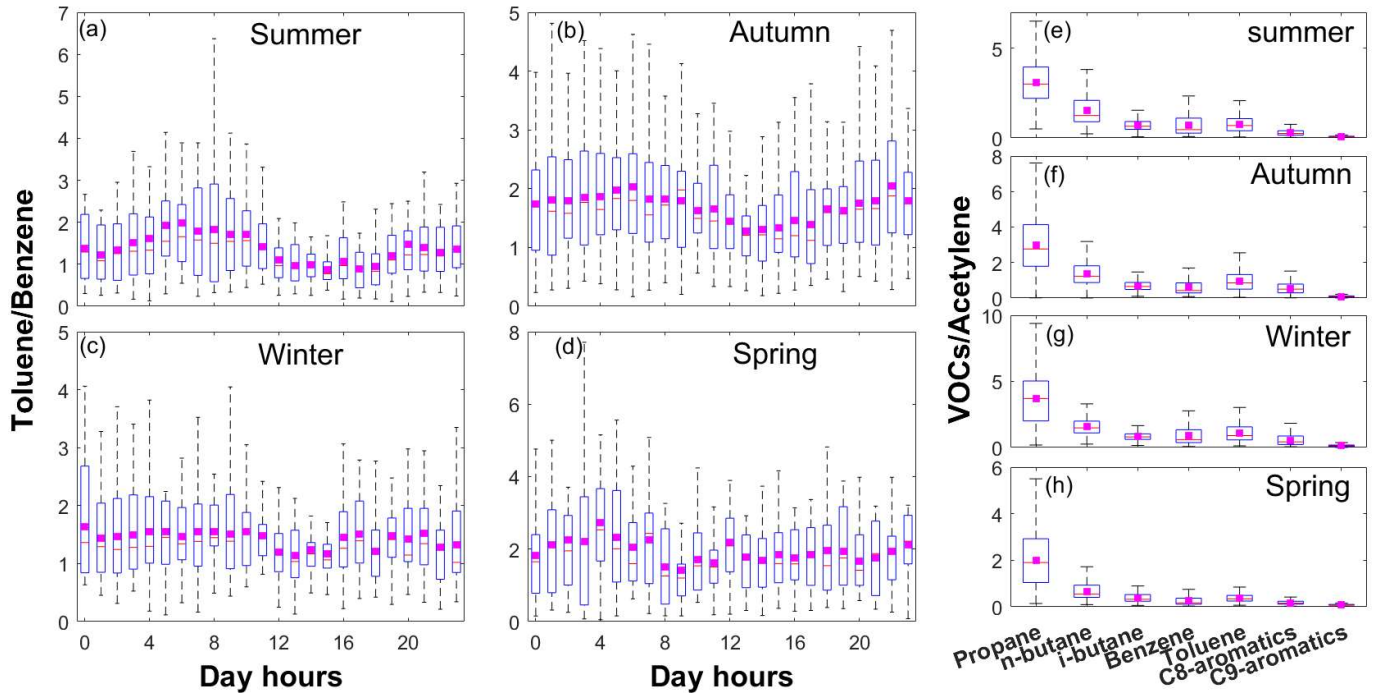
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Figure 2: Diurnal variations in TVOCs and different VOC-groups, TVOCs, TVOCs without halocarbons concentrations in different seasons (a, b, d, & e) and seasonal variations in average concentrations and proportion of different VOC-groups, TVOCs, TVOCs without halocarbons TVOCs and different VOC-groups (c & f).



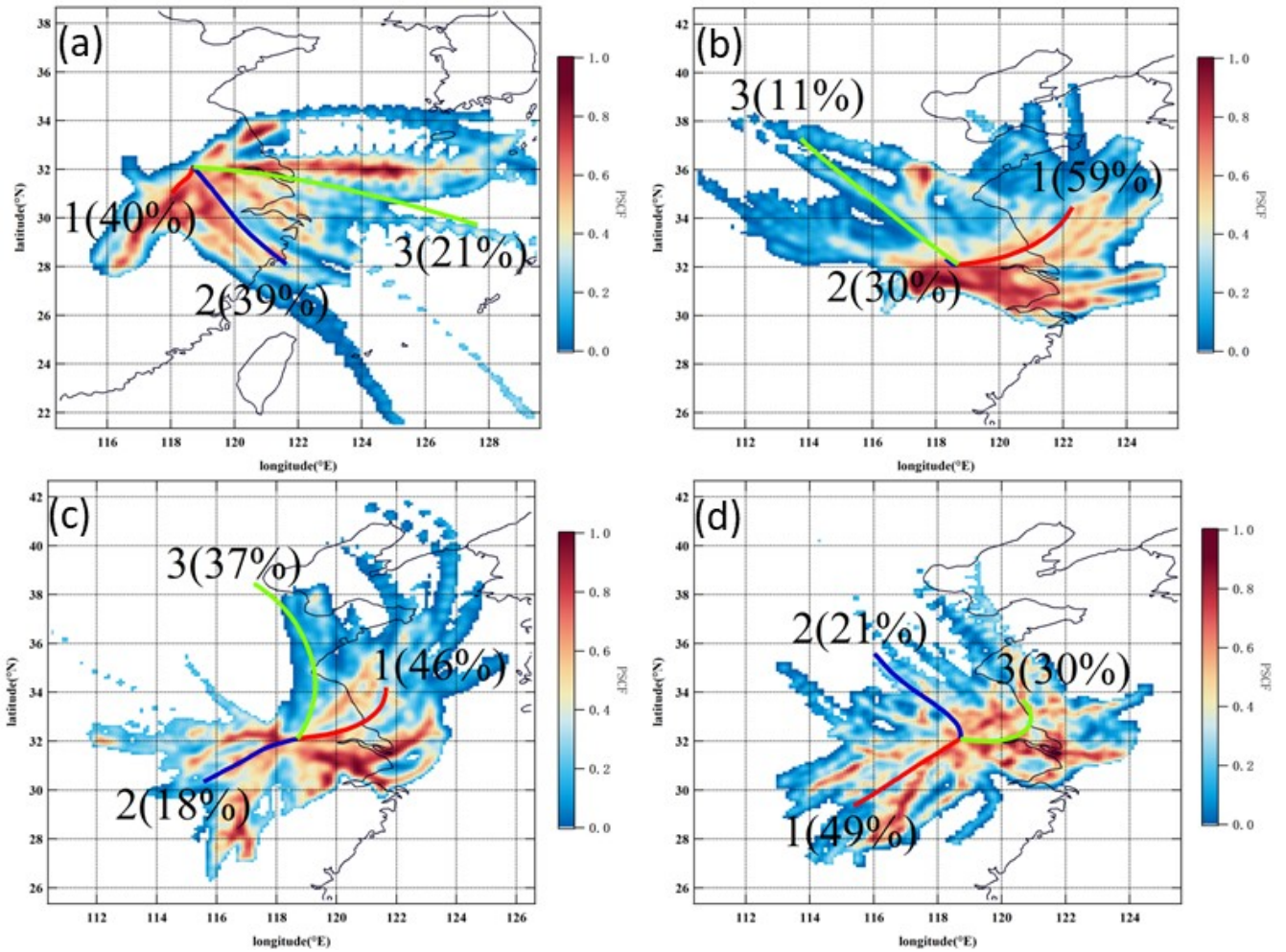
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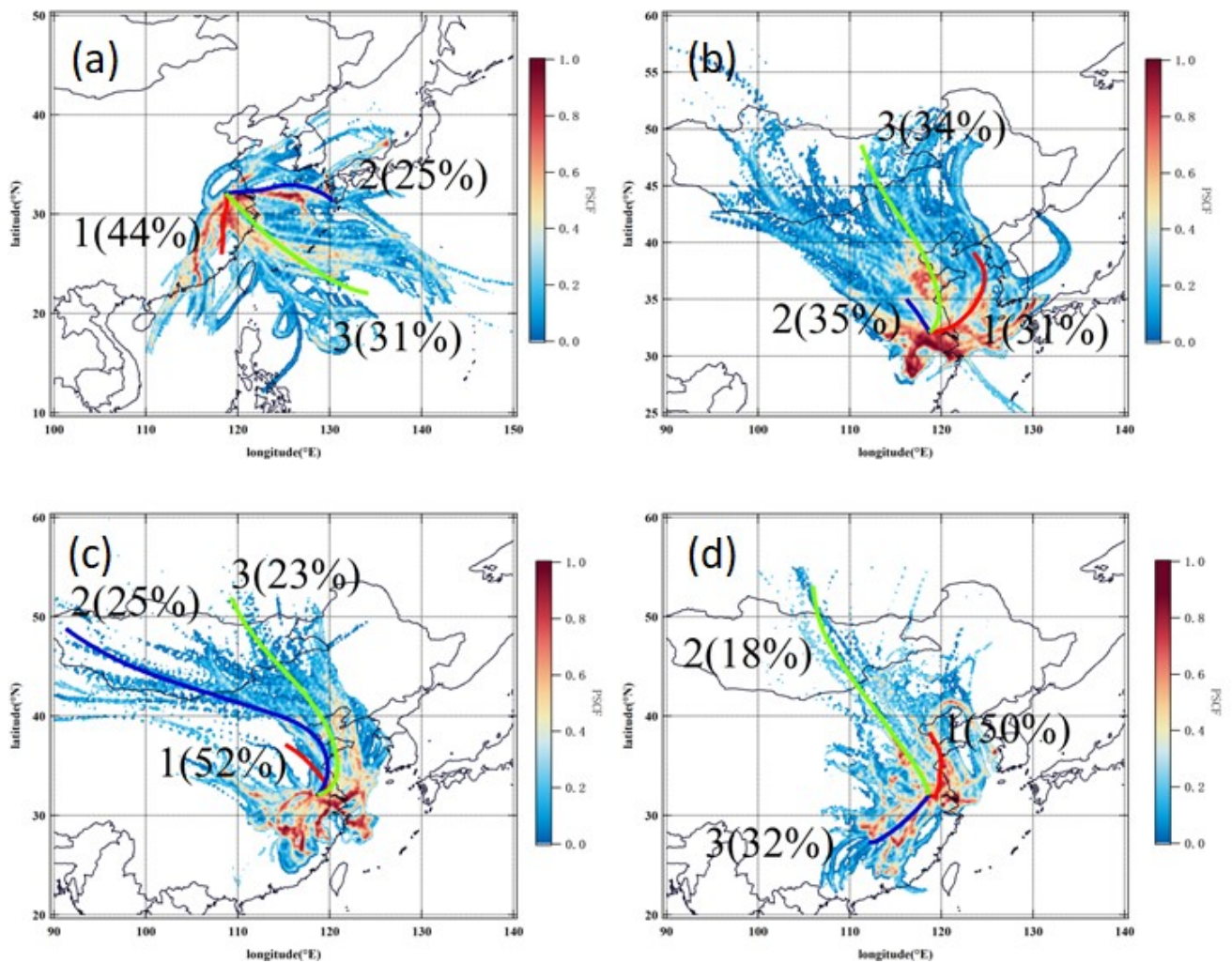
Figure 3: Diurnal variations in weather conditions and NO<sub>x</sub>, O<sub>3</sub>, CO, and SO<sub>2</sub> concentrations in different seasons. Note that the plotted CO concentrations and solar radiation values are reduced by 10-folds for a better visualization.



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**Figure 4: Diurnal variations in toluene/benzene ratios (a, b, c, & d) and in the ratios of different VOCs to acetylene in different seasons (e, f, g, & h). The pink-colored squares in the box-plots represent the average values.**

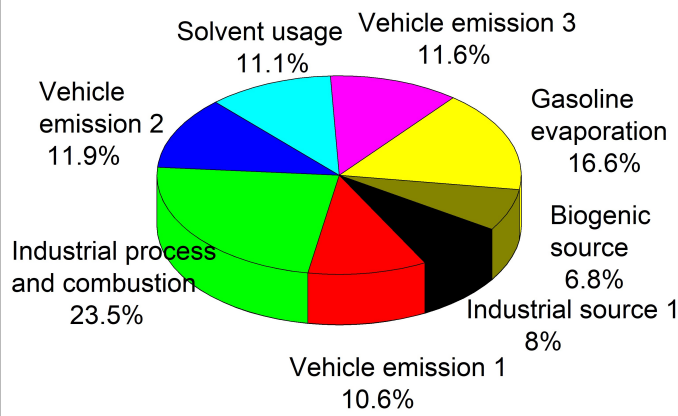




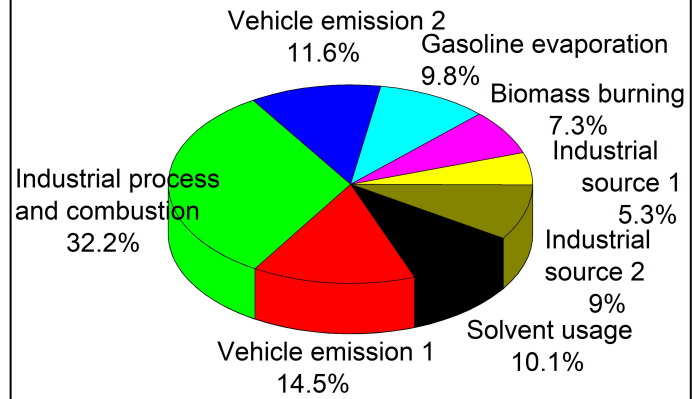
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Figure 5: Wind cluster and PSCF analysis during (a) summer (b) autumn, (c) winter, and (d) spring based on the 24-72 hours backward air mass trajectories from the study area.

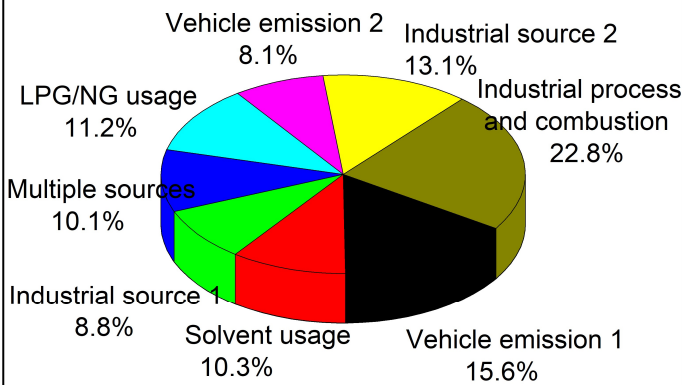
(a) Summer



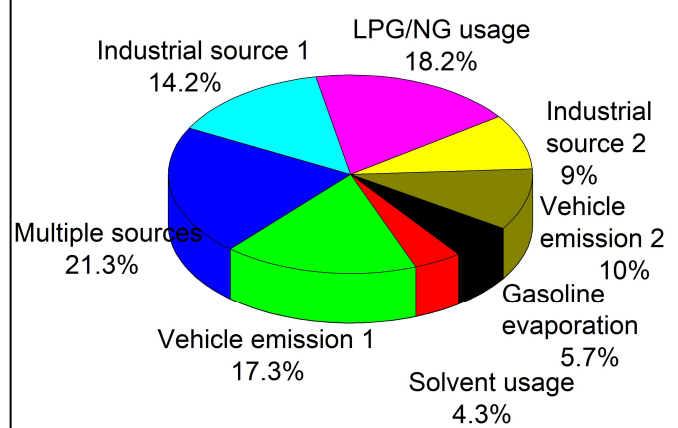
(b) Autumn

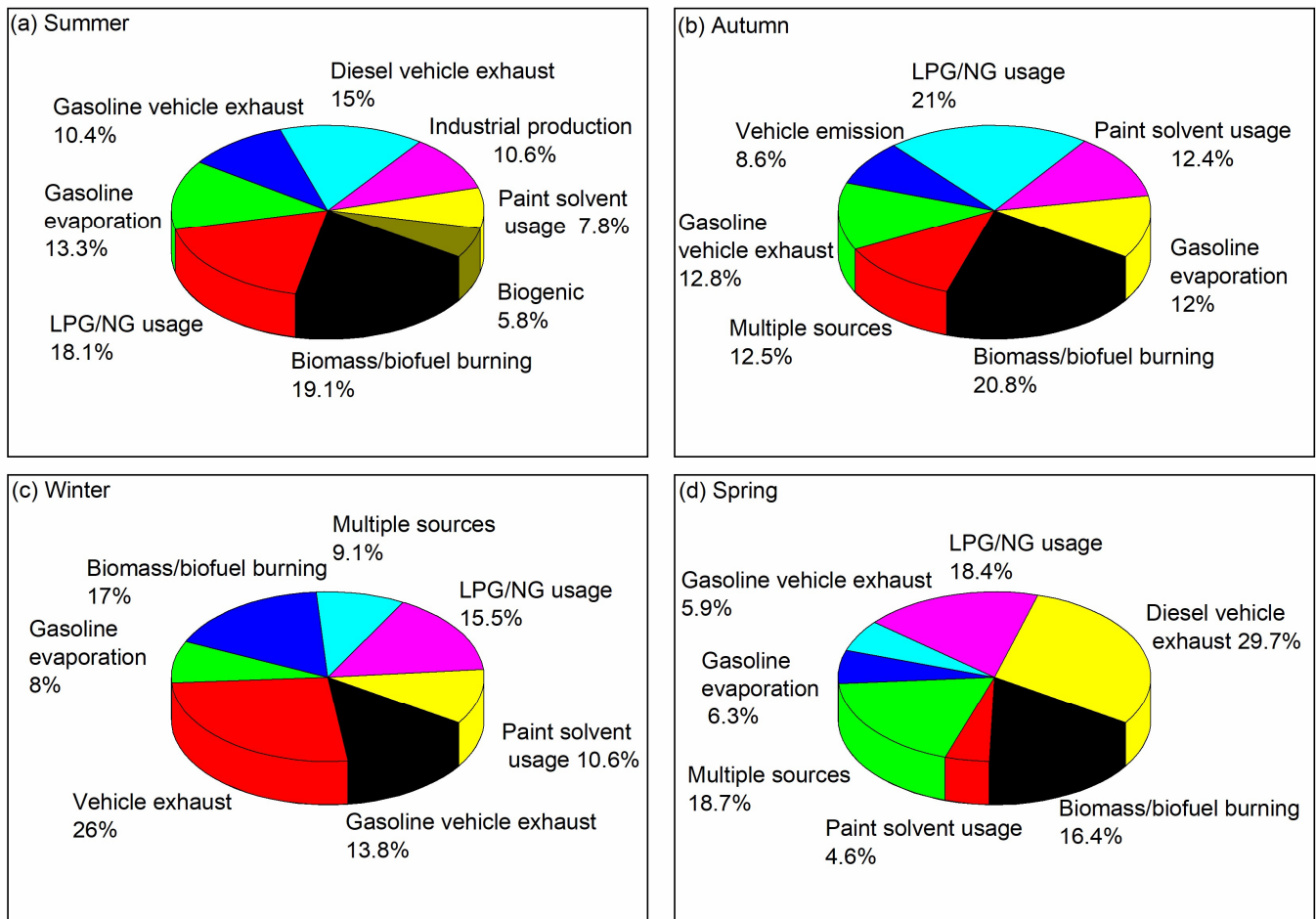


(c) Winter



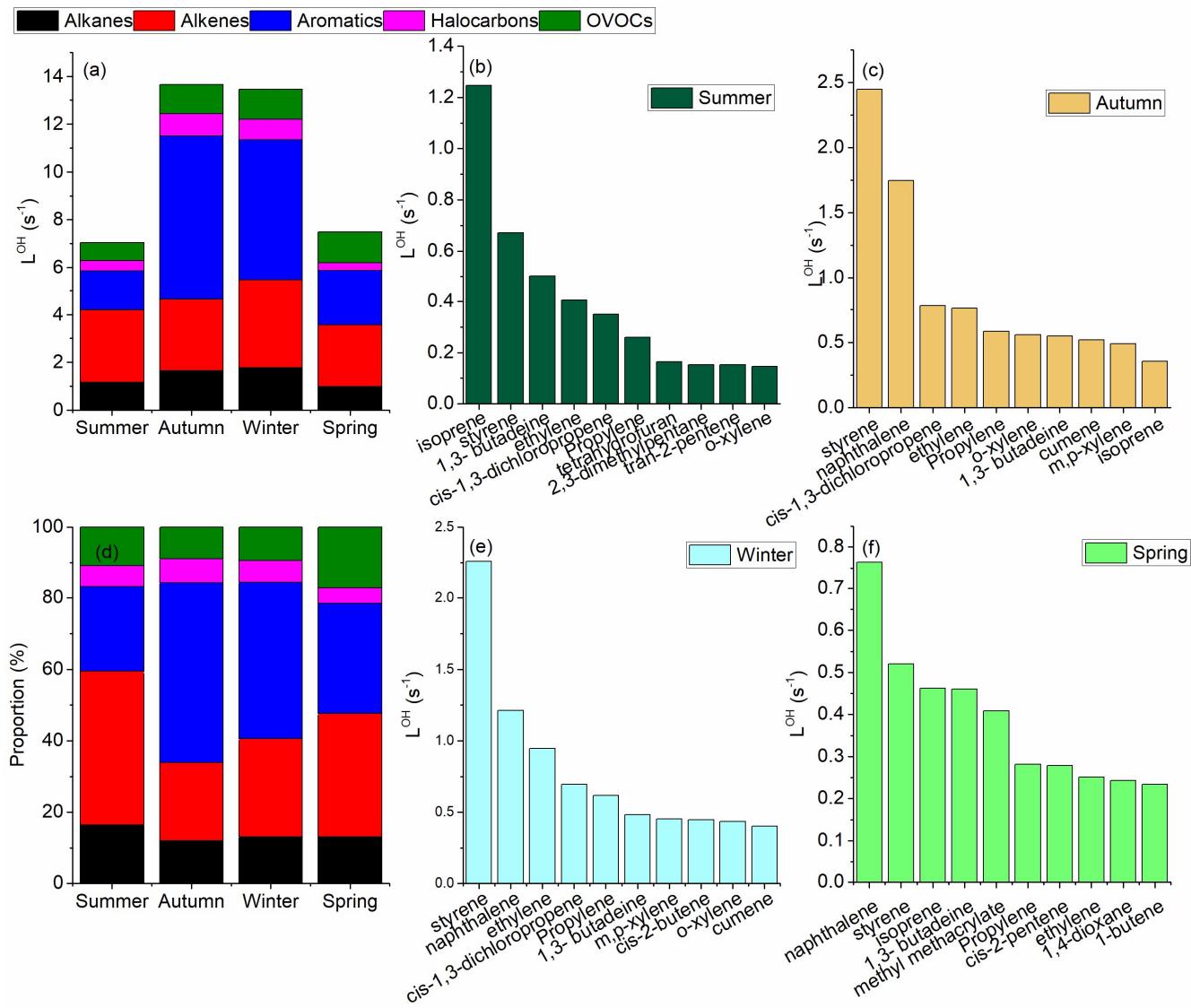
(d) Spring





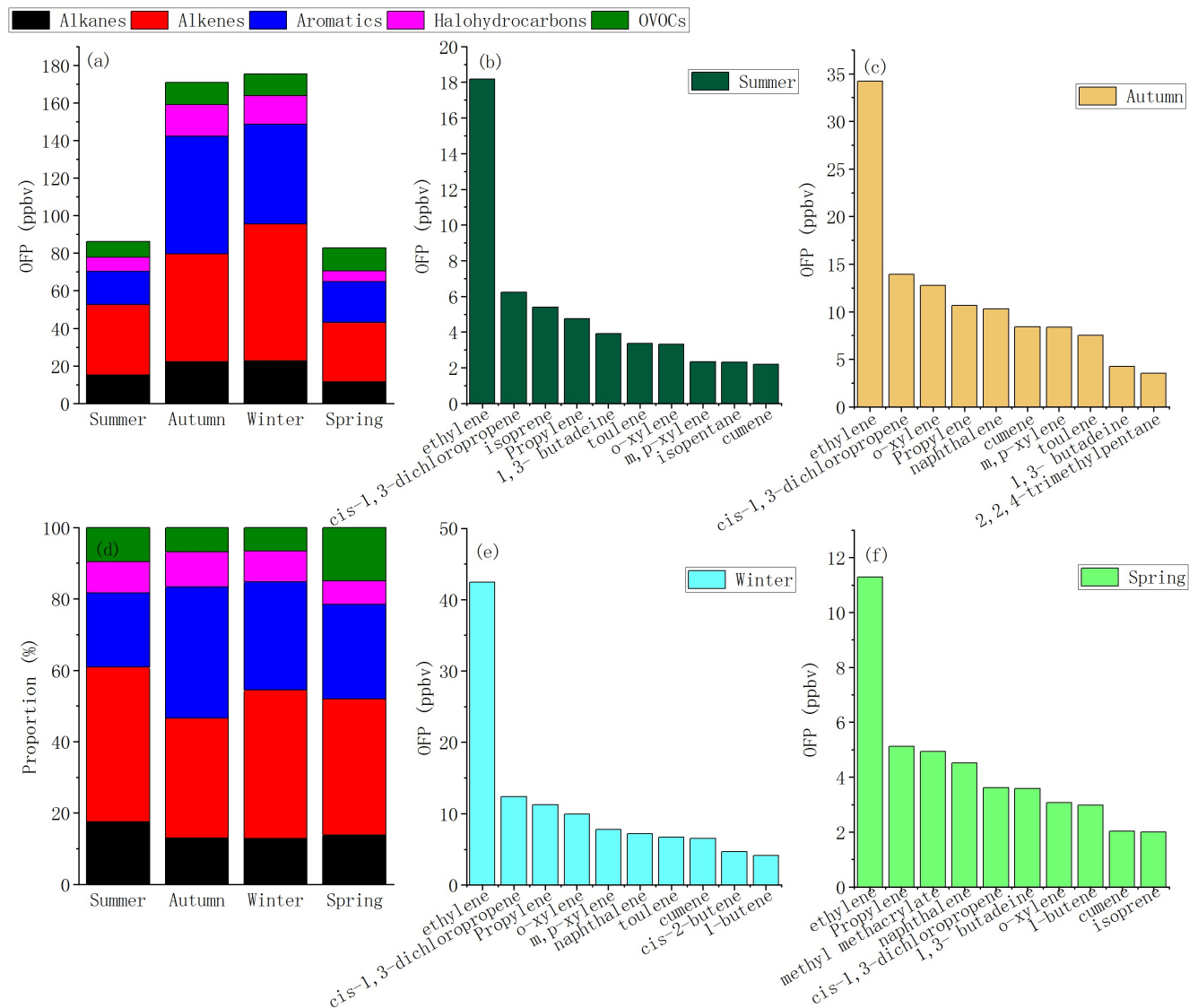
900 **Figure 6: relative contributions of different sources to ambient VOCs in Nanjing industrial area during different seasons**



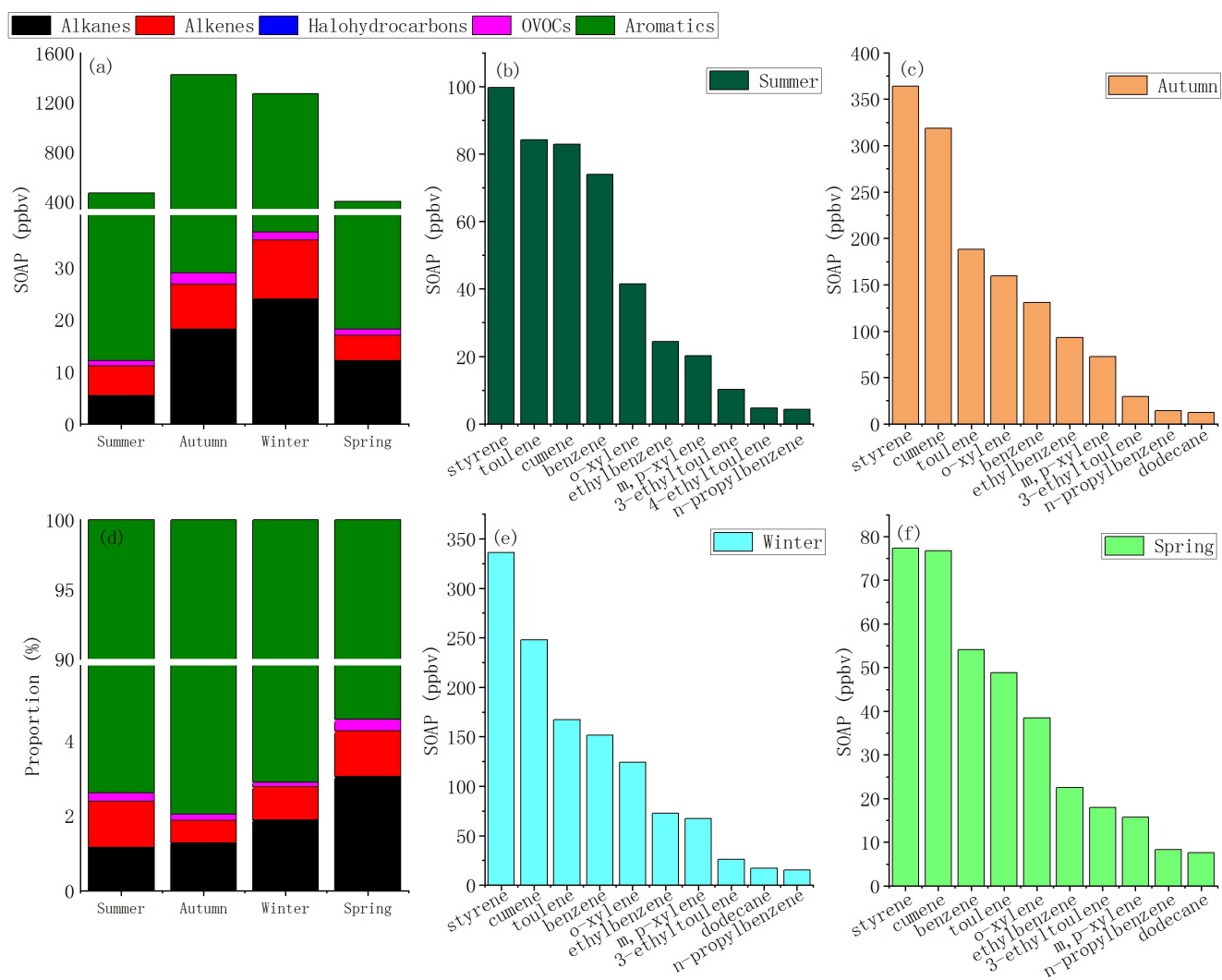


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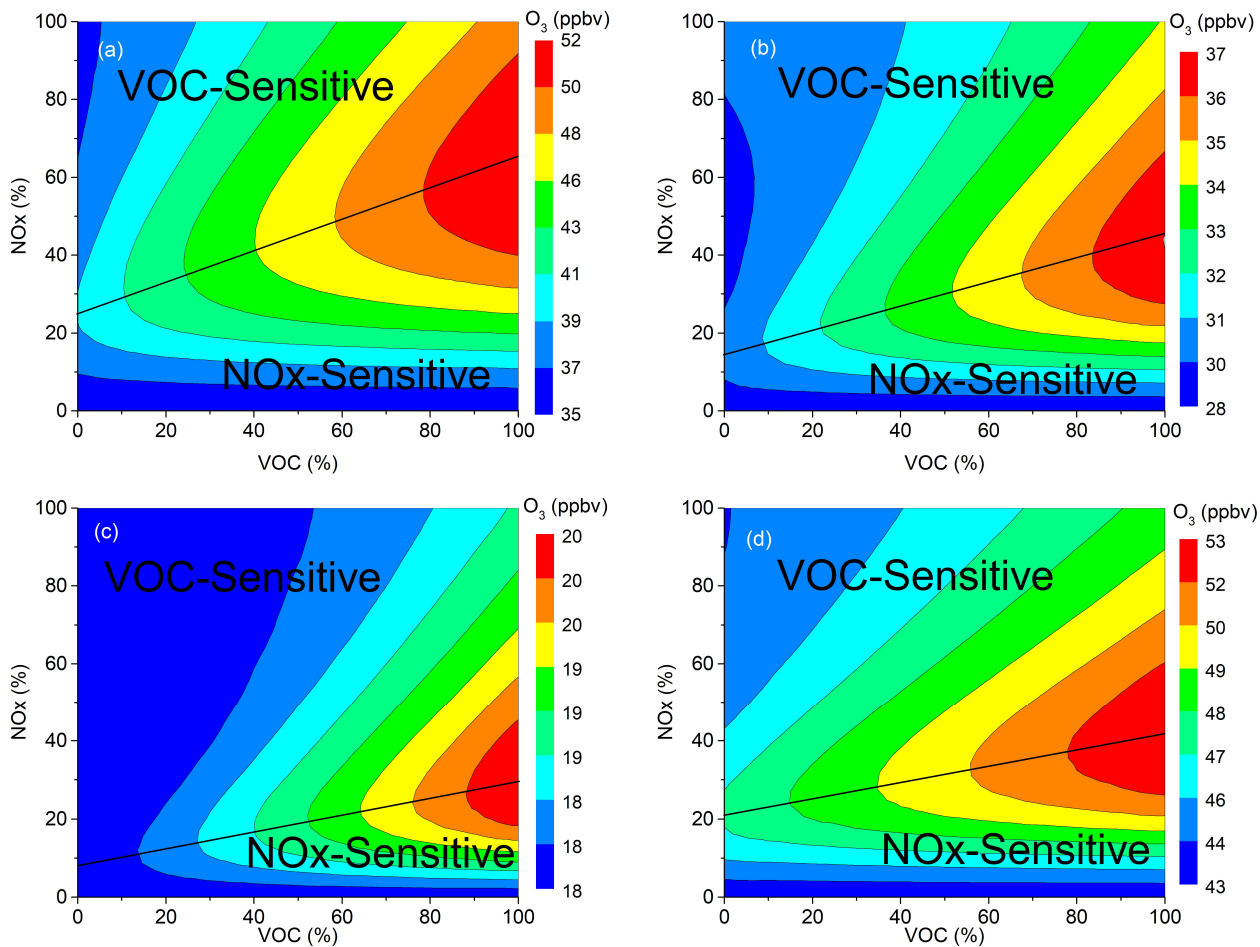
**Figure 7: Contribution to OH loss rates of different VOC-groups and the top 10 VOC species in different seasons**



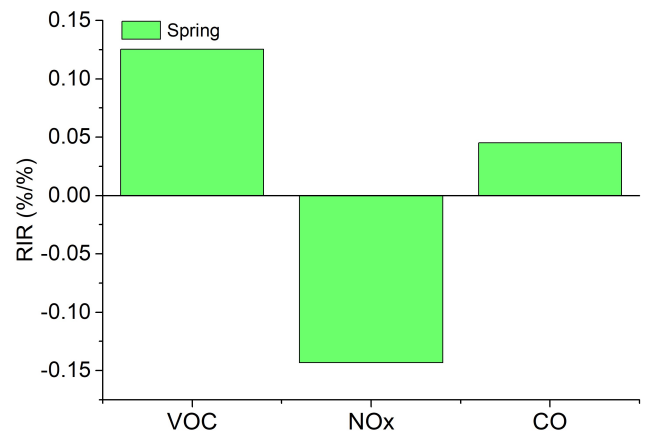
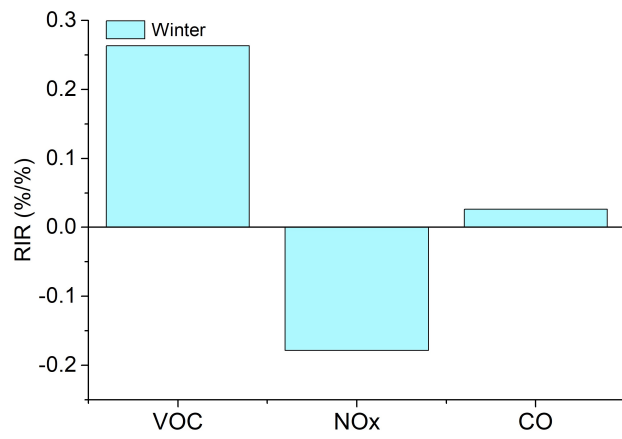
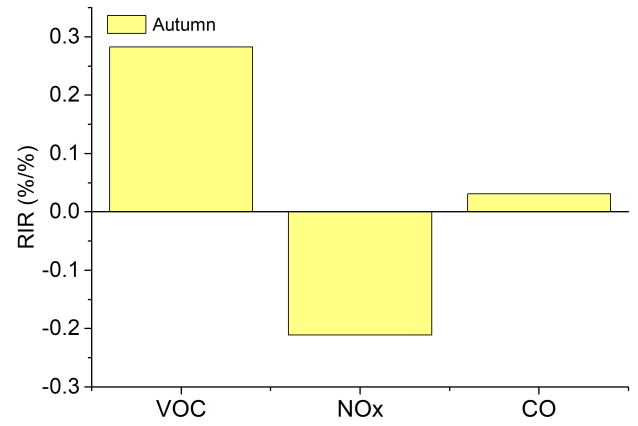
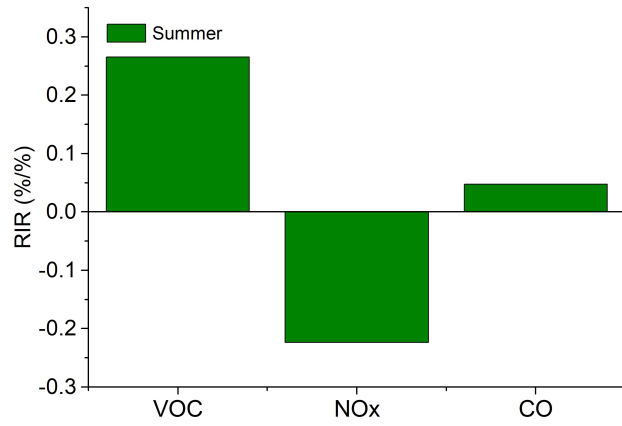
**Figure 8: Contribution to ozone formation potential of different VOC groups and the top 10 VOC species in different seasons**



**Figure 9: Contribution to secondary organic aerosol formation potential of different VOC groups and the top 10 VOC species in different seasons**



**Figure 10: O<sub>3</sub> isopleth diagram for (a) summer (b) autumn, (c) winter, and (d) spring based on percentage changes in VOCs and NO<sub>x</sub> concentrations in Nanjing and corresponding modelled O<sub>3</sub> production.**



**Figure 11: The RIR values of the VOC, NOx, and CO for the different seasons in Nanjing**

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## Supplement

### Measurement report: High Contributions of Halohydrocarbon and Aromatic Compounds to Emissions and Chemistry of Atmospheric VOCs in Industrial Area

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**Table S1: OH reaction rate constant ( $K^{\text{OH}}$ ) of VOCs**

Compounds	$K^{\text{OH}}$ (Carter, 2010)
ethane	2.54E-13
propane	1.11E-12
isobutane	2.14E-12
n-butane	2.38E-12
isopentane	3.60E-12
n-pentane	3.84E-12
2,2 dimethylbutane	2.27E-12
2,3 dimethyl butane	5.79E-12
2-methyl pentane	5.20E-12
cyclopentane	5.02E-12
3-methylpentane	5.20E-12
n-hexane	5.25E-12
2,4-dimethylpentane	4.77E-12
methylcyclopentane	5.68E-12
isoheptane	6.81E-12
cyclohexane	7.02E-12

2,3-dimethylpentane	7.15E-12
3-methylhexane	7.17E-12
2,2,4-trimethylpentane	3.38E-12
heptane	6.81E-12
methylcyclohexane	9.64E-12
2-methylheptane	8.31E-12
n-octane	8.16E-12
n-nonane	9.75E-12
decane	1.10E-11
n-hendecane	1.23E-11
dodecane	1.32E-11
ethylene	8.15E-12
Propylene	2.60E-11
trans-2-butene	6.32E-11
cis-2-butene	5.58E-11
1-butene	3.11E-11
1,3- butadiene	6.59E-11
1-pentene	3.14E-11
trans-2-pentene	6.70E-11
isoprene	9.96E-11
cis-2-pentene	6.50E-11
1-hexene	3.70E-11
acetylene	7.56E-13
benzene	1.22E-12
toulene	5.58E-12
ethylbenzene	7.00E-12
m,p-xylene	2.31E-11
o-xylene	1.36E-11
styrene	5.80E-11
cumene	6.30E-12
n-propylbenzene	5.80E-12
3-ethyltoulene	1.86E-11
4-ethyltoulene	1.18E-11
mesitylene	5.67E-11
2-ethyltoulene	1.19E-11
1,2,4-trimethylbenzene	3.25E-11
1,2,3-trimethylbenzene	3.27E-11
1,3-diethylbenzene	2.55E-11
1,4-diethylbenzene	1.64E-11
naphthalene	2.30E-11
chloromethane	4.48E-14

vinyl chloride	6.90E-12
methyl bromide	4.12E-14
chloroethene	0
trichlorofloromethane	0
Vinylidene chloride	0
1,1,2-Trichlor-1,2,2-trifluorethan	0
dichloromethane	1.45E-13
trans-1,2-dichloroethylene	0
1,1-dichloroethane	2.60E-13
cis-1,2-dichloroethylene	0
chloroform	1.06E-13
carbon tetrachloride	0
1,2-dichloroethane	2.53E-13
trichloroethylene	2.34E-12
1,2-dichloropropane	4.50E-13
bromodichloromethane	0
trans-1,3-dichloropropene	1.44E-11
cis-1,3-dichloropropene	8.45E-12
1,1,2-trichloroethane	2.00E-13
tetrachloroethylene	0
1,2-dibromoethane	2.27E-13
chlorobenzene	7.70E-13
bromoform	0
1,1,2,2-tetrachloroethane	0
1,3-dichlorobenzene	5.55E-13
1,4 dichlorobebezne	5.55E-13
benzyl chloride	0
1,2-dichlorobenzene	5.55E-13
1,2,4-trichlorobenzene	0
hexachloro-1,3-butadiene	0
carbon disulfide	2.76E-12
Acrolein	1.99E-11
acetone	1.91E-13
isopropanol	5.09E-12
MTBE	0
vinyl acetate	3.16E-11
MEK	1.20E-12
ethyl acetate	1.60E-12
tetrahydrofuran	1.61E-11
methyl methacrylate	5.25E-11
1,4-dioxane	3.83E-11



4-methyl-2-pentanone	1.27E-11
2-hexanone	9.10E-12

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954 **Table S2: VOC concentrations measured in the industrial area in Nanjing. VOC concentrations observed in previous studies**  
 955 **in Nanjing are also listed.**

Compounds	Current study										(An et al., 2017), Nanjing		(Wu et al., 2020), Nanjing
	Summer		Autumn		Winter		Spring		Yearly		Summer	Winter	Yearly
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Mean	Mean
ethane	2.81	0.58	8.06	1.77	7.66	1.39	4.76	1.25	5.82	2.49	2.76	7.66	2.89
propane	3.12	0.63	6.09	1.21	4.92	0.91	2.73	0.92	4.22	1.57	1.70	4.51	3.29
isobutane	0.75	0.16	1.25	0.26	1.16	0.15	0.48	0.14	0.91	0.36	1.04	2.25	0.9
n-butane	1.75	0.39	2.61	0.63	2.32	0.26	0.87	0.29	1.89	0.76	1.09	2.35	1.53
isopentane	1.59	0.29	1.56	0.47	1.63	0.31	0.42	0.19	1.30	0.59	0.86	1.13	1.26
n-pentane	0.66	0.17	1.06	0.29	1.36	0.25	0.31	0.10	0.85	0.46	0.50	0.86	0.78
2,2 dimethylbutane	0.08	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.28	0.03	0.04
2,3 dimethyl butane	0.13	0.03	0.18	0.03	0.11	0.00	0.20	0.02	0.16	0.04	0.12	0.35	0.04
2-methyl pentane	0.26	0.08	0.32	0.10	0.44	0.11	0.29	0.06	0.33	0.08	0.25	0.41	0.16
cyclopentane	0.15	0.03	0.10	0.02	0.08	0.01	0.22	0.03	0.14	0.06	0.08	0.12	0.08
3-methylpentane	0.25	0.06	0.38	0.09	0.37	0.12	0.25	0.08	0.31	0.07	0.22	0.31	0.26
n-hexane	0.17	0.04	0.33	0.09	0.41	0.17	0.21	0.06	0.28	0.11	0.41	0.48	0.47
2,4- dimethylpentane	0.06	0.00	0.06	0.01	0.06	0.00	0.13	0.01	0.08	0.03	0.05	0.08	0.01

methylcyclopentane	0.12	0.03	0.16	0.04	0.14	0.04	0.13	0.03	0.14	0.02	0.08	0.13	0.26
isoheptane	0.13	0.04	0.12	0.04	0.11	0.04	0.16	0.03	0.13	0.02			
cyclohexane	0.44	0.29	0.37	0.15	0.43	0.31	0.21	0.13	0.36	0.10	0.41	0.60	0.15
2,3-dimethylpentane	0.86	0.59	0.73	0.30	0.85	0.63	0.42	0.25	0.72	0.21	0.11	0.20	0.02
3-methylhexane	0.10	0.02	0.12	0.03	0.09	0.02	0.14	0.02	0.11	0.02	0.04	0.05	0.08
2,2,4-trimethylpentane	1.59	0.37	2.81	0.82	3.26	0.78	1.16	0.74	2.21	0.99	0.03	0.02	0.03
heptane	0.10	0.01	0.12	0.02	0.12	0.01	0.10	0.01	0.11	0.01	1.92	0.2	0.11
methylcyclohexane	0.18	0.02	0.18	0.04	0.19	0.03	0.16	0.03	0.18	0.01	0.08	0.12	0.08
2-methylheptane	0.08	0.00	0.08	0.01	0.08	0.00	0.17	0.01	0.10	0.04	0.01	0.05	0.02
n-octane	0.09	0.01	0.08	0.01	0.09	0.01	0.20	0.01	0.11	0.06	0.19	0.21	0.05
n-noane	0.06	0.00	0.08	0.02	0.08	0.02	0.07	0.00	0.07	0.01	0.03	0.05	0.03
decane	0.05	0.00	0.06	0.01	0.06	0.01	0.05	0.00	0.06	0.01	0.05	0.06	0.04
n-hendecane	0.04	0.01	0.16	0.01	0.22	0.01	0.17	0.01	0.15	0.07	0.06	0.09	0.02
dodecane	0.08	0.00	0.36	0.02	0.50	0.01	0.22	0.02	0.29	0.18	0.07	0.13	0.03
ethylene	2.02	0.58	3.80	0.89	4.71	1.09	1.25	0.71	2.95	1.59	3.08	6.62	1.21
Propylene	0.41	0.34	0.91	0.46	0.97	0.31	0.44	0.58	0.68	0.30	0.98	2.09	0.70
trans-2-butene	0.02	0.00	0.06	0.02	0.23	0.01	0.03	0.01	0.09	0.10	0.07	0.14	0.07
cis-2-butene	0.07	0.00	0.16	0.03	0.33	0.03	0.09	0.01	0.16	0.12	0.06	0.10	0.05
1-butene	0.07	0.00	0.10	0.02	0.43	0.02	0.31	0.13	0.22	0.17	0.18	0.23	0.15

1,3- butadiene	0.31	0.07	0.34	0.05	0.30	0.03	0.28	0.00	0.31	0.02			
1-pentene	0.16	0.03	0.14	0.03	0.08	0.03	0.10	0.03	0.12	0.04	0.04	0.05	0.04
tran-2-pentene	0.09	0.03	0.06	0.02	0.05	0.01	0.09	0.02	0.07	0.02	0.03	0.04	0.03
isoprene	0.51	0.37	0.15	0.06	0.09	0.02	0.19	0.02	0.23	0.19	0.58	0.07	0.18
cis-pentene	0.07	0.02	0.06	0.01	0.07	0.01	0.17	0.02	0.09	0.05	0.03	0.02	0.02
1-hexene	0.05	0.03	0.06	0.02	0.06	0.03	0.24	0.01	0.10	0.09	0.03	0.02	0.01
acetylene	1.02	0.15	1.77	0.24	1.59	0.15	1.20	0.13	1.40	0.35	2.63	6.46	
benzene	0.80	0.19	1.41	0.41	1.63	0.39	0.58	0.37	1.10	0.50	1.86	3.21	0.82
toulene	0.84	0.40	1.88	0.51	1.67	0.31	0.49	0.12	1.22	0.66	1.47	3.20	1.07
ethylbenzene	0.22	0.05	0.83	0.21	0.65	0.15	0.20	0.10	0.48	0.32	1.27	1.79	0.43
m,p-xylene	0.24	0.07	0.86	0.24	0.80	0.17	0.19	0.07	0.52	0.36	0.46	0.59	0.67
o-xylene	0.43	0.09	1.67	0.42	1.30	0.29	0.40	0.21	0.95	0.63	0.28	0.39	0.21
styrene	0.47	0.15	1.71	0.49	1.58	0.35	0.36	0.15	1.03	0.71	0.17	0.30	0.12
cumene	0.87	0.19	3.34	0.84	2.60	0.59	0.80	0.41	1.90	1.27			
n-propylbenzene	0.04	0.01	0.13	0.02	0.14	0.01	0.08	0.11	0.10	0.05	0.09	0.08	0.03
3-ethyltoulene	0.10	0.02	0.29	0.06	0.26	0.05	0.18	0.21	0.21	0.09	0.05	0.05	0.03
4-ethyltoulene	0.07	0.00	0.08	0.01	0.08	0.01	0.10	0.06	0.08	0.01	0.19	0.29	0.03
mesitylene	0.03	0.00	0.06	0.02	0.08	0.03	0.04	0.00	0.05	0.02			
2-ethyltoulene	0.04	0.01	0.07	0.02	0.07	0.02	0.06	0.07	0.06	0.02	0.51	0.08	
1,2,4-trimethylbenzen e	0.06	0.01	0.06	0.02	0.08	0.03	0.13	0.11	0.08	0.03	0.33	0.42	0.09

1,2,3-trimethylbenzene	0.08	0.01	0.20	0.03	0.22	0.01	0.10	0.01	0.15	0.07	0.05	0.05	0.05
1,3-diethylbenzene	0.09	0.00	0.18	0.02	0.17	0.01	0.16	0.01	0.15	0.04	0.03	0.05	0.01
1,4-diethylbenzene	0.09	0.00	0.17	0.02	0.20	0.01	0.17	0.01	0.16	0.05	0.04	0.10	0.04
naphthalene	0.13	0.02	3.09	0.98	2.14	0.22	1.35	0.29	1.68	1.25			
chloromethane	0.16	0.02	0.56	0.08	1.21	0.33	0.15	0.01	0.52	0.50			
vinyl chloride	0.05	0.00	0.07	0.02	0.09	0.02	0.16	0.01	0.09	0.05			
methyl bromide	0.04	0.00	0.05	0.01	0.04	0.01	0.03	0.00	0.04	0.01			
chloroethene	0.08	0.01	0.08	0.02	0.10	0.03	0.05	0.01	0.08	0.02			
trichlorofluoromethane	0.23	0.01	0.18	0.01	0.30	0.02	0.21	0.04	0.23	0.05			
Vinylidene chloride	0.05	0.01	0.05	0.01	0.04	0.00	0.05	0.01	0.05	0.00			
1,1,2-Trichloro-1,2,2-trifluoroethane	0.08	0.00	0.08	0.01	0.10	0.00	0.08	0.01	0.08	0.01			
dichloromethane	1.26	0.09	3.09	0.54	2.62	0.47	1.97	0.53	2.23	0.80			
trans-1,2-dichloroethylene	0.05	0.00	0.05	0.01	0.05	0.01	0.14	0.01	0.07	0.05			
1,1-dichloroethane	0.33	0.08	0.65	0.18	0.82	0.34	0.41	0.13	0.55	0.22			
cis-1,2-dichloroethylene	0.07	0.00	0.07	0.01	0.03	0.00	0.20	0.01	0.09	0.07			

chloroform	0.17	0.02	0.57	0.16	0.53	0.18	0.18	0.04	0.36	0.22
carbon tetrachloride	0.12	0.01	0.18	0.02	0.17	0.03	0.18	0.02	0.16	0.03
1,2- dichloroethane	0.95	0.14	3.19	0.40	2.95	0.43	1.15	0.31	2.06	1.17
trichloroethylene	0.13	0.02	0.14	0.02	0.10	0.02	0.06	0.00	0.11	0.04
1,2- dichloropropane	0.57	0.21	1.48	0.53	0.96	0.23	0.14	0.05	0.79	0.57
bromodichlorom ethane	0.06	0.00	0.03	0.01	0.03	0.00	0.06	0.00	0.04	0.01
trans-1,3- dichloropropene	0.10	0.00	0.08	0.01	0.13	0.00	0.17	0.01	0.12	0.04
cis-1,3- dichloropropene	1.68	0.79	3.76	1.02	3.35	0.62	0.98	0.23	2.44	1.33
1,1,2- trichloroethane	0.06	0.01	0.12	0.04	0.11	0.07	0.05	0.05	0.09	0.03
tetrachloroethyle ne	0.06	0.00	0.09	0.02	0.08	0.02	0.06	0.01	0.07	0.01
1,2- dibromoethane	0.03	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.01
chlorobenzene	0.31	0.18	1.89	0.91	1.73	1.14	0.20	0.16	1.03	0.90
bromoform	0.02	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.00
1,1,2,2- tetrachloroethan e	0.94	0.30	3.43	0.97	3.16	0.70	0.73	0.30	2.06	1.43
1,3-	0.02	0.00	0.09	0.03	0.14	0.05	0.04	0.01	0.07	0.05

dichlorobenzene										
1,4 dichlorobezne	0.11	0.01	0.65	0.20	0.40	0.05	0.09	0.01	0.31	0.27
benzyl chloride	0.12	0.02	0.10	0.05	0.13	0.07	0.24	0.23	0.15	0.06
1,2- dichlorobenzene	0.03	0.01	0.25	0.11	0.15	0.04	0.08	0.01	0.13	0.10
1,2,4- trichlorobenzene	0.04	0.00	0.17	0.04	0.25	0.01	0.14	0.02	0.15	0.09
hexachloro-1,3- butadiene	0.02	0.00	0.17	0.04	0.15	0.04	0.02	0.00	0.09	0.08
carbon disulfide	0.42	0.11	0.59	0.13	0.66	0.15	0.21	0.07	0.47	0.20
Acrolein	0.09	0.02	0.07	0.02	0.05	0.01	0.07	0.02	0.07	0.01
acetone	1.60	0.29	2.98	0.25	1.94	0.22	2.61	0.61	2.28	0.63
isopropanol	0.46	0.07	2.34	0.60	1.28	0.34	0.44	0.10	1.13	0.90
MTBE	0.37	0.11	0.66	0.23	0.35	0.11	0.35	0.13	0.43	0.15
vinyl acetate	0.17	0.04	0.33	0.09	0.42	0.18	0.26	0.08	0.30	0.11
MEK	0.69	0.06	1.14	0.10	0.73	0.09	0.77	0.43	0.84	0.21
ethyl acetate	1.06	0.17	1.56	0.25	1.43	0.18	1.34	0.95	1.35	0.21
tetrahydrofuran	0.41	0.56	0.08	0.11	0.43	0.45	0.24	0.03	0.29	0.16
methyl methacrylate	0.11	0.01	0.21	0.01	0.20	0.01	0.32	0.00	0.21	0.09
1,4-dioxane	0.05	0.00	0.07	0.01	0.09	0.00	0.26	0.01	0.12	0.10
4-methyl-2- pentanone	0.23	0.08	0.31	0.07	0.28	0.06	0.30	0.03	0.28	0.03

2-hexanone	0.15	0.00	0.23	0.01	0.28	0.01	0.29	0.02	0.23	0.07
<b>TVOC</b>	<b>38.81</b>	<b>10.21</b>	<b>83.05</b>	<b>20.07</b>	<b>77.51</b>	<b>16.77</b>	<b>39.62</b>	<b>13.12</b>	<b>59.75</b>	<b>28.57</b>

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## S1. Source apportionment of VOCs

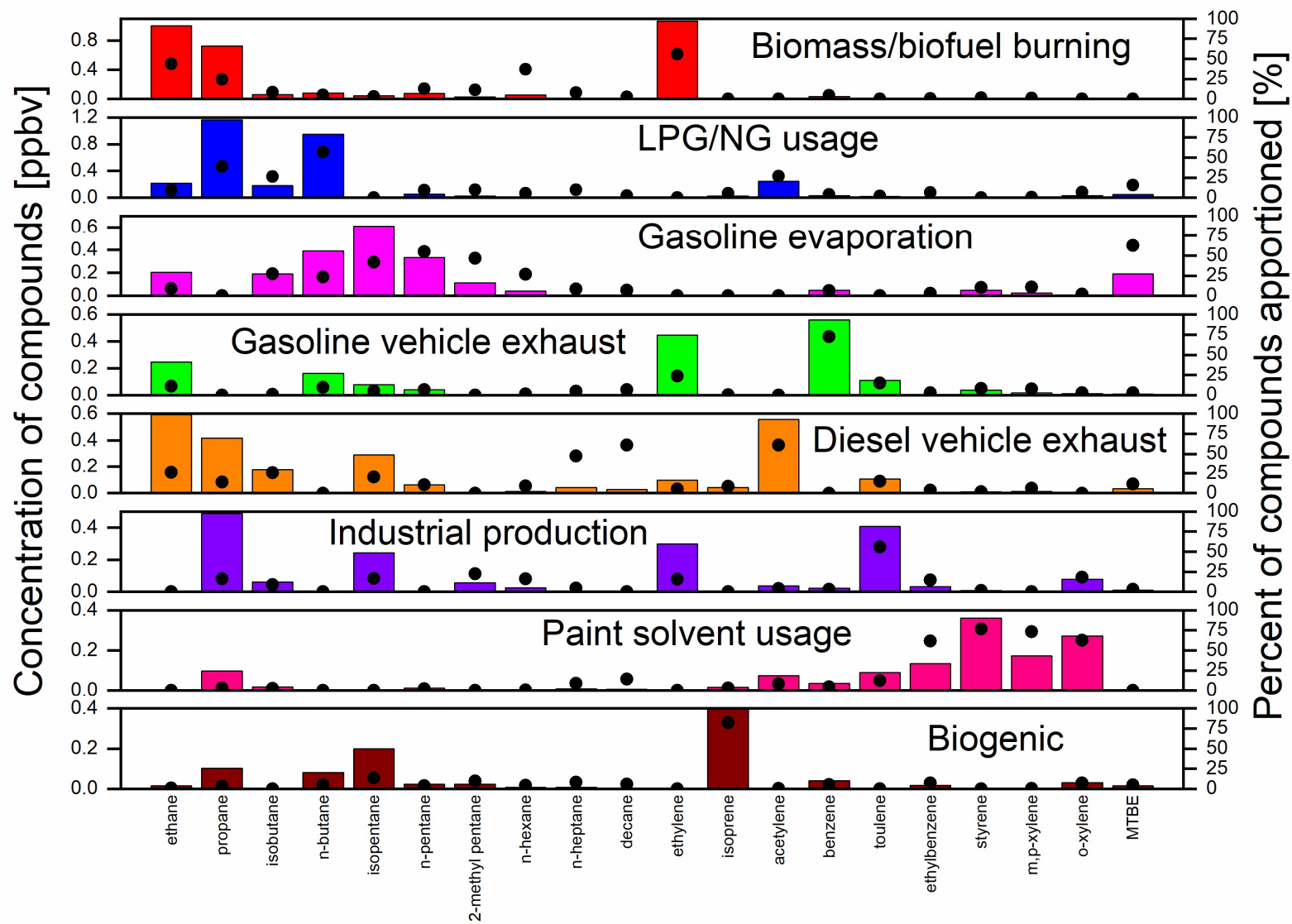
Figure S1 shows the source profile of summertime VOCs obtained from the PMF model. The resolved factors were identified as biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, diesel vehicle exhaust, industrial production, paint solvent usage, and biogenic source. Factor 1 was characterized by high concentrations of ethane and ethylene. These compounds are tracers of incomplete combustion which emitted from vehicle exhaust and biomass/biofuel burning (An et al., 2017). Benzene, toluene, pentane, and decane concentrations were low in factor 1, therefore, it was identified as biomass/biofuel burning. Factor 2 was distinguished by a significant presence of LPG/NG VOCs propane, isobutene, and n-butane (Shao et al., 2016). So, factor 2 was identified as LPG/NG usage. Factor 3 was dominated by high concentrations of isopentane, n-pentane, and MTBE. Therefore, factor 3 was identified as gasoline evaporation (Song et al., 2018; Wang et al., 2016). Factor 4 possessed high concentrations of vehicle exhaust VOCs benzene and toluene (Song et al., 2018). Although these VOCs are also emitted by industrial processes, the contribution of benzene was several folds higher than toluene in this factor. Therefore, factor 4 was related to vehicle exhaust emission and it was assigned to gasoline vehicle exhaust (An et al., 2017). Factor 5 was characterized by high concentrations of acetylene, n-heptane, and decane. These are related to vehicle emission, especially diesel vehicle exhaust emission as diesel engine produce more acetylene than the gasoline engine does (Song et al., 2018; An et al., 2017). Therefore, factor 5 was attributed to diesel vehicle exhaust. Factor 6 was dominated by toluene and the sampling site was beside an industrial area. So, we identified this factor as industrial production. Due to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene, factor 7 was assigned to paint solvent usage sources (Li et al., 2018). Factor 8 was attributed to the biogenic source, which was mainly distinguished by a high concentration of isoprene (Song et al., 2018).

During autumn, the possible VOC sources were biomass/biofuel burning, multiple sources, gasoline vehicle exhaust, vehicle emission, LPG/NG usage, paint solvent usage and gasoline evaporation (Fig.S2). Factor 1 was represented by a high concentration of ethane and ethylene, so, it was identified as biomass/biofuel burning (An et al., 2017). Factor 2 was dominated by isoprene, n-heptane, decane, and acetylene. Among these compounds, isoprene is mainly emitted by trees and the rest of the compounds are related to diesel vehicle exhaust emission. Therefore,

Factor 2 was identified as multiple sources. Factor 3 was identified as gasoline vehicle exhaust due to the high contribution of benzene and a relatively small contribution of toluene. In factor 3, benzene was several folds higher than toluene. The 4<sup>th</sup> factor was mainly composed of vehicle emission-related compounds 2-methyl pentane, n-hexane, n-heptane, n-pentane, and isopentane, therefore, identified as vehicle emission (Song et al., 2018). Factor 5 was assigned to LPG/NG usage as propane, isobutene, and n-butane were the main contributor to it (Shao et al., 2016). Factor 6 was characterized by a high concentration of o-xylene, m,p-xylene, ethylbenzene and styrene, which are typical tracer of paint solvent usage. Factor 7 was identified as gasoline evaporation, it was dominated by high concentrations of isopentane, n-pentane, and MTBE (Song et al., 2018).

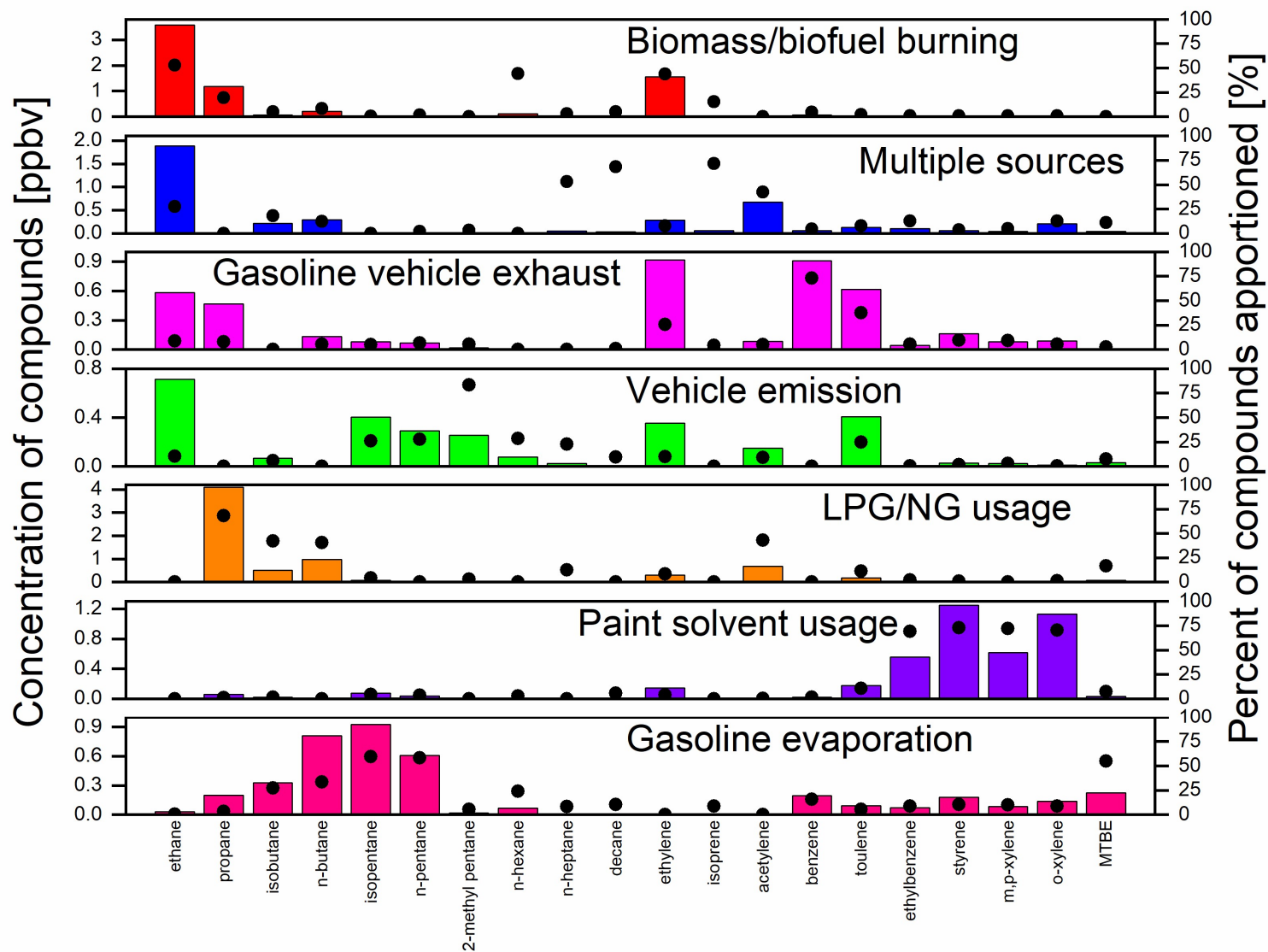
During winter, the source factors were identified as gasoline vehicle exhaust, vehicle exhaust, gasoline evaporation, biomass/biofuel burning, multiple sources, LPG/NG usage, and paint solvent usage (Fig. S3). Factor 1 was assigned to gasoline vehicle exhaust; it was dominated by benzene and toluene and the contribution of benzene was twice of toluene. Factor 2 was represented by a high concentration of isobutene, n-butane, acetylene, ethylene, ethane, n-heptane and decane. Isobutene and n-butane are related to LPG/NG usage, but, the contribution of propane was zero in factor 2. Acetylene, ethylene, and ethane emitted from combustion sources like vehicle exhaust and biomass burning. Decane and n-heptane are related to vehicle emission. By considering the above information, factor 2 was identified as vehicle exhaust. Factor 3 was identified as gasoline evaporation and it was characterized by high concentrations of isopentane and n-pentane. Factor 4 was characterized by a high contribution of ethylene and ethane; therefore, it was identified as biomass/biofuel burning. Factor 5 was characterized by high concentrations of isoprene, propane, n-hexane and n-heptane. Propane is related to LPG/NG usage, isoprene mainly emitted from trees (evergreen trees in winter), and n-hexane and n-heptane are related to vehicle emission. By considering the above information, factor 5 was assigned to multiple sources. Factor 6 was dominated by high concentrations of propane. Therefore, it was identified as LPG/NG usage. Factor 7 was identified as paint solvent usage due to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene (Zhang et al., 2018; Song et al., 2020).

1015 During spring, the possible VOC sources were biomass/biofuel burning, paint solvent usage,  
multiple sources, gasoline evaporation, gasoline vehicle exhaust, LPG/NG usage, and diesel  
vehicle exhaust (Fig. S4). Factor 1 was identified as a biomass/biofuel burning source for the  
high loading of ethylene and ethane and relatively lower contribution from the vehicle emission  
related compounds. Due to the high contribution of o-xylene, styrene, m,p-xylene, and  
1020 ethylbenzene, factor 2 was assigned to paint solvent usage sources (Li et al., 2018). Factor 3 had  
a high contribution of isoprene, n-hexane, n-heptane, decane, MTBE, toluene, ethylbenzene, and  
o-xylene. Therefore, factor 3 was identified as multiple sources. Factor 4 was represented by a  
high concentration of isopentane, n-pentane, and MTBE. Therefore, factor 4 was identified as  
gasoline evaporation. Factor 5 was represented by high concentrations of benzene, therefore,  
1025 identified as gasoline vehicle exhaust. Factor 6 was assigned to LPG/NG usage due to the high  
contribution of propane, n-butane, and isobutane (Shao et al., 2016). Factor 7 was identified as  
diesel vehicle exhaust due to the high contribution of acetylene, n-heptane, and decane.



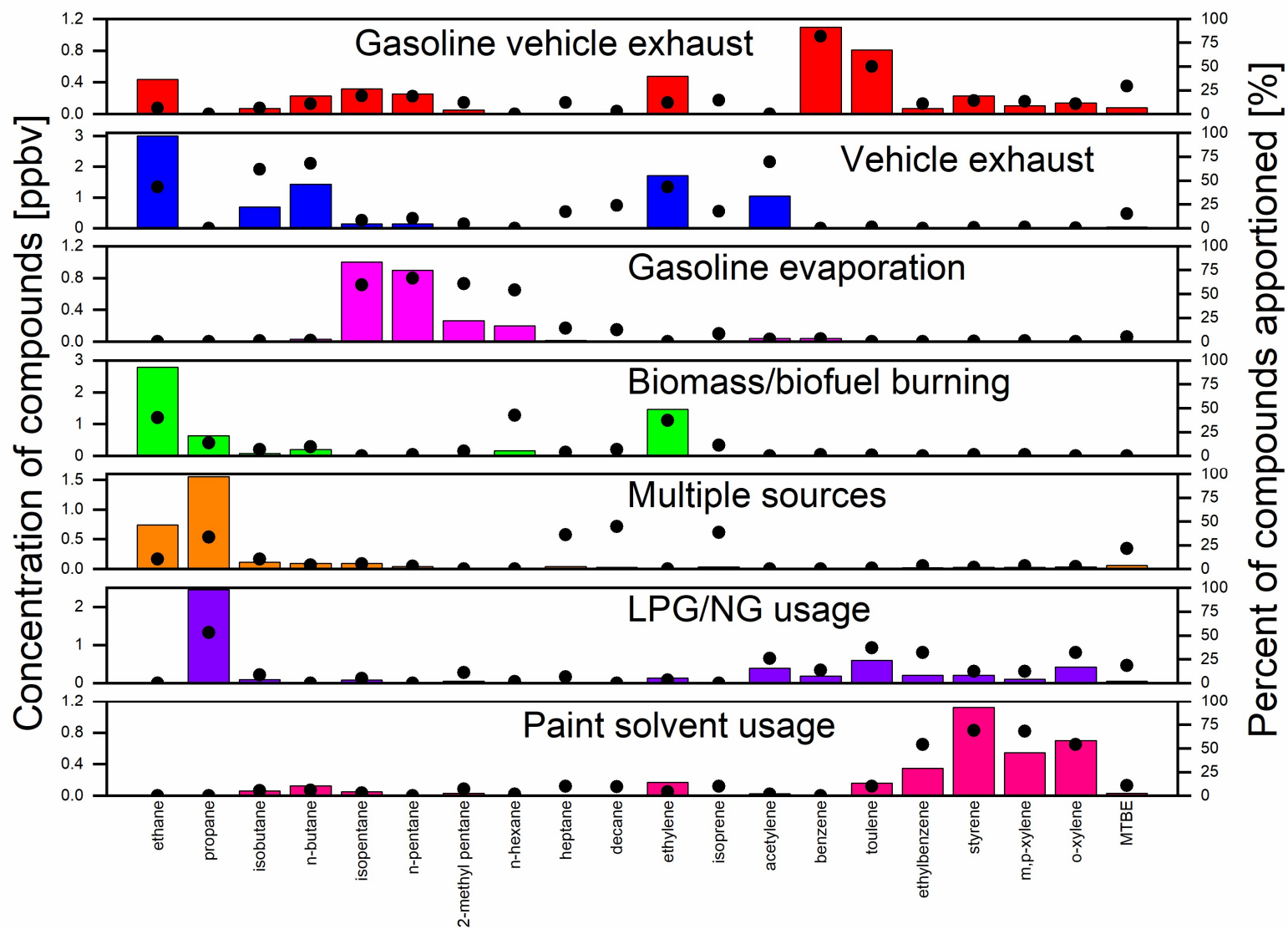
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1029 **Figure S1: Source profile of VOCs during summer in Nanjing industrial area**



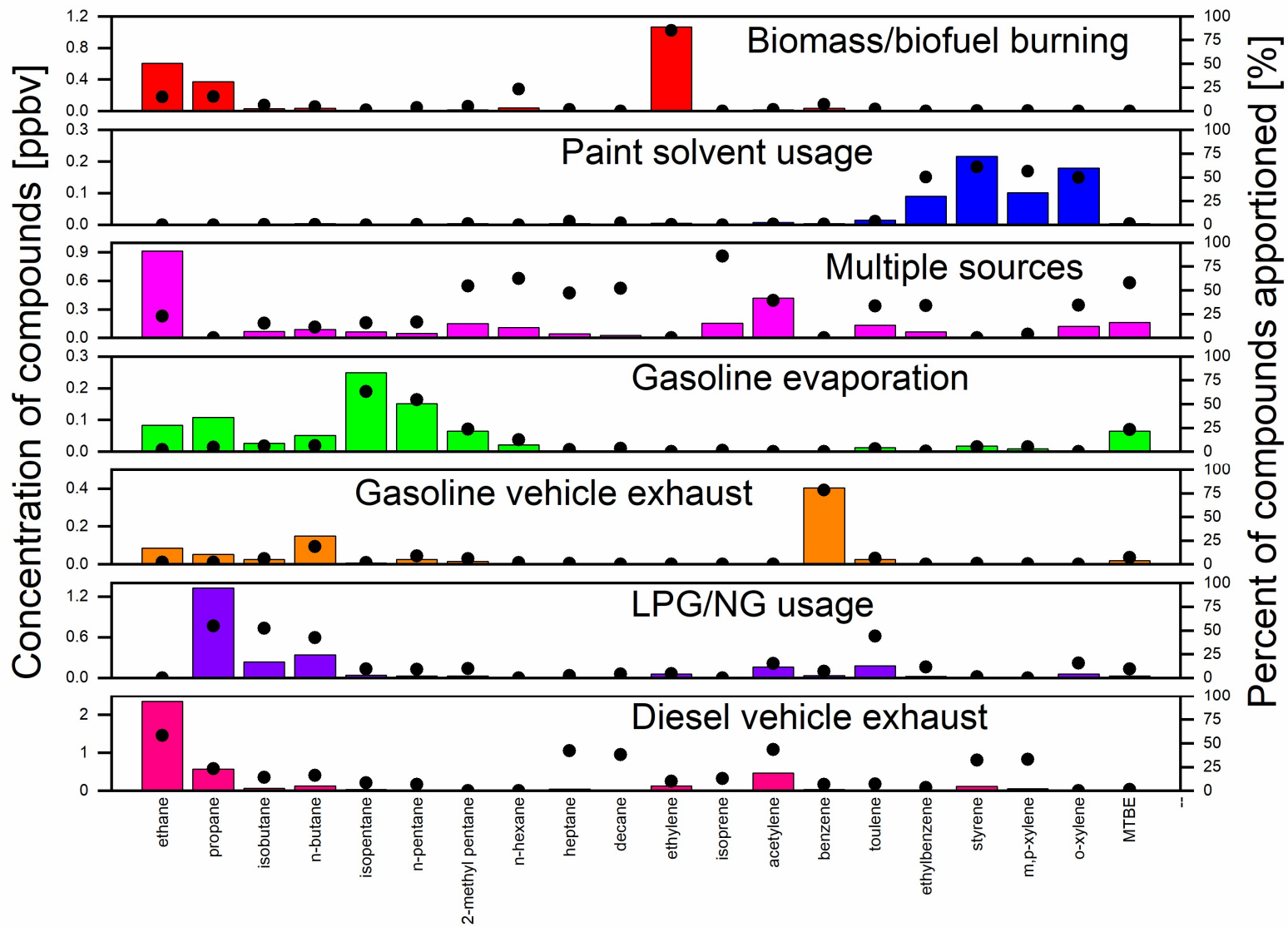
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1031 **Figure S2: Source profile of VOCs during autumn in Nanjing industrial area**



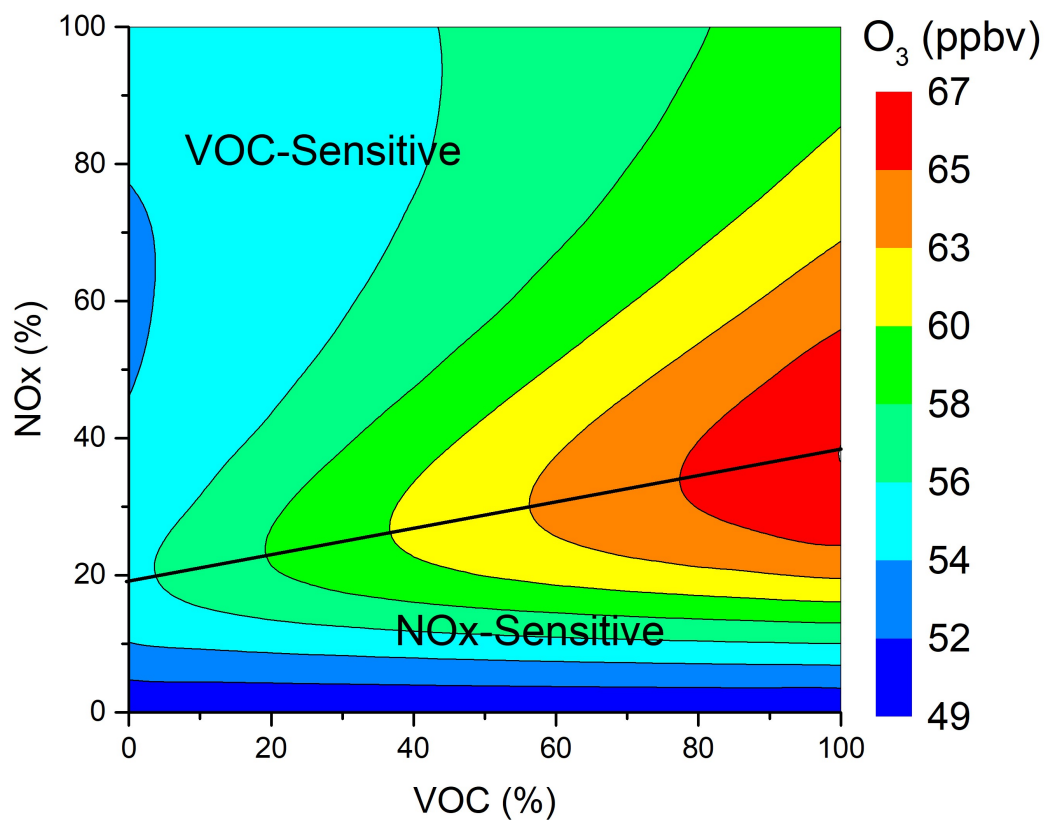
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1033 **Figure S3: Source profile of VOCs during winter in Nanjing industrial area**



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1035 **Figure S4: Source profile of VOCs during spring in Nanjing industrial area**



**Figure S5: O<sub>3</sub> isopleth diagram on a high O<sub>3</sub> episode day (July 29 2018) in Nanjing industrial area.**

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# Authors' response to referee 3

The authors are grateful to the anonymous referee #3 for his/her constructive comments and suggestions. Here, we present the response for each of the comments. The revised manuscript and supplement with tracked changes can be found at the end of the document.

5        **1. PMF analysis-**

- **PMF was performed separately on each season. Was there enough data in during 2020 to draw meaningful conclusions? It is difficult to tell the duration of measurements from figure 1.**

10        Authors' response: We presented 20 days data (464 data points) for the spring season in 2020 (April 15 - May 4). Due to the instruments failure, we could not continue the measurements for a longer period. Still, PMF model analysis on 464 hourly data points is enough to draw a meaningful conclusion.

- **Do the PMF results indicate that there is seasonality in source sector emissions, or are the fingerprints consistent?**

15        Authors' response: Yes, the PMF results indicate that there is seasonality in source sector emissions, for instance, (i) contribution from gasoline evaporation was much higher in summer than those in autumn and spring (ii) biogenic source was clearly distinguished in  
20        summer (due to high emission), but mixed with other sources during the rest of the seasons.

- **Why was an 8 factor solution chosen (v. 7 v. 6 factors, etc)?**

25        Authors' response: The reason for choosing 7 to 8-factor solution has been mentioned in the material and methods (section 2.2) of the revised manuscript (added at the end of this document).

- **The supplemental figures are difficult to read due to the number of species included in the figure. It should be noted which axis should be read with each dataset.**

30        Authors' response: Both the issues have been solved in the revised manuscript.

- **As noted by reviewer 2, the results are odd (e.g., biogenic isopentane; propane from**

solvents). **The revised and trimmed-down PMF submitted in response to the reviewer still has these oddities.**

35 Authors' response: It has been solved in the revised manuscript added below. For instance, isopentane is assigned to gasoline evaporation and propane is assigned to LPG/NG usages sources.

## 2. PSCF analysis-

40 • **I do not think this method is ubiquitous enough to merit the brevity of explanation. For example, what do the colors mean in figure 5? What does the impact of a 24 v. 48 v. 72 h back-trajectory have on the analysis? Does this assume that VOCs have the same lifetime as the back-trajectory?**

45 Authors' response: PSCF has been widely used to determine potential source areas of particulate pollutants, and in recent years, it has been also used to determine the potential source areas of VOCs (Hao et al., 2019; Ming et al., 2017; Sun et al., 2015; Song et al., 2018; Hui et al., 2019). The PSCF value itself is a probability (from 0 to 1) indicating the probability of being a possible source of a pollutant (e.g. colorbar in Figure 5). This probability is calculated by dividing the number of trajectories with a high air pollutant concentration (higher than the mean TVOCs concentration in our case) by the total number  
50 of trajectories at the receptor. Areas in Figure 5 with higher PSCF values indicate that the corresponding region is a potential source region of severe VOC pollution. We generally choose backward trajectories of different duration depending on the studied species, for example, if it is an inert pollutant such as Black Carbon, a backward trajectory of 120h or longer will be chosen. The biggest difference between 24h vs 48h vs 72h analysis is that we  
55 assume different atmospheric lifetimes of the pollutants, so that the potential source area obtained is also different, e.g., the range of 72h is larger and the high probability range (high PSCF value) is larger too, but if the pollutants themselves are not able to remain for 72h, there will be some bias in the estimation of the potential source area.

60 • **It is not clear what useful/new information is derived from this analysis. The main results of this analysis (line 428-430) seems to be that the VOCs measured at the site**

**come primarily come from industries located near the site. Would there be a reason to think otherwise?**

65 Authors' response: Long-distance transport of VOC pollution to the receptor site is not uncommon (Derstroff et al., 2017; Patokoski et al., 2015). So, it is not always the case that the VOC should come to the measurement site from the nearby areas.

70 **3. OFP/EKMA/RIR**

**• Discussion of wintertime OFP seems unusual, as photochemical ozone production in the winter is not a primary concern.**

75 Authors' response: The OFP analysis has already been removed following the suggestion of referee #2.

**• There are not enough details in the description of the F0AM model. For example: Which VOCs were constrained (not all are in MCM)?**

80 Authors' response: More information has been added in the methods, and the list of constrained VOCs has been added in Table S1.

**Other comments-**

85 **• I find the title “High Contributions of Halohydrocarbon and Aromatic Compounds to Emissions and Chemistry of Atmospheric VOCs in Industrial Area” to be misleading. Halocarbons do not contribute significantly to either SOA or ozone chemistry. Neither halocarbons nor aromatics dominate calculated OFP in the summer (Figure 5).**

90 Authors' response: The title has been modified in the revised version.

**• It seems a major conclusion (line 431) is that industries and vehicles should have the most priority in reducing emissions. Nearly all anthropogenic VOCs in this area could**

95 **be classified as industry/vehicles, so this conclusion seems too vague to be meaningful. Is it a new finding?**

Authors' response: This part has been modified in the revised manuscript. According to the revised PMF model analysis vehicle-related emissions were the major VOC sources in the industry affected area.

100 **• It is unusual to see the notation KOH (typically lowercase/supscripts are for kinetics, uppercase for equilibrium reactions).**

Authors' response: Amended.

105 **• There are no units in supplemental tables.**

Authors' response: Units have been added in the supplemental tables.

110 **• It is not clear how to interpret numbers given in lines 272 (e.g., 0.9-2 (1.4 +/- 0.3))**

115 Authors' response: It was the range and mean value of toluene to benzene ratio in ppbv/ppbv unit. The toluene to benzene ratio analysis section has already been removed following the suggestion of referee #2.

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**Measurement report: High Contributions of Halocarbon and Aromatic Compounds to  
Emissions and Chemistry of Atmospheric VOCs in Industrial Area**

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**Abstract.** Volatile organic compounds (VOCs) are key components for tropospheric chemistry and air quality. We investigated ambient VOCs in an industrial area in Nanjing, China for about 1 month in winter, spring, and summer and 3 months in autumn from between July 2018 ~~to and~~ May 2020. The total VOCs (TVOCs) concentration was 59.8±28.6 ppbv during the investigation period. About twice TVOCs concentrations were observed in autumn (83±20 ppbv) and winter (77.5±16.8 ppbv) seasons compared to those in spring (39.6±13.1 ppbv) and summer (38.8±10.2 ppbv). Unlike in previous studies in Nanjing, oxygenated-VOCs (OVOCs) and halocarbons were not measured, the observed TVOCs was about 1.5 and 3 times higher than those previously reported in the same study area and a nonindustrial suburban area in Nanjing, respectively the current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2 folds higher than the one reported in the nonindustrial suburban area in Nanjing. Observed TVOCs concentrations ~~were was~~ similar to ~~those the one~~ in the metropolitan city Beijing, ~~and but,~~ 1.3 fold smaller than the one reported in Shanghai, Observed TVOCs concentration was similar to those in Lanzhou, Chengdu, Tokyo, and Xi'an, however, it was about 1.5-~~3~~-1.7 folds higher than those in ~~Lanzhou,~~ Wuhan, Tianjin, ~~and~~ Ningbo, ~~Chengdu, London, Los Angeles, and Tokyo.~~ Due to the industrial influence,

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halocarbons ( $14.3 \pm 7.3$  ppbv, 24%) VOC-group was the second largest contributor to the TVOCs after alkanes ( $21 \pm 7$  ppbv, 35%), which is in contrast with the previous studies in Nanjing and also in almost other regions in China. Relatively high proportions of haloalkanes and aromatics were observed in autumn (25.7 and 19.3%, respectively) and winter (25.8 and 17.6%, respectively) compared to those in summer (20.4 and 11.8%, respectively) and spring (20.3 and 13.6%, respectively). According to the potential source contribution function (PSCF), short-distance transports from the surrounding industrial areas and cities were the main reason for high VOC concentration in the study area. According to positive matrix factorization (PMF) model results, ~~industry-related sources (23–47%) followed by~~ vehicle-related emissions (24.3–34.4%) contributed the major portion to the ambient VOC concentrations. ~~Whereas aromatics~~ Aromatics followed by alkenes were the top contributors to the loss rate of OH radicals ( $L_{OH}$ ) (37 and 32%, respectively), ~~alkenes followed by aromatics contributed most to the ozone formation potential (OFP) (39 and 28%, respectively). Besides, the aromatics VOC group was also the major contributor to the secondary organic aerosol potential (SOAP) (97%).~~ According to the empirical kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis in assistance with a photochemical box model, the study area was in the VOC-sensitive regime for ozone ( $O_3$ ) formation during all the measurements seasons. Therefore, mainly alkenes and aromatics emissions chiefly from ~~industries and~~ automobiles should be reduced to decrease the secondary air pollution formation in the study area.

## 1 Introduction

Air pollution characterized by severe ozone ( $O_3$ ) and haze pollution is a big problem in urban and industrial areas in China (He et al., 2019; Hui et al., 2018; Tan et al., 2018; Jia et al., 2016; Feng et al., 2016; Hui et al., 2019). In recent years,  $O_3$  concentration above the national standard, and severe haze events are frequently reported (He et al., 2019; Hui et al., 2019; Sheng et al., 2018; Feng et al., 2016; Tan et al., 2018; Jia et al., 2016). As a precursor of  $O_3$  and secondary organic aerosol (SOA), volatile organic compounds (VOCs) are largely responsible for the severe air pollution in China (Song et al., 2018; Hui et al., 2019; Hui et al., 2018; He et al., 2019). Unfortunately, anthropogenic VOC emissions have been increasing over the last 2 decades in China and it is expected to do so in the future (Mozaffar & Zhang, 2020, and references therein).

Atmospheric VOC has plenty of sources; it can be emitted from various anthropogenic and biogenic sources. Besides, it can also be formed in the atmosphere. Anthropogenic VOC sources mainly include industrial emission, vehicle exhaust, solvent usages, biomass burning, and fuel evaporation. On the other hand, vegetation is the main biogenic sources of VOC. In developed areas in China, vehicle exhaust and industrial emission are the 2 major VOC sources (He et al., 2019; Hui et al., 2018; Hui et al., 2019; Mo et al., 2017; Song et al., 2018; An et al., 2014; Mozaffar & Zhang, 2020). Whereas vehicle-related sources are more dominant in the North China Plain (NCP), Central China (CC), and Pearl River Delta region (PRD), industry-related sources are more influential in the Yangtze River Delta (YRD) area (Zhang et al., 2017; Meng et al., 2015; Sun et al., 2019; He et al., 2019; Zhang et al., 2018; An et al., 2017; Mozaffar & Zhang, 2020; Shao et al., 2016). Alkanes, Alkenes, aromatics, oxygenated-VOCs (OVOCs), and halocarbons are the most common VOC-groups in the atmosphere (Hui et al., 2019; Hung-Lung et al., 2007; Song et al., 2018; Tiwari et al., 2010; He et al., 2019; Na et al., 2001; Hui et al., 2018). VOC concentration and composition changes depending on seasons, for example, the contribution from biogenic and solvent utilization increases in summer, and contribution from combustion sources increases in winter (Mo et al., 2017; Song et al., 2018; An et al., 2014). The chemical reactivity of VOC depends on its chemical composition, for instance, alkenes and aromatics are generally more reactive than alkanes (Carter, 2010). To understand the chemical reactivity ~~and secondary product formation ability~~ of VOCs, analysis of OH radical loss rate ( $L_{OH}$ ), ~~ozone formation potential (OFP), and secondary organic aerosol potential (SOAP) are~~ is commonly used (Song et al., 2018; He et al., 2019; Hui et al., 2018); ~~Hui et al., 2019~~.

Industries are an important source of VOC, and different reactive and hazardous VOCs emissions from industries are already reported in different areas on earth (Zhang et al., 2018; Na et al., 2001; Hung-Lung et al., 2007; Yan et al. 2016; Tiwari et al., 2010; Shi et al., 2015; Zhang et al., 2018b). For instance, Zhang et al. (2018) reported a high concentration of alkanes (82%) and lifetime cancer risk of different aromatics and halocarbons in a petroleum refinery in Guangzhou, China. A high concentration of OVOCs (63%) was observed in an industrial area in Ulsan, Korea (Na et al., 2001). Hung-Lung et al.(2007) mentioned a high concentration of aromatics in an industrial area in Taiwan. A high concentration of halocarbons (49%) was observed in an iron smelt plant in Liaoning, China (Shi et al., 2015). Zhang et al. (2018) mentioned a high concentration of alkanes (42%) and aromatics (20%) in a petrochemical and

other industries affected area in Shanghai, China. High concentrations of aliphatic and aromatics were observed in a petrochemical industrial area in Yokohama, Japan (Tiwari et al., 2010).  
255 Therefore, VOC composition varied among the industries/industrial areas in different regions. Mostly short-term investigations were performed to characterize the VOCs in industry-affected areas. In the current study, we carried out a comprehensive investigation on VOC in an industrial area in Nanjing for about 1 month in winter, spring, and summer and 3 months in autumn between July 2018 and May 2020. Nanjing is located in the YRD region which is mainly  
260 affected by industrial emissions. Several VOC investigations have already been performed in the Nanjing industrial area but OVOCs and halocarbons were not measured in those studies (An et al., 2017; An et al., 2014). However, OVOCs and halocarbons are already mentioned as one of the highest concentrated VOC-groups in other industrial regions (Na et al., 2001; Shi et al., 2015). In the current study area, a high concentration of alkanes (45%) and alkenes (25%) were  
265 observed in a previous investigation (An et al., 2014). Besides the incomplete VOC measurements, O<sub>3</sub> formation sensitivity to its precursors was not investigated properly using a photochemical box model in Nanjing. Moreover, source apportionment of VOCs was not conducted for different seasons of a year.

270 In the current study, we report the variations in concentrations and compositions of VOC during the observation period. We present the possible source areas and potential sources of VOC based on potential source contribution function (PSCF) and positive matrix factorization (PMF) model analysis. We also present the contributions of different sources to ambient VOC during the measurement period. We report the chemical reactivity ~~and secondary product formation~~  
275 ~~capacity~~ of the VOC using L<sub>OH</sub>, ~~OFP, and SOAP analysis~~. We also present the sensitivity analysis of O<sub>3</sub> formation using empirical kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis. Therefore, this study provides valuable information to the scientific community and policymakers.

## 2 Material and Methods

### 280 2.1 Sampling Site Description, Gases Analysis, and Meteorology Data

Field measurements were carried out ~~for about 1 month in winter, spring, and summer and 3 months in autumn from-between~~ July 2018 ~~to-and~~ May 2020 at Nanjing University of Information Science and Technology (32.1°N, 118.4°E), which is located in an industrial area in Nanjing, China. The sampling site was on the rooftop of a building (~20 m). The sampling site  
285 is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high traffic roads, and residential areas. A detailed description of the sampling site can be found elsewhere (Mozaffar et al., 2020).

We analysed ambient air VOCs using an online GC-FID/MS instrument (AC-GCMS 1000, Guangzhou Hexin Instrument Co., Ltd., China). FID detector analysed C2-C5 VOCs and MS  
290 analysed C6-C12 VOCs. The instrument analysed one sample at every hour. During the investigation period, we inspected and calibrated the instrument regularly to ensure the accuracy of the data. We monitored the O<sub>3</sub> concentrations using a 49i O<sub>3</sub> analyser (Thermo Fisher Scientific Inc., USA), NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations were measured using a 42i NO-NO<sub>2</sub>-NO<sub>x</sub> analyser (Thermo Fisher Scientific Inc., USA), SO<sub>2</sub> concentrations were followed using a  
295 43i SO<sub>2</sub> analyser (Thermo Fisher Scientific Inc., USA), and CO concentrations were measured using a 48i CO analyser (Thermo Fisher Scientific Inc., USA). We also measured temperature and relative humidity, wind speed, wind direction, and solar radiation by HMP155 (Vaisala, Finland), 010C (Met One Instruments, Inc., USA), 020CC (Met One Instruments, Inc., USA), and CNR4 (Kipp & Zonen, The Netherlands) analysers, respectively. A detailed description of  
300 the instrumentation, sampling procedure, analysis, quality control, and calibration procedure can be found elsewhere (Mozaffar et al., 2020).

### 2.2 Positive Matrix Factorization (PMF) model and Potential Source Contribution Function (PSCF)

We used the positive matrix factorization (PMF) model (US Environmental Protection Agency, USEPA, version 5.0) for the source apportionments of VOCs. A detailed description of the  
305 model can be found elsewhere (Hui et al., 2019; Song, ~~Tan, Feng, Qu, Liu,~~ et al., 2018). In this study, we used ~~620~~ potential VOC tracers (Fig. S1 - S4) in the PMF model to analyse the VOC sources for different seasons. The error fraction was set to 20% for the sample data uncertainty

estimation. We explored the PMF factor number from 4-8 to determine the optimal number of sources. Finally, we decided to choose an 7 to 8-factor solution ( $Q_{\text{true}}/Q_{\text{robust}} \sim 1.0$ ) for different seasons as  $Q_{\text{true}}/Q_{\text{robust}}$  was  $\sim 1.0$ ,  $Q_{\text{true}}/Q_{\text{expected}}$  was ranging from 0.99-1.45 (Hui et al., 2019), and strong correlations (0.7-0.8) were observed between the concentrations extracted from the model and the observed concentrations of each compounds (He et al., 2019).

We used the potential source contribution function (PSCF) to locate possible source areas of VOCs for different seasons during the investigation period. We used Zefir analysis software to do the PSCF analysis and the Hysplit4 model to cluster the backward trajectories (Petit et al., 2017). Backward trajectories in the sampling site were estimated using the data provided by the National Centers for Environmental Prediction (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1>). We estimated 24-72 hr backward trajectories 24 times a day arriving at 500 m above the ground surface using the hysplit4 model. For the PSCF analysis, we divided the geographic region covered by the back trajectories into an array of  $0.1^\circ \times 0.1^\circ$  grid cells and used the mean TVOCs concentration as the VOC reference value. More details about the PSCF analysis can be found in previous studies (Chen et al., 2018).

### ~~2.3 OH radical loss rate ( $L_{\text{OH}}$ ), Ozone formation potential (OFP), and Secondary organic aerosol potential (SOAP)~~

To evaluate the daytime photochemistry of VOCs, we estimated their OH radical loss rate ( $L_{\text{OH}}$ ). The following equation was used to estimate the  $L_{\text{OH}}$  ( $\text{s}^{-1}$ ) (Zhang et al., 2020).

$$L_{\text{OH}} = [\text{VOC}]_i \times K_{\text{OH}i} \quad (1)$$

Where  $[\text{VOC}]_i$  is the concentration of VOC species  $i$  ( $\text{molecule cm}^{-3}$ ),  $K_{\text{OH}i}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is the reaction rate constant of  $i$  VOC with OH radical. The  $K_{\text{OH}}$  values for the VOCs are collected from Carter (2010) (Table S1).

~~The Ozone formation potential (OFP) of the VOCs is their maximum contribution to the  $\text{O}_3$  formation (Hui et al., 2018a). The OFP (ppbv) of the VOCs was estimated using the following equation:~~

$$\text{OFP} = [\text{VOC}]_i \times \text{MIR}_i \quad (2)$$

Where  $MIR_i$  is the maximum incremental reactivity of the  $i$  VOC. The MIR values for the VOCs are also collected from Carter (2010) (Table S1).

The contribution of VOCs to the formation of secondary organic aerosol is estimated by secondary organic aerosol potential (SOAP) (Song et al., 2018). We estimated the SOAP (ppbv) of VOCs using the following equation.

$$SOAP = [VOC]_i \times SOAP_i^p$$

(3)

Where  $SOAP_i^p$  is the SOA formation potential of the  $i$  VOC on a mass basis relative to toluene (Derwent et al., 2010). In this study, the  $SOAP_i^p$  factors of the VOCs are collected from Derwent et al. (2010) (Table S1).

#### 2.4 Empirical Kinetic Modelling Approach (EKMA) and Relative Incremental Reactivity (RIR)

The empirical kinetic modelling approach (EKMA) is a well-known procedure to develop the O<sub>3</sub> formation reduction strategy by testing the relationship between ambient O<sub>3</sub> and its precursors (He et al., 2019; Hui et al., 2018; Vermeuel et al., 2019; Tan et al., 2018). In this study, we used the Framework for 0-D Atmospheric Model (F0AM v 3.2, Wolfe et al., 2016), a photochemical box model run by Master Chemical Mechanism (MCM) v3.2 chemistry (Jenkin et al., 1997; 2003, 2015; Saunders et al., 2003), to get the data for the EKMA isopleth. The FOAM-MCM box model can simulate 16940 reactions of 5733 chemical species. The box model was run using the VOCs and gas concentrations and the meteorological data as input. 61 VOCs were constrained in the model as all the observed VOC species reactions are not included in MCM. These constrained VOCs are listed in Table S1. To generate the O<sub>3</sub> isopleth from the model simulated data, a total of 121 reduction scenarios (11 NO<sub>x</sub> × 11 VOC) were simulated and the maximum O<sub>3</sub> produced in each scenario was saved.

The O<sub>3</sub> formation sensitivity to its precursors' concentrations can also be assessed by the relative incremental reactivity (RIR, Cardelino & Chameides, 1995). We also utilized the FOAM-MCM box model data to estimate the RIR. The RIR is simply defined as the percentage change in O<sub>3</sub> formation per percentage change in precursor's concentration. In this study, we reduced the precursor's concentration by 10% for the RIR estimation. The RIR was estimated using the following equation.



$$RIR(X) = \frac{[P_{O_3}(X) - P_{O_3}(X - \Delta X)] / P_{O_3}(X)}{[\Delta X] / [X]} \quad (2)$$

Where [X] is the observed concentration of a precursor X, [ΔX] is the changes in the concentration of X. P<sub>O<sub>3</sub></sub>(X) and P<sub>O<sub>3</sub></sub>(X- ΔX) are the simulated net O<sub>3</sub> production with the observed and the reduced concentration of the precursor X, respectively.

### 3 Results and discussion

#### 3.1 Overview of the metrological conditions and air pollutants concentrations

The time series of the hourly inorganic air pollutants, meteorological parameters, and TVOC concentrations estimated with all the measured VOCs and without halocarbons are shown in Fig. 1. The discontinuity of the time series data is due to the failure of the instruments. The measured data from July to August 2018, September to November 2018, December 2018 to January 2019, and April to May 2020 are termed as summer, autumn, winter, and springtime data, respectively. Overall, the observed temperature and solar radiation gradually decreased from summer to winter and increased back to the summertime level in spring. The temperature ranged between -5.7 and 41.4 °C during the measurement period. The relative humidity values varied from 18 to 100% and high values were generally observed in winter and autumn. During the observation period, wind speed ranged between 0.1 and 7.5 ms<sup>-1</sup>. Wind prevailed at the sampling site from many directions during the measurement periods; more details about the wind direction will be discussed in Sect.3.3.2. The O<sub>3</sub> and NO<sub>x</sub> concentrations varied from 2 to 160 ppbv and 0.4 to 90 ppbv, respectively. Whereas high O<sub>3</sub> concentrations (>80 ppbv) were observed in summer and spring, high NO<sub>x</sub> concentrations were measured in winter and at the end of autumn. The CO and SO<sub>2</sub> concentrations ranged from 83 to 3398 ppbv and 0.5 to 21 ppbv, respectively. Generally, high concentrations of CO and SO<sub>2</sub> were observed in winter and spring. The measured NO and NO<sub>2</sub> concentrations varied from 0.4 to 51 ppbv and 1 to 79 ppbv, respectively. In general, the high NO and NO<sub>2</sub> concentrations were observed in autumn and winter. The TVOCs concentrations estimated with all the measured VOCs varied between 9 and 393 ppbv during the observation period and the high values were measured in autumn and winter. More details about the abovementioned parameters will be discussed in the following section.

### 3.2 Concentration and composition of VOCs

In total 100 VOCs were observed in Nanjing industrial area, including 27 alkanes, 11 alkenes, 1 alkyne, 17 aromatics, 31 halocarbons, 12 OVOCs, and 1 other (carbon disulfide) (Table S2).  
400 Ethane ( $5.8 \pm 2.5$  ppbv), propane ( $4.2 \pm 1.5$  ppbv), and ethylene ( $3 \pm 1.6$  ppbv) were the most abundant VOCs in the study area during the observation period. However, we observed season-wise variations in the order of abundant VOC species (Table S2). For instance, acetone was the 3<sup>rd</sup> highest concentrated VOC in spring. The abovementioned 4 VOC species are also frequently mentioned as the most abundant VOCs in different regions in China (Deng et al., 2019; He et al.,  
405 2019; J. Li et al., 2018; Ma et al., 2019). We compared the individual VOC concentrations with the available data presented in recent investigations. The individual VOC concentrations in the current observation were similar to those in the previous investigations in the same study area, however, they were almost twice of those found in a nonindustrial suburban area in Nanjing (Table S2). Some of the differences in comparison to the study performed in nonindustrial suburban area in Nanjing (Wu et al., 2020) may be due to the differences in observation period. The yearly concentrations reported in the study performed in nonindustrial suburban area in Nanjing were probably estimated over a continuous measurement data for a year. However, the yearly concentrations in the current observation were estimated using the data which were not continuously measured during all the days of a year. The autumn time individual VOC  
410 concentrations in the current observation were about 1.4 fold lower than those measured in Beijing during October-November (Li et al., 2015). The winter time individual VOC concentrations in the current observation were also about 1.4 fold lower than those measured in  
415 and Shanghai during November-January (Zhang et al., 2018), ~~but~~ But, the yearly individual VOC concentrations in the current observation were similar to those measured in Guangzhou during  
420 June-May (Zou et al., 2015). During the observation period, the concentrations of different VOC-groups were in the order of alkanes ( $21 \pm 7$  ppbv, 35%)> halocarbons ( $14.3 \pm 7.3$  ppbv, 24%)> aromatics ( $9.9 \pm 5.8$  ppbv, 17%)> OVOCs ( $7.5 \pm 1.9$  ppbv, 13%)> alkenes ( $5 \pm 1.9$  ppbv, 8%)> alkynes ( $1.4 \pm 0.3$  ppbv, 2%)> others ( $0.5 \pm 0.2$  ppbv, 1%). However, we noticed relatively higher proportions of OVOCs (14% and 18%) than the aromatics (12% and 14%) in summer  
425 and spring (Fig. 2c & f). The relatively higher contribution of OVOCs in summer and spring could be related to the biogenic emissions (e.g. acetone, MEK from trees). Indeed, the relative contribution of acetone and MEK to the TVOCs were higher in summer and spring than those in

autumn and winter (Table S2). Huang et al. (2019) reported that the industries, biogenic emissions, and secondary formation are the main source of OVOCs in southern China. Relatively high proportions of halo-hydrocarbons and aromatics were observed in autumn (25.7 and 19.3%, respectively) and winter (25.8 and 17.6%, respectively) compared to those measured in summer (20.4 and 11.8%, respectively) and spring (20.3 and 13.6%, respectively) (Fig. 2f). The high proportions of halo-hydrocarbons and aromatics in autumn and winter could be related to the burning of biomass and fossil fuel for additional heating. Similar to the observation in the current study, the alkane is generally the most abundant VOC group in China (Mozaffar & Zhang, 2020). The relatively high contribution from halocarbons to the TVOCs could be related to the industrial emissions in the study area. In previous studies in an iron smelt plant in Liaoning, China, a high concentration of halocarbons (49%) was observed (Shi et al., 2015). However, halocarbons and OVOCs were not measured in previous investigations in the same study area (An et al., 2014; An et al., 2017; Shao et al., 2016) and also in another suburban area in Nanjing (Wu et al., 2020). Either aromatics or alkenes was mentioned as the second most abundant VOC-group in those studies in Nanjing, which is the 3<sup>rd</sup> and 5<sup>th</sup> most abundant VOC group in the current investigation. In Shanghai, a nearby city, alkanes (42%) and alkenes (26%) were two major VOC-groups and halocarbons and OVOCs were not reported (Zhang et al., 2018). The TVOCs concentration including halocarbons was 59.8±28.6 ppbv over the whole observation period, and relatively higher TVOCs concentrations were measured in autumn (83±20 ppbv) and winter (77.5±16.8 ppbv) compared to those in spring (39.6±13.1 ppbv) and summer (38.8±10.2 ppbv). The TVOCs concentration without halocarbons were 45.4±20.4, 61.7±14.6, 57.4±11.8, 31.6±10.9, and 30.9±8.2 ppbv during the whole observation period, autumn, winter, spring and summer, respectively. About 1.5-times higher TVOCs concentration was observed relative to the previous investigation in the same study area (An et al., 2014; An et al., 2017). Besides, we also found 3-times higher TVOCs concentration compared to the one in a nonindustrial suburban area in Nanjing (Wu et al., 2020). As mentioned before, halo-hydrocarbons and OVOCs were not measured reported in the previous investigation in the same study area (An et al., 2014; An et al., 2017) and in a nonindustrial suburban area in Nanjing (Wu et al., 2020). The current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2 folds higher than the one reported in the nonindustrial suburban area in Nanjing those previous studies in Nanjing, it could be one of the reasons for the relatively high

TVOCs concentration in the current study. Observed autumn ~~time and wintertime~~ TVOCs concentrations ~~including halocarbons were was~~ similar to ~~those the one~~ measured in urban Beijing (86.2 ppbv ~~in autumn during 17-31 October~~) (Li et al., 2015). ~~and Winter time TVOCs concentrations without OVOCs in~~ Shanghai (94.1 ppbv ~~during in winter Nov-Jan~~) was higher than ~~the current observation (70±15.1 ppbv)~~ (Li et al., 2015; Zhang et al., 2018). ~~Similarly,~~ ~~Observed summertime TVOCs concentration was similar to those found in urban Xi'an (42.6 ppbv, estimation includes halocarbons and OVOCs),~~ Wuhan (43.9 ppbv ~~estimation includes halocarbons and OVOCs~~) (Zeng et al., 2018; Sun et al., 2019). ~~Yearly TVOCs concentration including halocarbons and OVOCs was 1.7 folds higher than the one found in Wuhan~~ (Hui et al., 2018b). ~~Besides, yearly TVOCs concentration (37.9 ppbv) without halocarbons and OVOCs was similar to Lanzhou, Chengdu, and Tokyo, however, 1.5 times higher than those reported for Tianjin and Ningbo (Jia et al., 2016; Hui et al., 2018b; B. Liu et al., 2016a; Hoshi et al., 2008; Mo et al., 2017; Song et al., 2018). However, yearly TVOCs concentration was 1.5-3 folds higher than those in Lanzhou, Wuhan, Tianjin, Ningbo, Chengdu, London, Los Angeles, and Tokyo (Jia et al., 2016; Hui et al., 2018; B. Liu et al., 2016a; Mo et al., 2017; Song et al., 2018; von Schneidmesser et al., 2010; Warneke et al., 2012; Hoshi et al., 2008).~~ The diurnal variation of the TVOCs, alkenes, aromatics, halocarbons, OVOCs, and alkanes concentrations showed a double-hump structure (Fig. 2a, b, d, & e). This double-hump pattern indicates the contribution of traffic emission during the rush-hours in the morning and evening. The lowest concentration of the TVOCs and different VOC-groups reached 12:00-16:00. Oppositely, the highest concentration of O<sub>3</sub> reached at that period (Fig. 3). The lowest O<sub>3</sub> concentrations were observed in winter which was consistent with the solar radiations.

### 3.3 Sources of VOCs

#### 3.3.1 Specific Ratios

~~The use of the toluene/benzene (T/B) ratio is one of the simplest ways to preliminary analyse the VOC sources. If the T/B ratio is < 2, the study area is mainly affected by vehicle emissions (Hui et al., 2018, 2019). If the T/B ratio is > 2, the study area is influenced by other sources (e.g. industry, solvent utilization) beside vehicle emissions (Kumar et al., 2018; Niu et al., 2012; Li et al., 2019). Moreover, the T/B ratios are ranged between 0.2-0.6 in coal and biomass burning affected areas (Wang et al., 2009; Akagi et al., 2011). The diurnal variations in T/B ratios during~~

490 different seasons are depicted in Fig. 4 (a, b, c, & d). The mean values of T/B ratios were ranged  
between ~~0.9–2 (1.4±0.3), 1.3–2 (1.7±0.2), 1.1–1.6 (1.4±0.1), and 1.4–2.7 (1.9±0.3)~~ during  
summer, autumn, winter, and spring, respectively. As the mean values of T/B ratios were around  
2, the study area could be mainly affected by vehicle emissions. The double-hump pattern in the  
diurnal variations in T/B ratios also indicates that the rush-hour traffic had a significant influence  
on the VOCs concentrations in the study area. Besides, the 75<sup>th</sup> percentiles of T/B ratios were  
495 above 2 most of the investigation periods, therefore, the study area could also be influenced by  
industrial emissions.

Figure 4 (e, f, g, & h) shows the ratios of different alkanes and aromatics to acetylene. Acetylene  
is a tracer of combustion sources, the ratios of different alkanes and aromatics to acetylene are  
used to comprehend the contribution of other sources to combustion sources. The mean ratios of  
500 propane, n-butane, and i-butane to acetylene were around ~~2.0–4.0, 0.7–1.6, and 0.4–0.8,~~  
respectively during all the seasons, which were smaller than those (11.5, 1.8, and 2.6,  
respectively) observed in Guangzhou city centre, which was affected by liquefied petroleum gas  
(LPG) emissions (Zhang et al., 2013). Therefore, LPG usages probably contributed a little  
fraction to the alkanes in the study area. The mean ratios of benzene, toluene, C8-aromatics, and  
505 C9-aromatics to acetylene were around ~~0.3–1.0, 0.4–1.1, 0.2–0.6, and 0.1,~~ respectively during all  
the seasons. The observed ratios of benzene and toluene to acetylene were much higher than  
those found in Jianfeng Mountains in Hainan (0.2 and 0.1, respectively) but comparable to those  
measured in urban Guangzhou (0.4 and 0.4–1, respectively) (Tang et al., 2007). Besides, the  
observed ratios of C8-aromatics and C9-aromatics to acetylene were comparable to traffic  
510 emission influenced urban Guangzhou (0.68 and 0.2, respectively) and Wuhan (0.5 and 0.2,  
respectively) (Zhang et al., 2013; Hui et al., 2018). Therefore, vehicle exhaust probably  
contributed significantly to the aromatics in the study area.

### 3.3.2 Potential Source Contribution Function (PSCF)

Besides the local sources, both the long and short distance transport of air mass could bring  
515 VOCs to the study area. Figure 5 shows the wind cluster and PSCF analysis results for different  
seasons. During summer, the major air masses ~~were~~ was short-distance transports from the  
southwest (4044%) direction and two long distance transports from southeast (3931 and 25%)  
directions. ~~A minor air mass (21%) was transported from the east direction.~~ High PSCF values

were in the nearby south~~west, and~~ southeast, ~~and east~~ directions; therefore, VOC pollution in the study area was mainly affected by the short-distance transport from the south and east directions. During autumn, the dominant air masses were short-distance transport from the ~~northeast~~ northwest (5935%) and long distance transport from the north~~west (3034%)~~ directions. However, according to the PSCF analysis, VOC pollution was mainly influenced by the short distance transport from the south ~~and east~~ directions. During winter, short-distance transports from the ~~northeast (46%) and~~ northwest (3752%) directions ~~were was~~ the major incoming air masses to the study area. According to the PSCF values, the short-distance air masses from the south and ~~east-north~~ directions were mainly transported VOC to the receptor site. During spring, air mass was mainly transported from the ~~southwestern-north (4950%) and eastern-southwest (3032%)~~ directions. A minor long distance air mass transported from the northwest (18%) direction. Atmospheric VOCs to the study area were mainly transported by these ~~two~~ air masses mostly from the nearby areas. Overall, the high PSCF values were concentrated around the measurement site, therefore, short distance transports from the surrounding areas and cities were the main reason for the high VOC concentration. The above conclusion perfectly makes sense as the sampling site is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high traffic roads, and residential areas.

### 3.3.3 PMF Model Analysis

~~Differences were observed among the source profiles of VOCs obtained for different seasons (Sect. S1). For instance, the biogenic source was identified in summer, biomass burning source was distinguished in autumn, and LPG/NG usage source was found in winter and spring. However, industry and vehicle-related VOC sources were identified during all the measurement seasons. According to PMF model results, aromatics were emitted from solvent usages, vehicle, and industry related sources. Besides, industry and combustion processes were the main sources of halocarbons and OVOCs. Moreover, alkanes and alkenes were emitted from vehicle exhaust and fuel usage sources.~~

~~Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, industry related sources contributed to the major portion of the ambient VOC concentrations followed by vehicle emission. Industrial emission accounted for about 32%, 47%,~~

45%, and 23% in summer, autumn, winter, and spring, respectively. The contributions of vehicle emission were about 34%, 26%, 24%, and 27% in summer, autumn, winter, and spring, respectively. The contribution of vehicle emission remained similar during the 4 seasons, however, the contribution of the industrial emission increased in autumn and winter. Previous investigations performed in Beijing, Tianjin, Wuhan, Chengdu, and Shuozhou also found that the industry and vehicle are the two most important VOC sources (Zhang et al. 2017; Liu et al. 2016; Hui et al. 2018; Song et al. 2018) Jia et al., 2016). Besides these two sources, solvent usage (11%, 10%, 10%, and 4%, respectively) and gasoline evaporation (17%, 10%, NA, 6%, respectively) were two important VOC sources during those 4 seasons. Moreover, source contribution from the biogenic source in summer (7%), biomass burning in autumn (7%), LPG/NG usage in winter (11%) and spring (18%), and multiple sources in winter (10%) and spring (23%) was observed.

According to the PMF model analysis, five VOC sources were common during all the measurement seasons. They were biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, and paint solvent usage (Sect. S1). The biogenic source was identified in summer. Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, vehicle-related sources contributed to the major portion of the ambient VOC concentrations. The total contributions of vehicle-related emission were about 39%, 33%, 48%, and 42% in summer, autumn, winter, and spring, respectively. The contributions of biomass/biofuel burning were about 19%, 21%, 17%, and 16.4% in summer, autumn, winter, and spring, respectively. Besides these two sources, LPG/NG usage (18%, 21%, 16%, and 18%, respectively) and paint solvent usage (8%, 12%, 11%, 5%, respectively) were two important VOC sources during those 4 seasons.

### **3.4 Chemical reactivity ( $L_{OH}$ ) and contribution to $O_3$ and SOA formation**

The estimated loss rates of OH radical ( $L_{OH}$ ) with VOCs were about 2-fold high in autumn ( $13.7 \text{ s}^{-1}$ ) and winter ( $13.5 \text{ s}^{-1}$ ) compared to those in summer ( $7 \text{ s}^{-1}$ ) and spring ( $7.5 \text{ s}^{-1}$ ) (Fig. 7 a). The relatively high  $L_{OH}$  values in autumn and winter were due to the relatively high VOC concentrations in those seasons (Fig.2). The average  $L_{OH}$  value was  $10.4 \pm 3.6 \text{ s}^{-1}$  over the four seasons. It was in a similar range with the values determined in Guangzhou ( $10.9 \text{ s}^{-1}$ ), Chongqing ( $10 \text{ s}^{-1}$ ), Xian ( $1.6\text{-}16.2 \text{ s}^{-1}$ ), and Tokyo ( $7.7\text{-}13.4 \text{ s}^{-1}$ ), however, higher than the values estimated

in Shanghai ( $2.9\text{-}5\text{ s}^{-1}$ ,  $6.2\text{ s}^{-1}$ ) and Beijing ( $7\text{ s}^{-1}$ ) (Tan et al., 2019; Zhu et al., 2019; Yoshino et al., 2012; Song et al., 2020). While alkene was the highest contributor to the  $L^{\text{OH}}$  in summer ( $3\text{ s}^{-1}$ , 43%) and spring ( $2.6\text{ s}^{-1}$ , 35%), aromatic was the maximum contributor in autumn ( $6.9\text{ s}^{-1}$ , 50%) and winter ( $5.9\text{ s}^{-1}$ , 44%) (Fig. 11 a & d). An increase in the OH loss rate by OVOCs was observed in spring (17%) compared to the other seasons (10, 8, and 9% in summer, autumn, and winter, respectively). Over the four seasons, the contribution of VOC-groups to  $L_{\text{OH}}$  exhibited the following trend: aromatics > alkenes > alkanes > OVOCs > halocarbons. Similar to the current study, aromatic is also mentioned as the maximum contributors to  $L_{\text{OH}}$  in different regions in China, however, the alkene is generally reported as the top contributor to  $L_{\text{OH}}$  (Zhang et al., 2020; Zhao et al., 2020; Hui et al., 2018; Song et al., 2020). Figure 7 also shows the top 10 VOCs contributing to  $L_{\text{OH}}$  for different seasons. Whereas isoprene was the highest contributor to  $L_{\text{OH}}$  in summer, styrene was the largest contributor in autumn and winter. On the other hand, naphthalene was the main contributor to  $L^{\text{OH}}$  in spring. Overall, styrene, naphthalene, ethylene, and isoprene were the main contributor to  $L_{\text{OH}}$  in the study area. In previous studies in China, these compounds are also mentioned as one of the highest contributors to  $L_{\text{OH}}$  (Zhao et al., 2020; Hui et al., 2018; Song et al., 2020).

~~The estimated  $\text{O}_3$  formation potential (OFP) of VOCs were about 2 times high in autumn (170.8 ppbv) and winter (175.4 ppbv) relative to those in summer (86.2 ppbv) and spring (82.8 ppbv) (Fig. 8 a). The average OFP value was  $128.8 \pm 51.2$  ppbv during the measurement period. The springtime OFP was similar to the one estimated in Beijing (80 ppbv) (Li et al., 2015). The summertime OFP was about 1.5 times higher than the one in Xi'an (Song et al., 2020), but, about 1.4-2 folds lower than those found in Shanghai (Liu et al., 2019). The average OFP was about 1.5 times higher than the one in Wuhan (Hui et al., 2018). Whereas alkene was the major contributor to OFP in summer (37.4 ppbv, 43%), winter (72.8 ppbv, 41%), and spring (31.6 ppbv, 38%), aromatics contributed the most to OFP in autumn (62.7 ppbv, 37%) (Fig. 12 a & d). During the measurement period, the contribution of VOC-groups to OFP showed the following trend: alkenes > aromatics > alkanes > OVOCs > halocarbons. The alkene is also mentioned as the top contributor to OFP in Nanjing and the same observation is commonly found in China (An et al., 2014; Hui et al., 2018; Song et al., 2018; Song et al., 2020). The top 10 VOCs contributing to OFP for different seasons are also shown in Fig. 8 (b, c, e, & f). Ethylene was the major contributor to OFP during all the season. Followed by ethylene, cis-1,3-dichloropropene was the~~



610 ~~main contributor to OFP from summer to winter. In spring, propylene was the second most contributors to OFP. Overall, different alkenes were the highest contributor to OFP in the study area. Alkenes are also mentioned as the top contributor to OFP in the previous investigations in Nanjing (An et al., 2014). Therefore, the reduction of these alkenes emissions in the study area could be one of the ways to reduce ambient O<sub>3</sub> concentration.~~

615 ~~The secondary organic aerosol potentials (SOAP) were about 3 times higher in autumn (1422 ppbv) and winter (1269 ppbv) than those in summer (466 ppbv) and spring (398 ppbv) (Fig. 9a). The average SOAP was 889±531 ppbv during the measurement period. The average SOAP was about 2-3 times higher than those estimated in Wuhan and Beijing (Hui et al., 2019; Li et al., 2020). Aromatics was the main contributor to SOAP during all the seasons (95-97%) (Fig. 9 a & d) which was consistent with the observations in Chengdu (Song et al., 2018), Beijing (Li et al., 2020), and Wuhan (Hui et al., 2019). During the measurement period, the contribution of VOC groups to SOAP exhibited the following trend: aromatics > alkanes > alkenes > OVOCs. Styrene, cumene, toluene, benzene, and o-xylene were the major contributor to SOAP during all the season (Fig. 9 b, c, e, & f). Therefore, the reduction of these aromatics emissions in the study area could be one of the ways to reduce ambient SOA concentration.~~

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### 3.5 Sensitivity analysis of O<sub>3</sub> formation

Figure 10 shows the EKMA isopleth diagrams of O<sub>3</sub> for different seasons. In all the diagrams, VOC and NO<sub>x</sub> = 100 % is the base case. The ridgeline divided the diagrams into two regimes, VOC-sensitive (above) and NO<sub>x</sub>-sensitive (below) regimes. For all the seasons, the study area fell above the ridgeline. Moreover, a decrease in O<sub>3</sub> production was noticed with the decrease in VOC concentration. Therefore, the study area was in the VOC-sensitive regime for O<sub>3</sub> formation during all the seasons. As a case study, O<sub>3</sub> formation sensitivity to its precursors was tested on a high O<sub>3</sub> concentration day (July 29 2018, maximum 126 ppbv). During the high O<sub>3</sub> episode, the study area was also in the VOC-sensitive regime for O<sub>3</sub> formation (Fig. S5). We also employed the RIR analysis to evaluate the O<sub>3</sub> production sensitivity to VOC, NO<sub>x</sub>, and CO concentrations (Fig. 11). The RIR value of VOC was the highest during all the seasons. It indicates that the O<sub>3</sub> production was more sensitive to the reduction of VOC concentration. This finding is consistent with the above results in the EKMA isopleth (Fig. 10). Except for the spring, the RIR values of CO were very small relative to those for the VOC. It indicates that the CO concentrations were

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640 relatively less important for the O<sub>3</sub> formation during those seasons. The RIR values for NO<sub>x</sub> were negative during all the seasons, implying that the O<sub>3</sub> formation was in the NO<sub>x</sub>-titration regime in the study area. From the above analysis, it is evident that a reduction of VOC concentration in the study area will be the most efficient way to reduce the O<sub>3</sub> formation. The previous two studies performed in Nanjing also concluded the same finding based on VOC/NO<sub>x</sub> ratios and RIR analysis (An et al., 2015; Xu et al., 2017). Our findings are also consistent with 645 the previous studies performed in other regions in China (Tan et al., 2018a; He et al., 2019; Feng et al., 2019; Ma et al., 2019). However, NO<sub>x</sub>-sensitive regions for O<sub>3</sub> formation are also found in China (Tan et al., 2018; Jia et al., 2016).

#### 4 Conclusions

650 Industries are an important anthropogenic source of VOCs. VOC plays a major role in tropospheric chemistry and air quality. Nanjing is one of the biggest industrial cities in China. We performed a long term investigation of ambient VOCs in an industrial area in Nanjing. ~~About 1.5~~ Similar and ~~3.2~~ folds high TVOCs concentrations were observed compared to those previously reported in the same study area and a nonindustrial suburban area in Nanjing, 655 ~~respectively. The relatively high TVOCs was due to halocarbons and OVOCs concentrations were not measured in those previous studies in Nanjing. Therefore, halocarbons and OVOCs were an important part of the TVOCs in Nanjing, and industrial emissions had a large influence on VOC concentration in the study area.~~ Observed TVOCs concentration was also ~~about 1.5~~ similar-~~3-1.7~~ folds higher than those reported in other cities in China and the world, but, 660 ~~similar 1.3 times smaller to than those the one~~ measured in urban ~~Beijing and~~ Shanghai. This high VOC concentration in the study area needs to be reduced to decrease O<sub>3</sub> concentration and improve the local air quality. TVOCs concentrations were about 2-times high in autumn and winter compared to those in summer and spring. Generally, haze pollutions frequently happen in autumn and winter, therefore, VOC concentration reduction in these seasons is an important step to reduce haze pollutions in the study area. After alkane, halocarbon was the 2<sup>nd</sup> largest contributor to the TVOCs, indicating a high influence of industrial emissions. Generally, alkenes/aromatics/OVOCs are the 2<sup>nd</sup> largest contributor to the TVOCs in China, therefore, industries in Nanjing emitted a high amount of halocarbons into the atmosphere. As halocarbons are carcinogenic, their emissions should be reduced. PSCF analysis indicated that the short

670 distance transports from the surrounding areas and cities were the main reason for high VOC  
concentration in the study area. Hence, local emissions should be reduced to decrease the haze  
and O<sub>3</sub> pollution in the study area. ~~Industries-Vehicle-related emissions~~ were the major VOC  
sources in the study area ~~followed by vehicles~~, thus, emission reduction from these ~~two~~ sources  
should get more priority. Aromatics and alkenes accounted for most of the L<sub>OH</sub>, ~~OFP, and SOAP~~,  
675 thus, these 2 kinds of VOCs should get more priority in emission reduction policies and  
strategies. During all the seasons, the study area was in the VOC-sensitive regime for O<sub>3</sub>  
formation. Therefore, VOCs especially aromatics and alkenes emission reduction is the most  
effective way to decrease the local O<sub>3</sub> formation.

#### 680 **Data availability**

All the data presented in this article can be accessed through <https://osf.io/bm6cs/>.

#### **Author contribution**

YLZ designed and supervised the project; MYF, FX, YCL, FC, and AM conducted the  
685 measurements; AM analysed the data and prepared the manuscript. All authors contributed in  
discussion to improve the article.

#### **Competing interests**

The authors declare that they have no conflict of interest.

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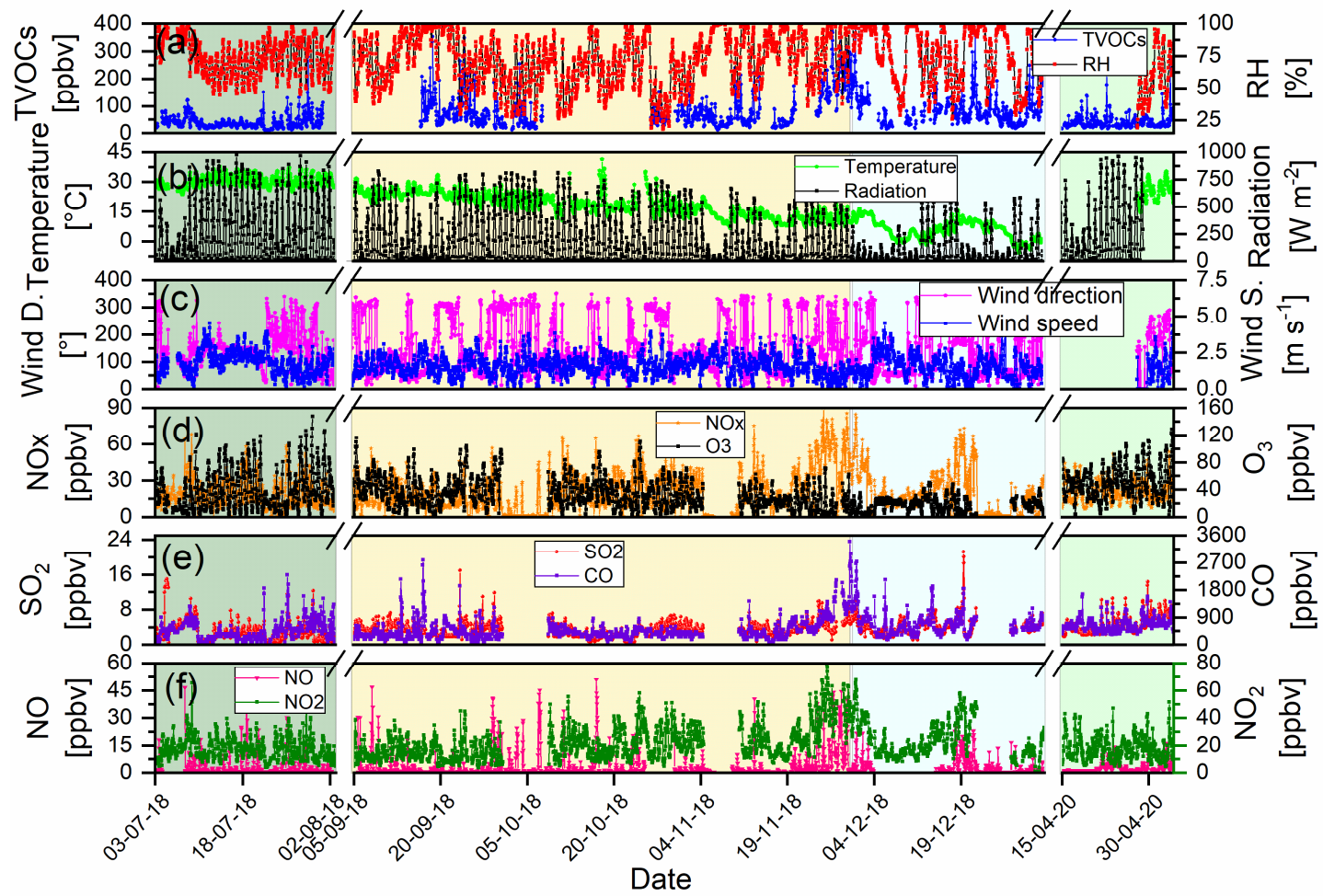
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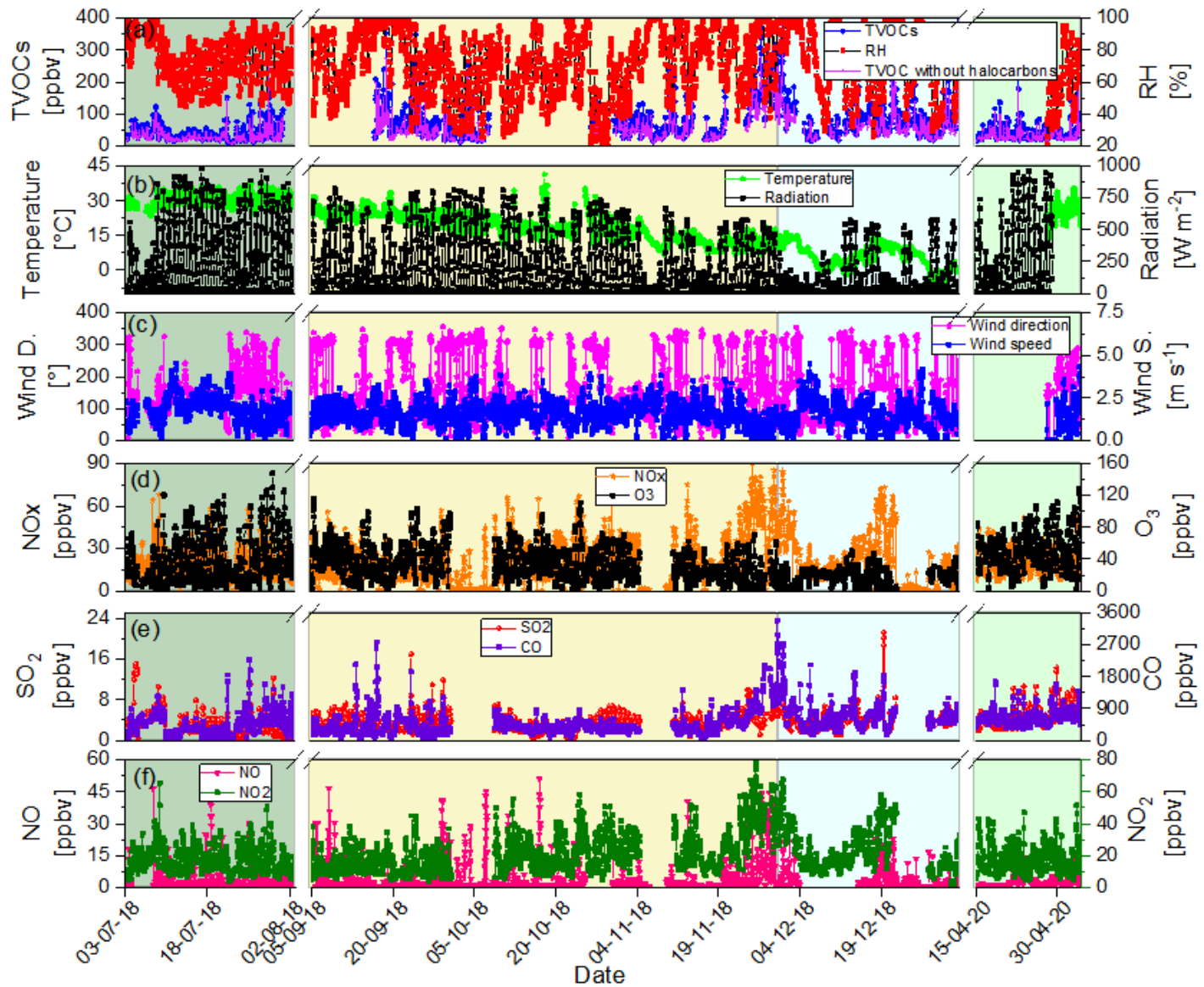
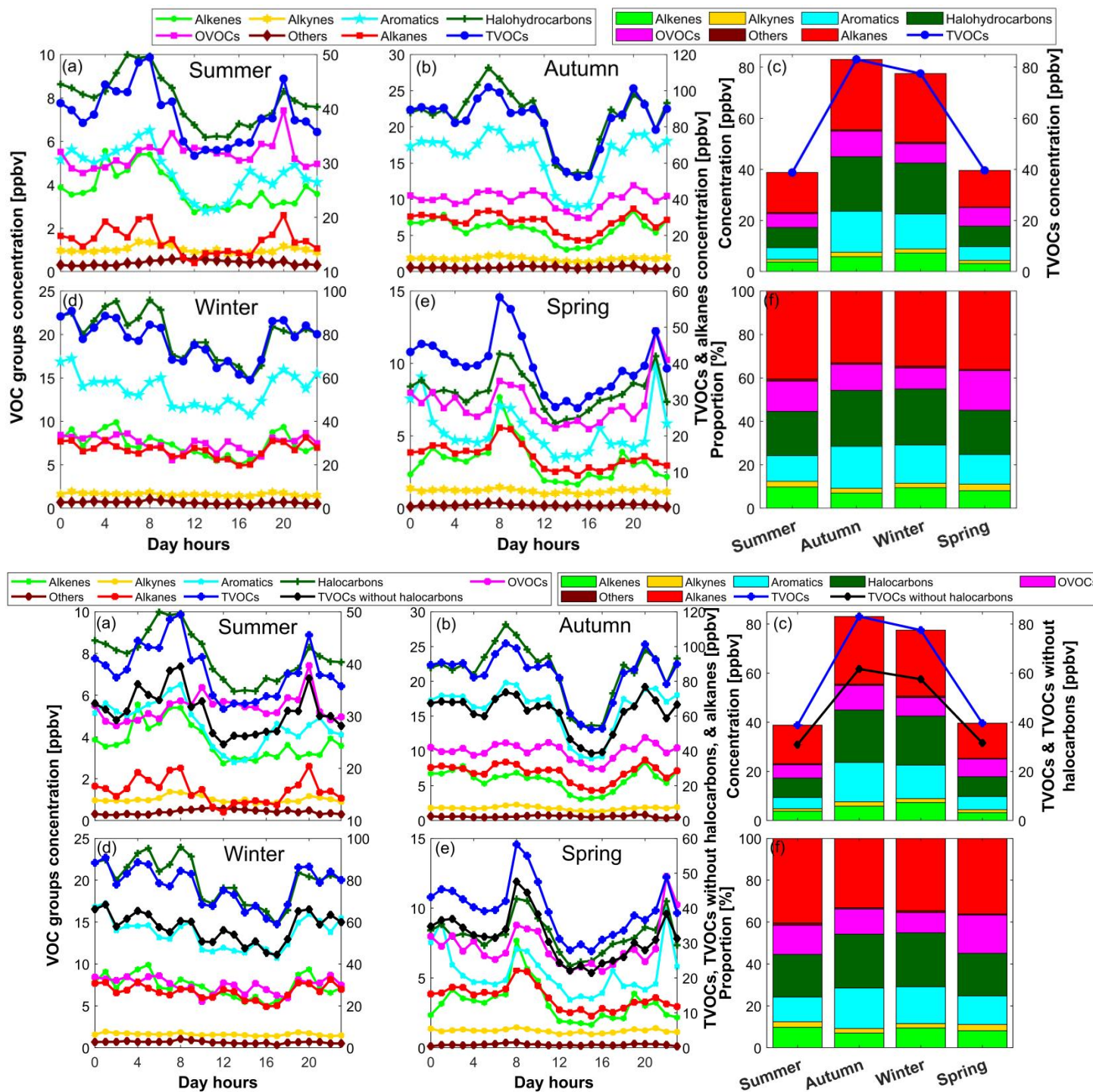
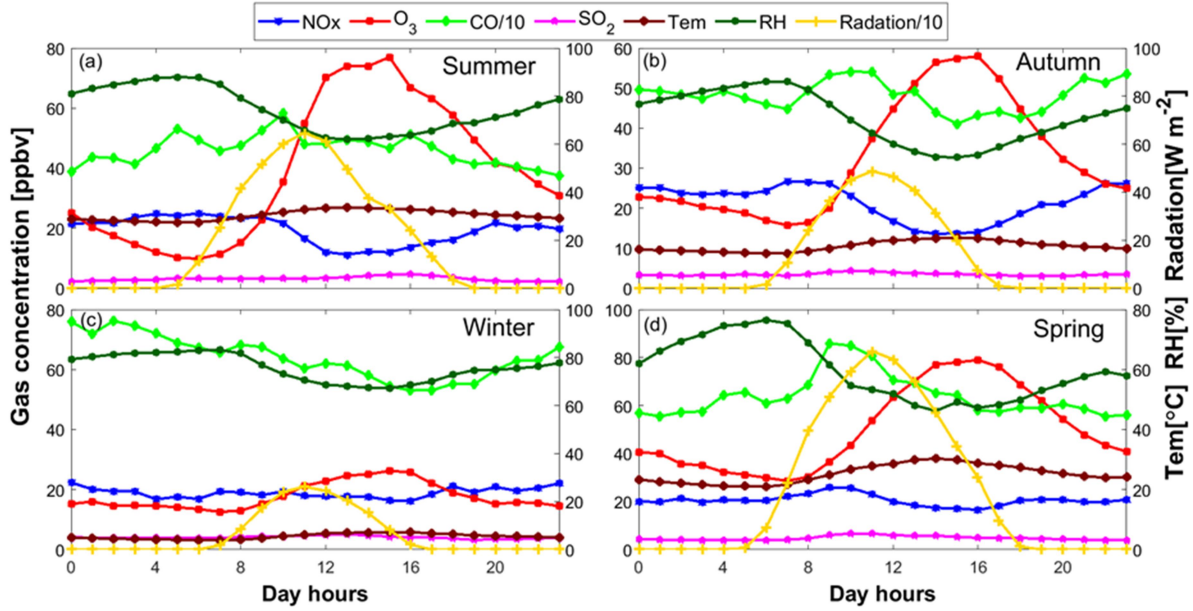


Figure 1: Time series of hourly meteorological parameters, inorganic air pollutants, ~~and~~ TVOCs, and TVOCs without halocarbons concentrations during the observation period at Nanjing. The green, yellow, cyan, and light-green shaded areas indicate summer, autumn, winter, and spring seasons, respectively. The discontinuity of the measured data is due to the instruments failure.

905

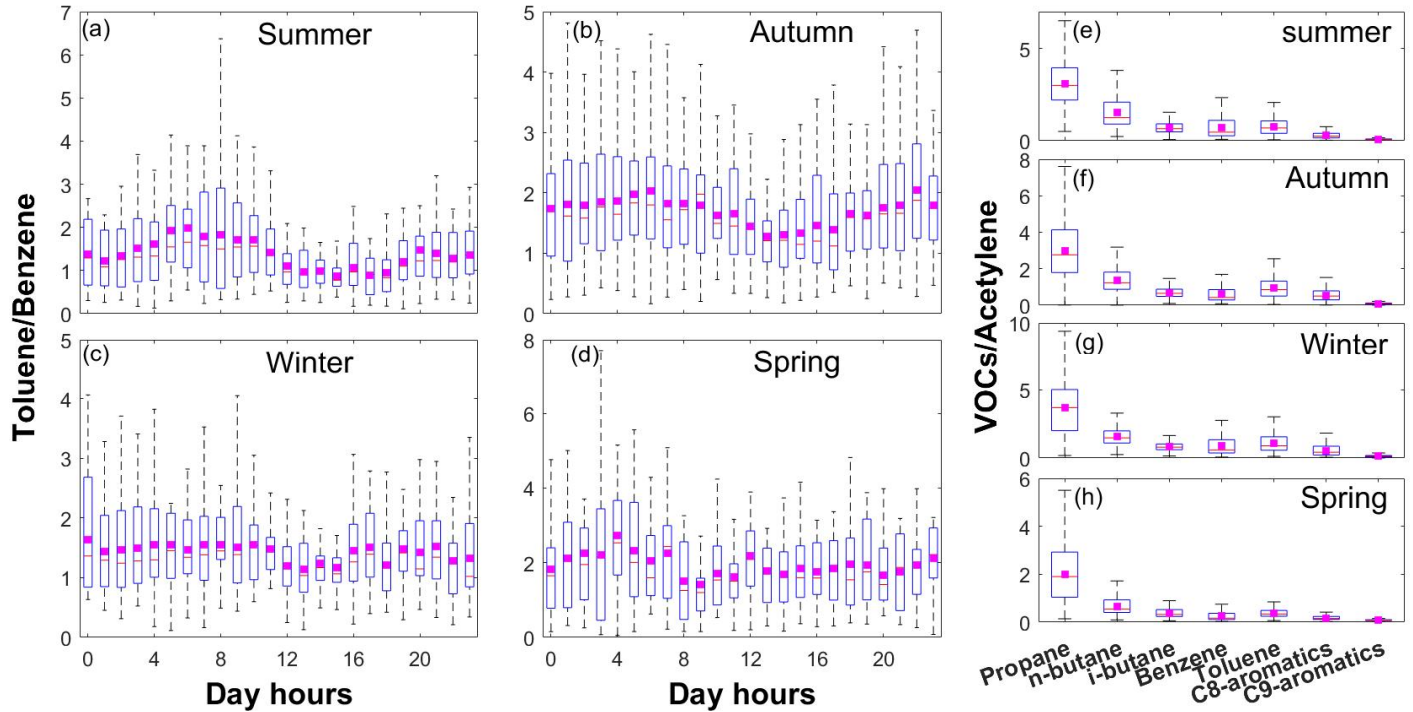


910 **Figure 2: Diurnal variations in TVOCs and different VOC-groups, TVOCs, TVOCs without halocarbons concentrations in different seasons (a, b, d, & e) and seasonal variations in average concentrations and proportion of different VOC-groups, TVOCs, TVOCs without halocarbons and different VOC-groups (c & f).**



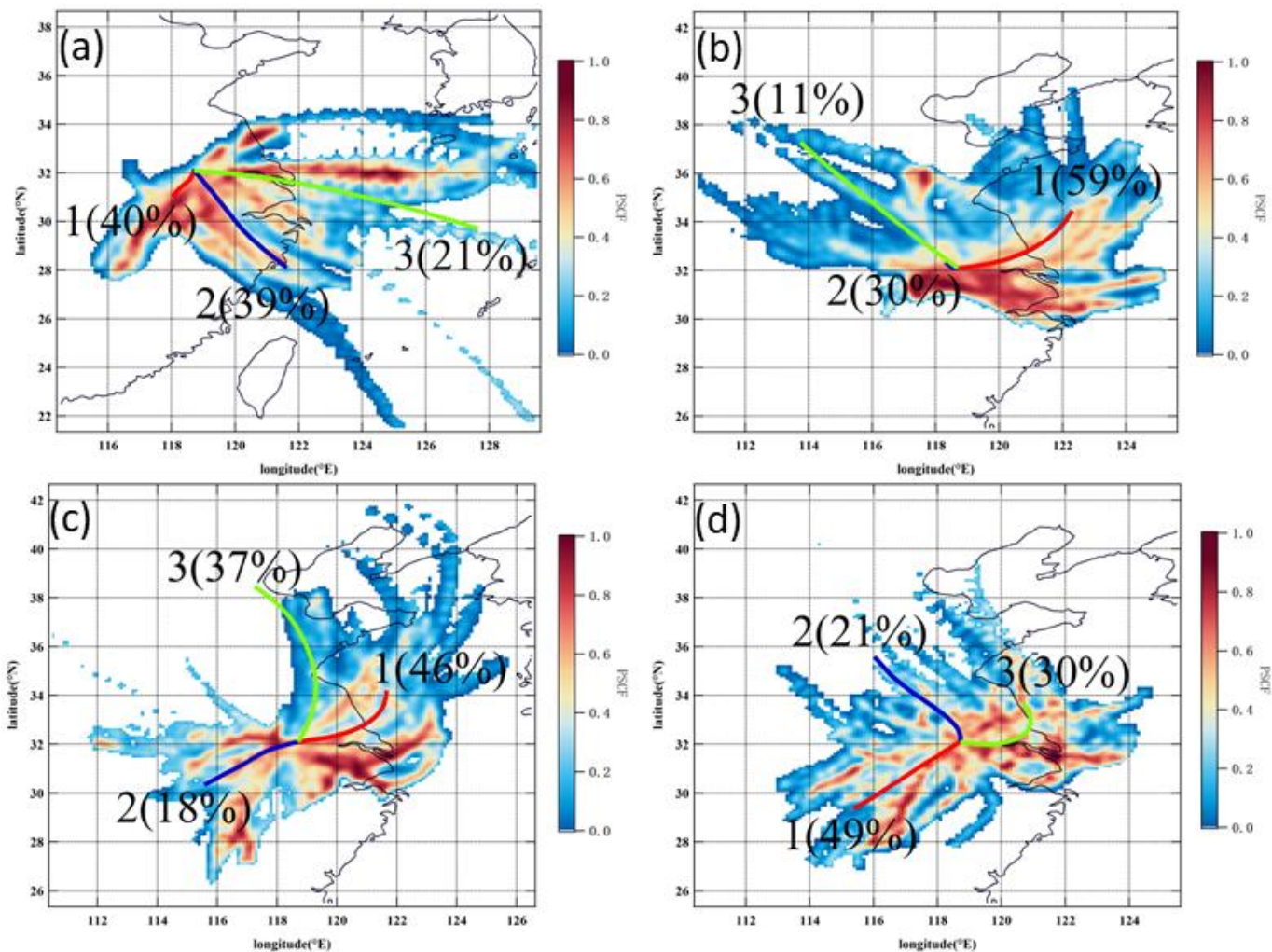
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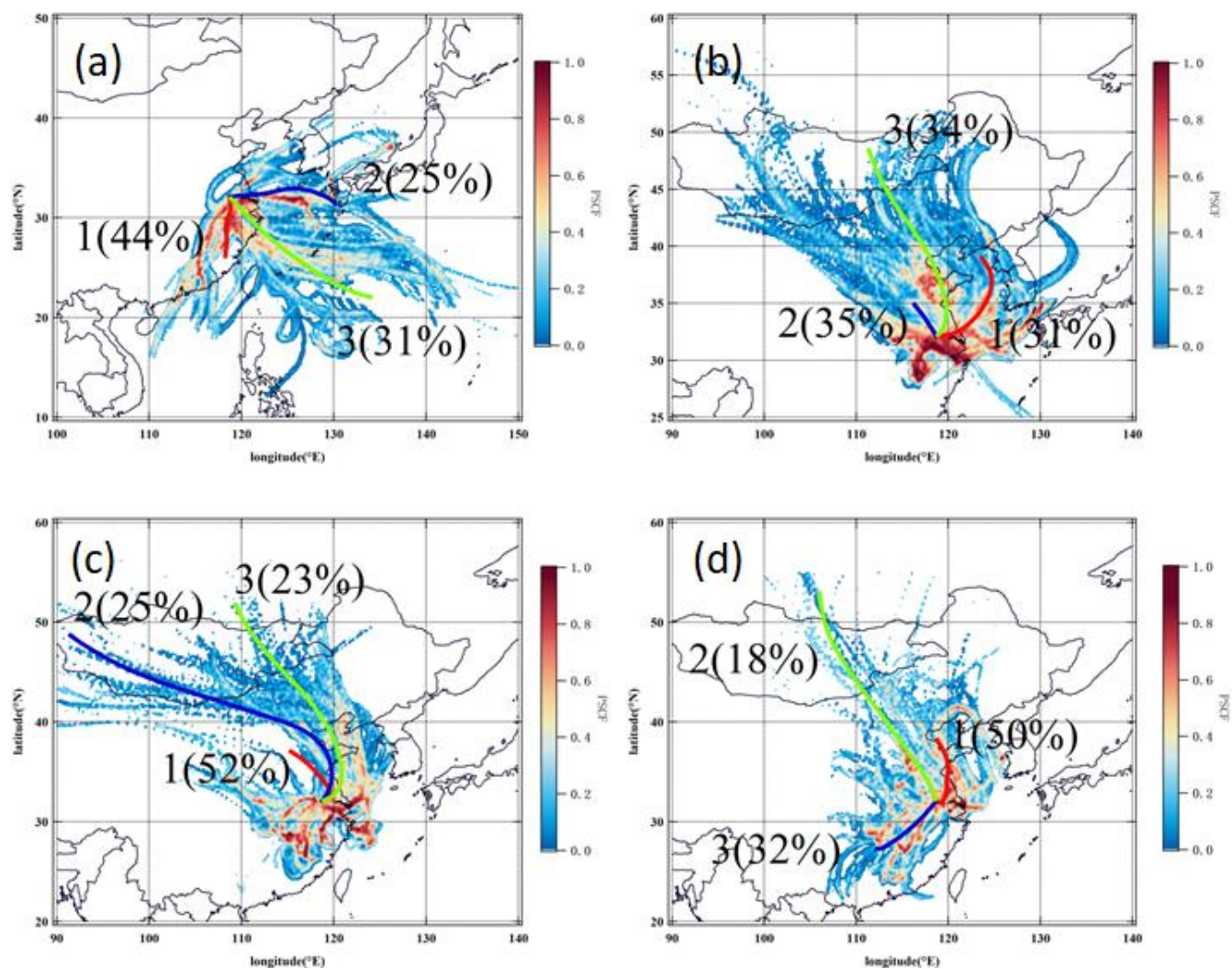
**Figure 3: Diurnal variations in weather conditions and NO<sub>x</sub>, O<sub>3</sub>, CO, and SO<sub>2</sub> concentrations in different seasons. Note that the plotted CO concentrations and solar radiation values are reduced by 10-folds for a better visualization.**



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**Figure 4: Diurnal variations in toluene/benzene ratios (a, b, c, & d) and in the ratios of different VOCs to acetylene in different seasons (e, f, g, & h). The pink-colored squares in the box-plots represent the average values.**

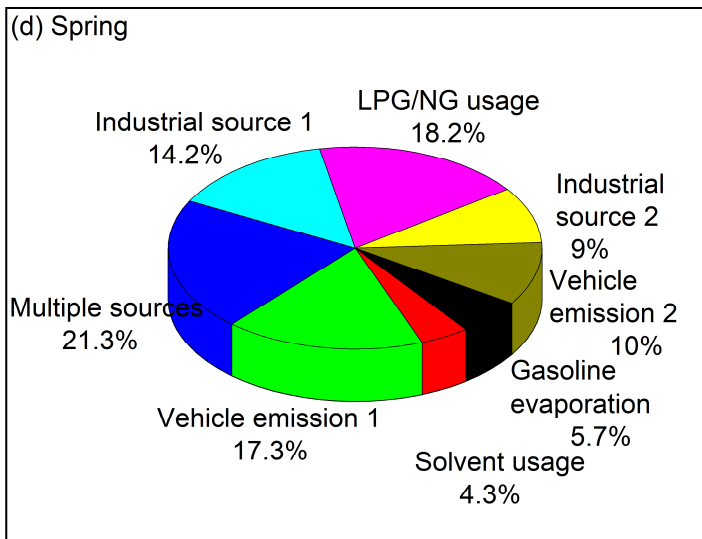
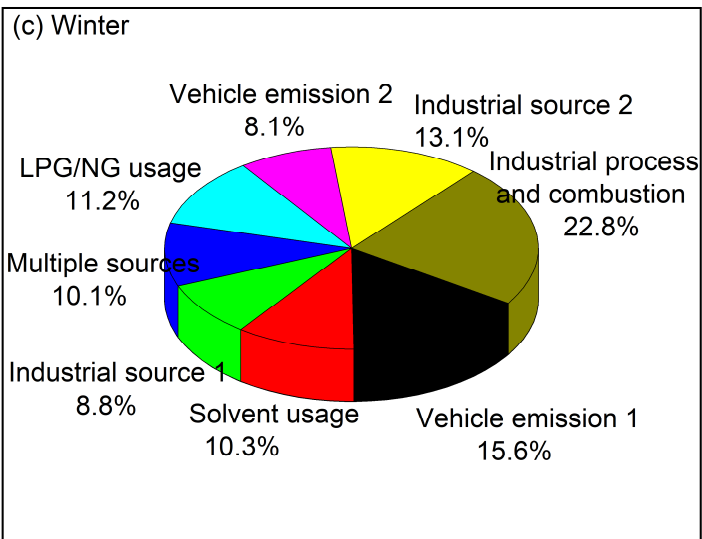
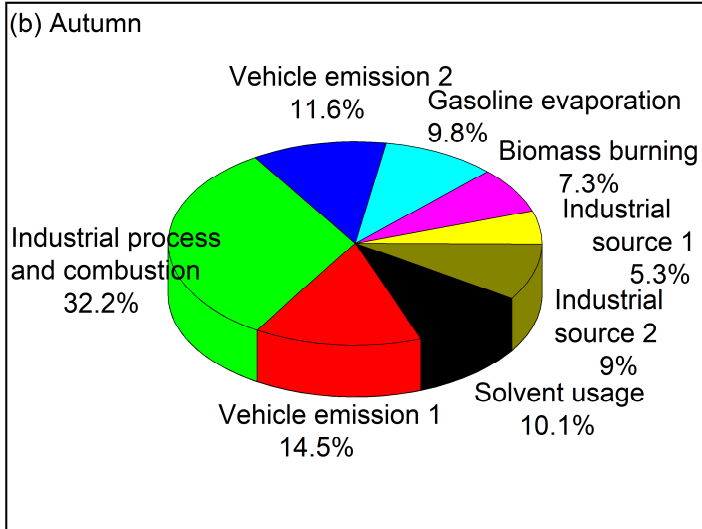
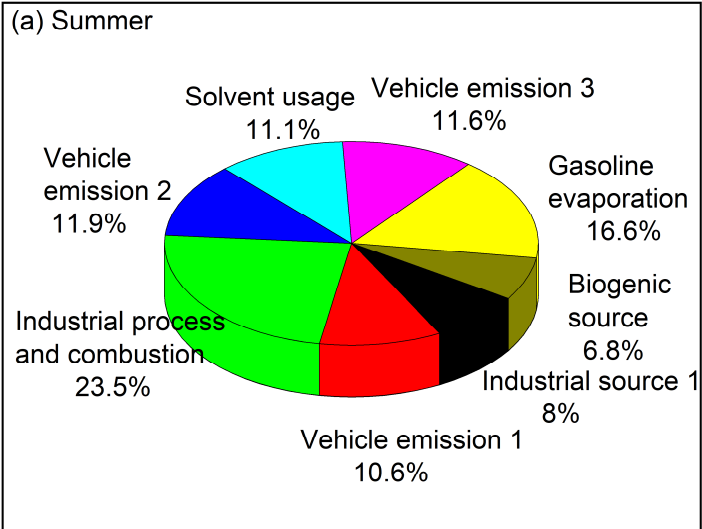


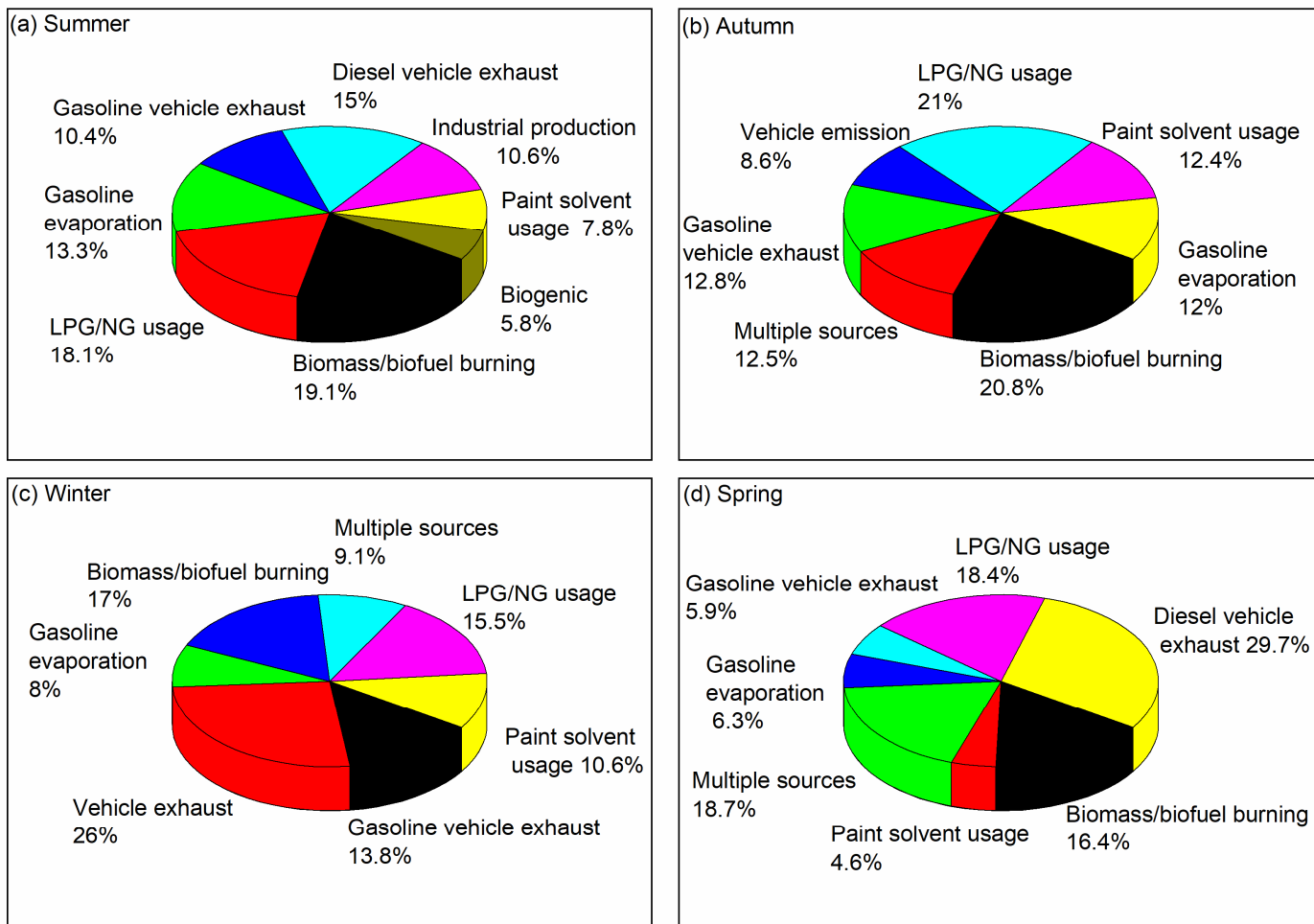


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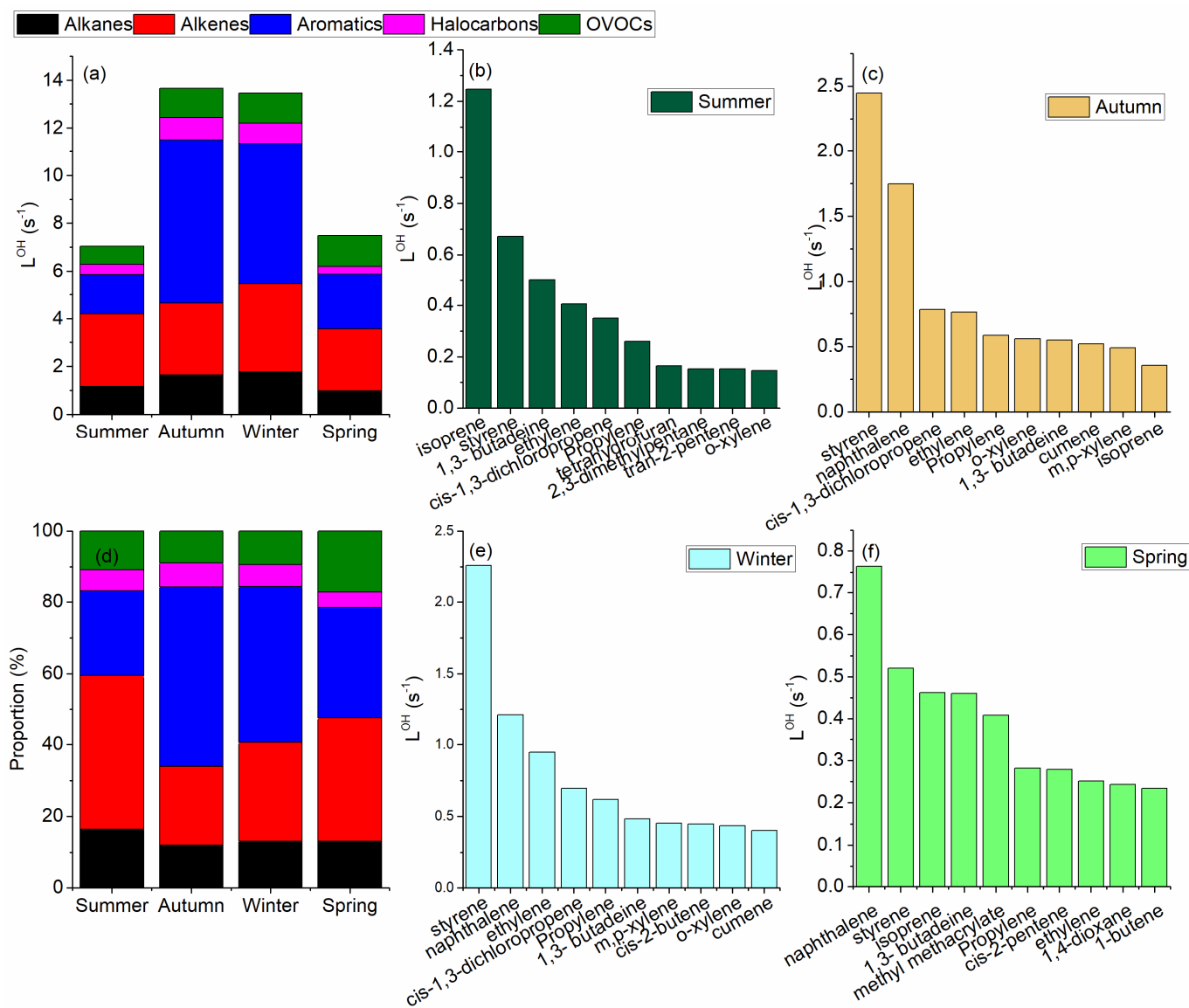
Figure 5: Wind cluster and PSCF analysis during (a) summer (b) autumn, (c) winter, and (d) spring based on the 24-72 hours backward air mass trajectories from the study area.



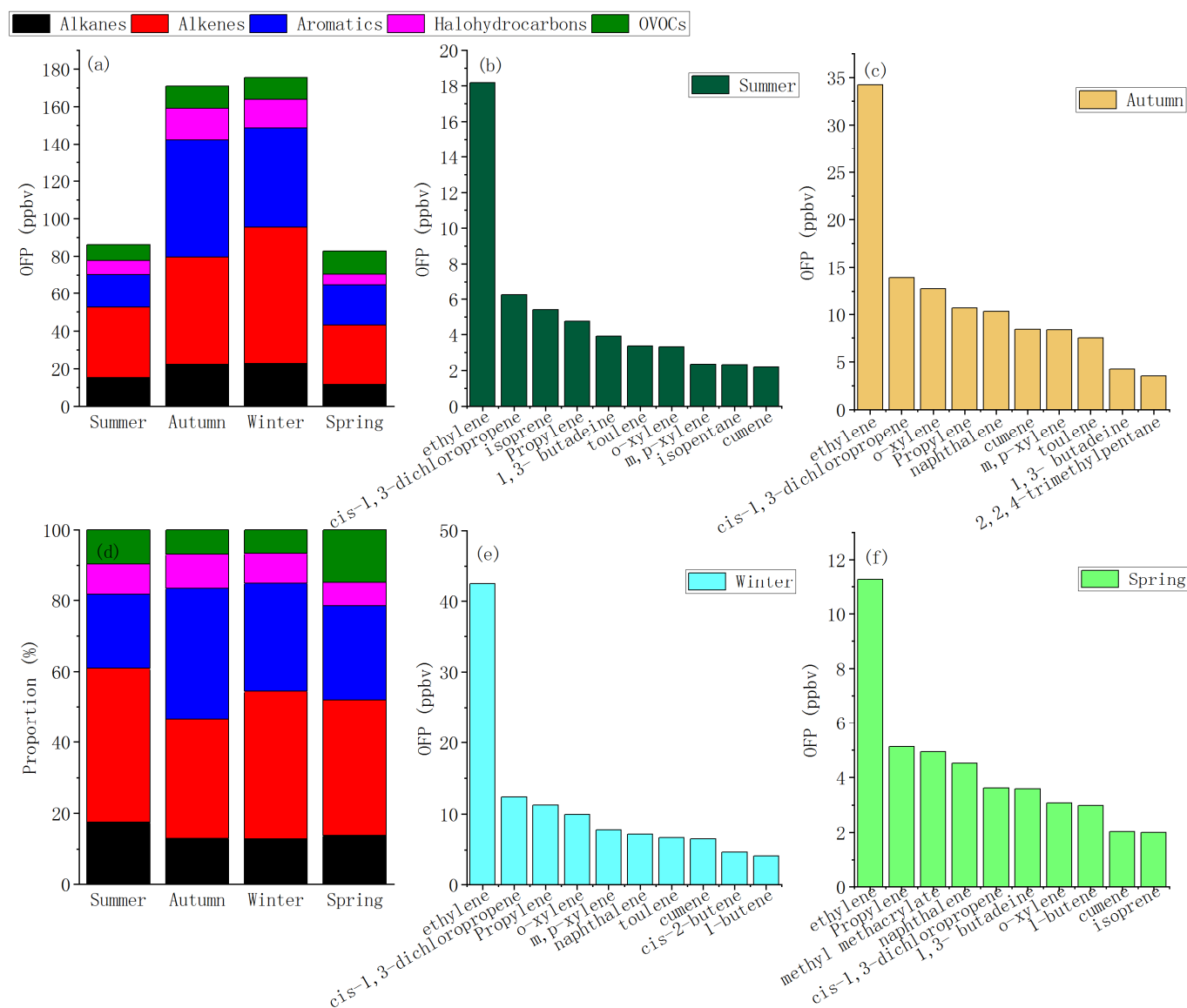




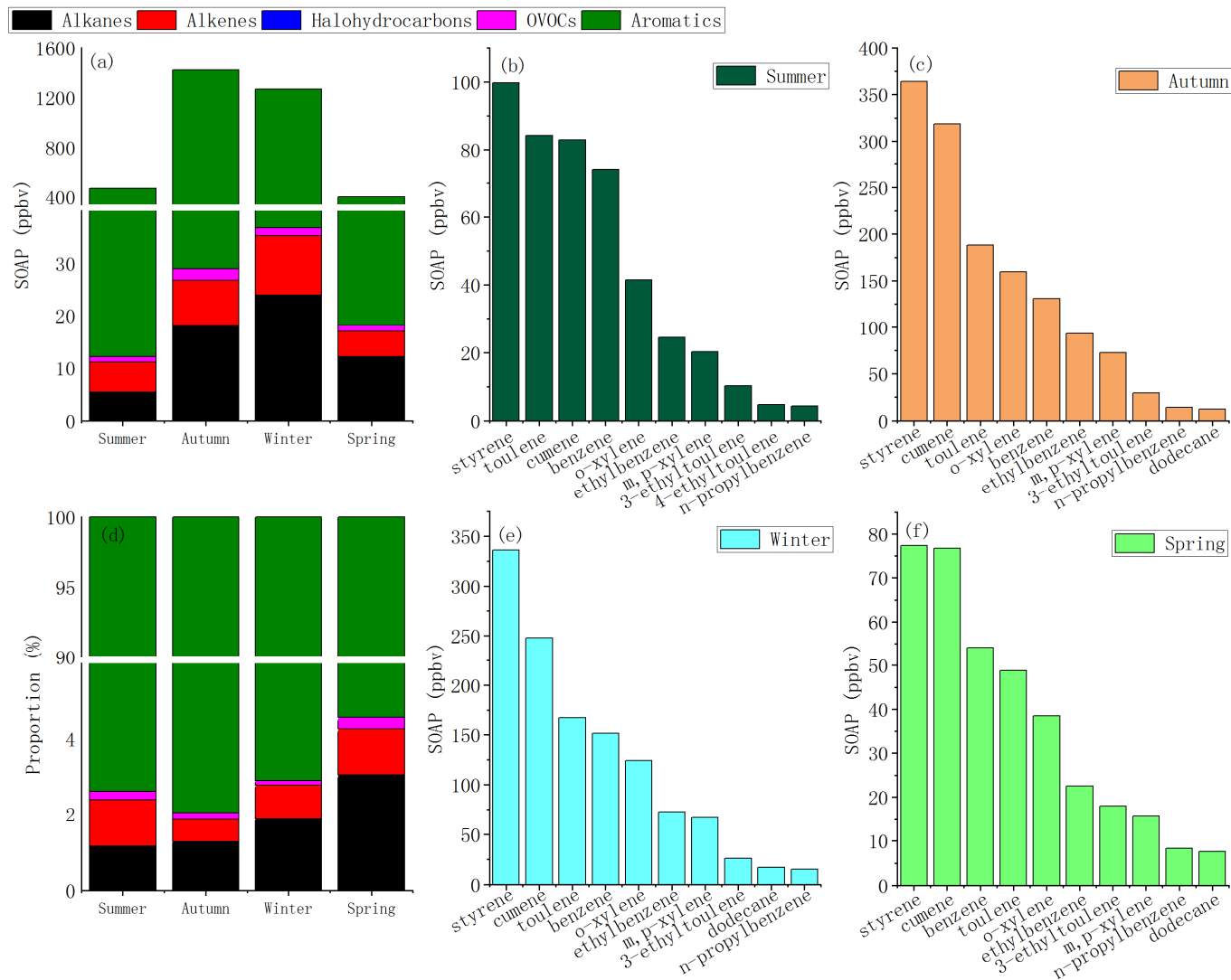
930 **Figure 6: relative contributions of different sources to ambient VOCs in Nanjing industrial area during different seasons**



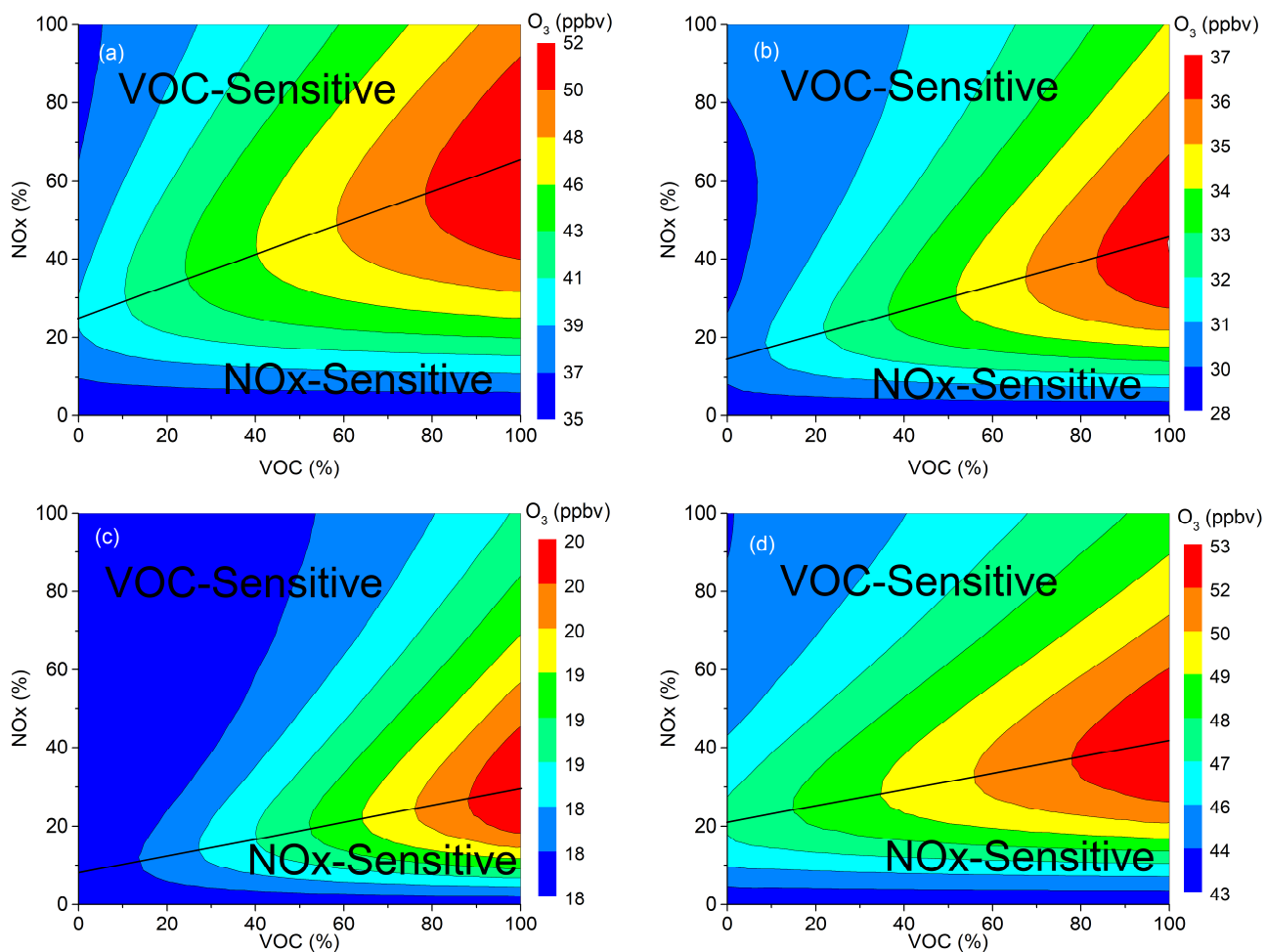
935 **Figure 7: Contribution to OH loss rates of different VOC-groups and the top 10 VOC species in different seasons**



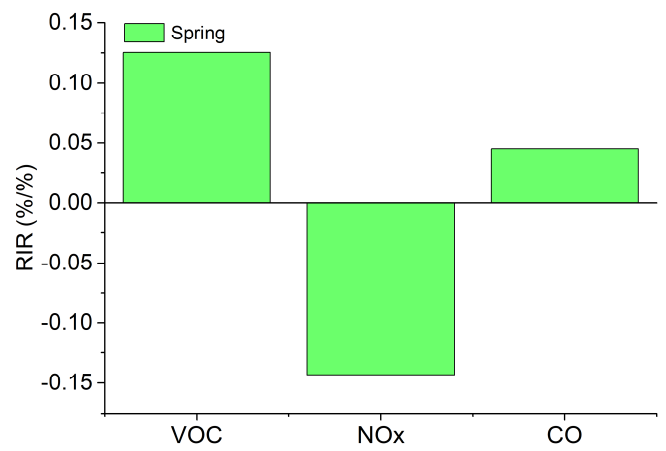
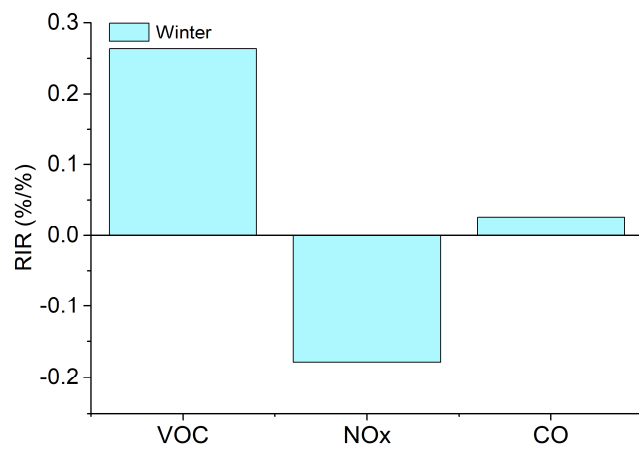
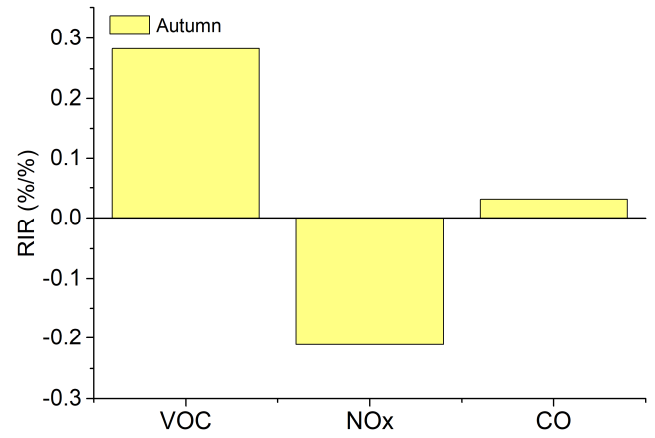
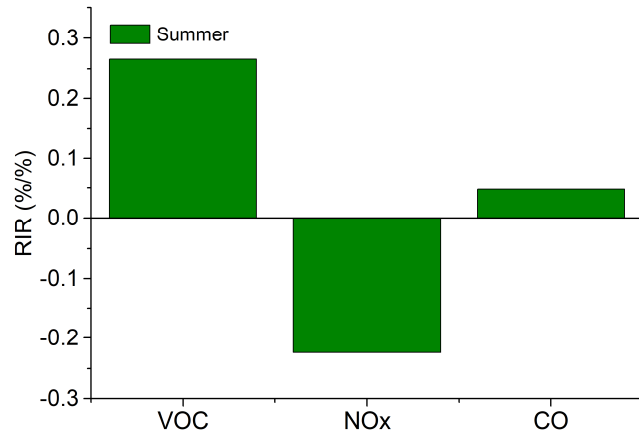
**Figure 8: Contribution to ozone formation potential of different VOC groups and the top 10 VOC species in different seasons**



**Figure 9: Contribution to secondary organic aerosol formation potential of different VOC groups and the top-10 VOC species in different seasons**



**Figure 10: O<sub>3</sub> isopleth diagram for (a) summer (b) autumn, (c) winter, and (d) spring based on percentage changes in VOCs and NOx concentrations in Nanjing and corresponding modelled O<sub>3</sub> production.**



**Figure 11: The RIR values of the VOC, NOx, and CO for the different seasons in Nanjing**

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## Measurement report: High Contributions of Halocarbon and Aromatic Compounds to Atmospheric VOCs in Industrial Area

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980 **Table S1: OH reaction rate constant ( $K_{OH}$ ) of VOCs and list of VOCs constrained in the F0AM model**

Compounds	$K_{OH}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) (Carter, 2010)	Constrained in F0AM model
Ethane	2.54E-13	Yes
propane	1.11E-12	Yes
isobutane	2.14E-12	Yes
n-butane	2.38E-12	Yes
isopentane	3.60E-12	Yes
n-pentane	3.84E-12	Yes
2,2 dimethylbutane	2.27E-12	
2,3 dimethyl butane	5.79E-12	
2-methyl pentane	5.20E-12	Yes
cyclopentane	5.02E-12	



3-methylpentane	5.20E-12	
n-hexane	5.25E-12	Yes
2,4-dimethylpentane	4.77E-12	
methylcyclopentane	5.68E-12	
isoheptane	6.81E-12	Yes
cyclohexane	7.02E-12	
2,3-dimethylpentane	7.15E-12	
3-methylhexane	7.17E-12	Yes
2,2,4-trimethylpentane	3.38E-12	
heptane	6.81E-12	Yes
methylcyclohexane	9.64E-12	
2-methylheptane	8.31E-12	
n-octane	8.16E-12	Yes
n-nonane	9.75E-12	Yes
Decane	1.10E-11	Yes
n-hendecane	1.23E-11	Yes
dodecane	1.32E-11	Yes
ethylene	8.15E-12	Yes
Propylene	2.60E-11	Yes
trans-2-butene	6.32E-11	Yes
cis-2-butene	5.58E-11	
1-butene	3.11E-11	Yes
1,3- butadiene	6.59E-11	
1-pentene	3.14E-11	Yes
trans-2-pentene	6.70E-11	
isoprene	9.96E-11	Yes
cis-2-pentene	6.50E-11	Yes
1-hexene	3.70E-11	Yes
acetylene	7.56E-13	Yes
benzene	1.22E-12	Yes
toluene	5.58E-12	Yes

ethylbenzene	7.00E-12	Yes
m,p-xylene	2.31E-11	Yes
o-xylene	1.36E-11	Yes
Styrene	5.80E-11	Yes
Cumene	6.30E-12	Yes
n-propylbenzene	5.80E-12	Yes
3-ethyltoluene	1.86E-11	Yes
4-ethyltoluene	1.18E-11	Yes
Mesitylene	5.67E-11	Yes
2-ethyltoluene	1.19E-11	Yes
1,2,4-trimethylbenzene	3.25E-11	Yes
1,2,3-trimethylbenzene	3.27E-11	Yes
1,3-diethylbenzene	2.55E-11	
1,4-diethylbenzene	1.64E-11	Yes
Naphthalene	2.30E-11	
Chloromethane	4.48E-14	Yes
vinyl chloride	6.90E-12	Yes
methyl bromide	4.12E-14	
Chloroethene	0	Yes
trichlorofluoromethane	0	
Vinylidene chloride	0	
1,1,2-Trichlor-1,2,2-trifluorethan	0	
Dichloromethane	1.45E-13	Yes
trans-1,2-dichloroethylene	0	
1,1-dichloroethane	2.60E-13	Yes
cis-1,2-dichloroethylene	0	
Chloroform	1.06E-13	Yes
carbon tetrachloride	0	
1,2-dichloroethane	2.53E-13	Yes

Trichloroethylene	2.34E-12	Yes
1,2-dichloropropane	4.50E-13	Yes
bromodichloromethane	0	
trans-1,3-dichloropropene	1.44E-11	
cis-1,3-dichloropropene	8.45E-12	
1,1,2-trichloroethane	2.00E-13	Yes
tetrachloroethylene	0	Yes
1,2-dibromoethane	2.27E-13	Yes
Chlorobenzene	7.70E-13	
Bromoform	0	
1,1,2,2-tetrachloroethane	0	Yes
1,3-dichlorobenzene	5.55E-13	
1,4 dichlorobezne	5.55E-13	
benzyl chloride	0	
1,2-dichlorobenzene	5.55E-13	
1,2,4-trichlorobenzene	0	
hexachloro-1,3-butadiene	0	
carbon disulfide	2.76E-12	
Acrolein	1.99E-11	Yes
Acetone	1.91E-13	Yes
Isopropanol	5.09E-12	Yes
MTBE	0	Yes
vinyl acetate	3.16E-11	
MEK	1.20E-12	Yes
ethyl acetate	1.60E-12	Yes
Tetrahydrofuran	1.61E-11	
methyl methacrylate	5.25E-11	
1,4-dioxane	3.83E-11	
4-methyl-2-pentanone	1.27E-11	Yes
2-hexanone	9.10E-12	Yes

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**Table S2: VOC concentrations (ppbv) measured in the industrial area in Nanjing. VOC concentrations observed in previous studies in Nanjing are also listed.**

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Compounds	Current study										(An et al., 2017), Nanjing		(Wu et al., 2020), Nanjing
	Summer		Autumn		Winter		Spring		Yearly		Summer	Winter	Yearly
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Mean	Mean
ethane	2.81	0.58	8.06	1.77	7.66	1.39	4.76	1.25	5.82	2.49	2.76	7.66	2.89
propane	3.12	0.63	6.09	1.21	4.92	0.91	2.73	0.92	4.22	1.57	1.70	4.51	3.29
isobutane	0.75	0.16	1.25	0.26	1.16	0.15	0.48	0.14	0.91	0.36	1.04	2.25	0.9
n-butane	1.75	0.39	2.61	0.63	2.32	0.26	0.87	0.29	1.89	0.76	1.09	2.35	1.53
isopentane	1.59	0.29	1.56	0.47	1.63	0.31	0.42	0.19	1.30	0.59	0.86	1.13	1.26
n-pentane	0.66	0.17	1.06	0.29	1.36	0.25	0.31	0.10	0.85	0.46	0.50	0.86	0.78
2,2-dimethylbutane	0.08	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.28	0.03	0.04
2,3-dimethylbutane											0.12	0.35	0.04
2-methylpentane	0.13	0.03	0.18	0.03	0.11	0.00	0.20	0.02	0.16	0.04	0.25	0.41	0.16
cyclopentane	0.26	0.08	0.32	0.10	0.44	0.11	0.29	0.06	0.33	0.08	0.08	0.12	0.08
3-methylpentane	0.15	0.03	0.10	0.02	0.08	0.01	0.22	0.03	0.14	0.06	0.22	0.31	0.26
n-hexane	0.25	0.06	0.38	0.09	0.37	0.12	0.25	0.08	0.31	0.07	0.41	0.48	0.47
2,4-dimethylpentane	0.17	0.04	0.33	0.09	0.41	0.17	0.21	0.06	0.28	0.11	0.05	0.08	0.01
methylcyclopentane	0.06	0.00	0.06	0.01	0.06	0.00	0.13	0.01	0.08	0.03	0.08	0.13	0.26
isohexane	0.12	0.03	0.16	0.04	0.14	0.04	0.13	0.03	0.14	0.02			
cyclohexane	0.13	0.04	0.12	0.04	0.11	0.04	0.16	0.03	0.13	0.02	0.41	0.60	0.15
2,3-dimethylpentane	0.44	0.29	0.37	0.15	0.43	0.31	0.21	0.13	0.36	0.10	0.11	0.20	0.02
	0.86	0.59	0.73	0.30	0.85	0.63	0.42	0.25	0.72	0.21			

3-methylhexane	0.10	0.02	0.12	0.03	0.09	0.02	0.14	0.02	0.11	0.02	0.04	0.05	0.08
2,2,4-trimethylpentane	1.59	0.37	2.81	0.82	3.26	0.78	1.16	0.74	2.21	0.99	0.03	0.02	0.03
heptane	0.10	0.01	0.12	0.02	0.12	0.01	0.10	0.01	0.11	0.01	1.92	0.2	0.11
methylcyclohexane	0.18	0.02	0.18	0.04	0.19	0.03	0.16	0.03	0.18	0.01	0.08	0.12	0.08
2-methylheptane	0.08	0.00	0.08	0.01	0.08	0.00	0.17	0.01	0.10	0.04	0.01	0.05	0.02
n-octane	0.09	0.01	0.08	0.01	0.09	0.01	0.20	0.01	0.11	0.06	0.19	0.21	0.05
n-noane	0.06	0.00	0.08	0.02	0.08	0.02	0.07	0.00	0.07	0.01	0.03	0.05	0.03
decane	0.05	0.00	0.06	0.01	0.06	0.01	0.05	0.00	0.06	0.01	0.05	0.06	0.04
n-hendecane	0.04	0.01	0.16	0.01	0.22	0.01	0.17	0.01	0.15	0.07	0.06	0.09	0.02
dodecane	0.08	0.00	0.36	0.02	0.50	0.01	0.22	0.02	0.29	0.18	0.07	0.13	0.03
ethylene	2.02	0.58	3.80	0.89	4.71	1.09	1.25	0.71	2.95	1.59	3.08	6.62	1.21
Propylene	0.41	0.34	0.91	0.46	0.97	0.31	0.44	0.58	0.68	0.30	0.98	2.09	0.70
trans-2-butene	0.02	0.00	0.06	0.02	0.23	0.01	0.03	0.01	0.09	0.10	0.07	0.14	0.07
cis-2-butene	0.07	0.00	0.16	0.03	0.33	0.03	0.09	0.01	0.16	0.12	0.06	0.10	0.05
1-butene	0.07	0.00	0.10	0.02	0.43	0.02	0.31	0.13	0.22	0.17	0.18	0.23	0.15
1,3-butadiene	0.31	0.07	0.34	0.05	0.30	0.03	0.28	0.00	0.31	0.02			
1-pentene	0.16	0.03	0.14	0.03	0.08	0.03	0.10	0.03	0.12	0.04	0.04	0.05	0.04
trans-2-pentene	0.09	0.03	0.06	0.02	0.05	0.01	0.09	0.02	0.07	0.02	0.03	0.04	0.03
isoprene	0.51	0.37	0.15	0.06	0.09	0.02	0.19	0.02	0.23	0.19	0.58	0.07	0.18
cis-pentene	0.07	0.02	0.06	0.01	0.07	0.01	0.17	0.02	0.09	0.05	0.03	0.02	0.02
1-hexene	0.05	0.03	0.06	0.02	0.06	0.03	0.24	0.01	0.10	0.09	0.03	0.02	0.01
acetylene	1.02	0.15	1.77	0.24	1.59	0.15	1.20	0.13	1.40	0.35	2.63	6.46	
benzene	0.80	0.19	1.41	0.41	1.63	0.39	0.58	0.37	1.10	0.50	1.86	3.21	0.82
toulene	0.84	0.40	1.88	0.51	1.67	0.31	0.49	0.12	1.22	0.66	1.47	3.20	1.07
ethylbenzene	0.22	0.05	0.83	0.21	0.65	0.15	0.20	0.10	0.48	0.32	1.27	1.79	0.43
m,p-xylene	0.24	0.07	0.86	0.24	0.80	0.17	0.19	0.07	0.52	0.36	0.46	0.59	0.67
o-xylene	0.43	0.09	1.67	0.42	1.30	0.29	0.40	0.21	0.95	0.63	0.28	0.39	0.21
styrene	0.47	0.15	1.71	0.49	1.58	0.35	0.36	0.15	1.03	0.71	0.17	0.30	0.12

cumene	0.87	0.19	3.34	0.84	2.60	0.59	0.80	0.41	1.90	1.27			
n-propylbenzene	0.04	0.01	0.13	0.02	0.14	0.01	0.08	0.11	0.10	0.05	0.09	0.08	0.03
3-ethyltoluene	0.10	0.02	0.29	0.06	0.26	0.05	0.18	0.21	0.21	0.09	0.05	0.05	0.03
4-ethyltoluene	0.07	0.00	0.08	0.01	0.08	0.01	0.10	0.06	0.08	0.01	0.19	0.29	0.03
mesitylene	0.03	0.00	0.06	0.02	0.08	0.03	0.04	0.00	0.05	0.02			
2-ethyltoluene	0.04	0.01	0.07	0.02	0.07	0.02	0.06	0.07	0.06	0.02	0.51	0.08	
1,2,4-trimethylbenzene											0.33	0.42	0.09
1,2,3-trimethylbenzene	0.06	0.01	0.06	0.02	0.08	0.03	0.13	0.11	0.08	0.03			
1,3-dimethylbenzene											0.05	0.05	0.05
1,3-diethylbenzene	0.08	0.01	0.20	0.03	0.22	0.01	0.10	0.01	0.15	0.07			
1,4-diethylbenzene	0.09	0.00	0.18	0.02	0.17	0.01	0.16	0.01	0.15	0.04			
naphthalene											0.04	0.10	0.04
chloromethane	0.09	0.00	0.17	0.02	0.20	0.01	0.17	0.01	0.16	0.05			
vinyl chloride	0.13	0.02	3.09	0.98	2.14	0.22	1.35	0.29	1.68	1.25			
methyl bromide	0.16	0.02	0.56	0.08	1.21	0.33	0.15	0.01	0.52	0.50			
chloroethene	0.05	0.00	0.07	0.02	0.09	0.02	0.16	0.01	0.09	0.05			
trichlorofluoromethane	0.04	0.00	0.05	0.01	0.04	0.01	0.03	0.00	0.04	0.01			
Vinylidene chloride	0.08	0.01	0.08	0.02	0.10	0.03	0.05	0.01	0.08	0.02			
1,1,2-Trichloro-1,2,2-trifluoroethane	0.23	0.01	0.18	0.01	0.30	0.02	0.21	0.04	0.23	0.05			
dichloromethane	0.05	0.01	0.05	0.01	0.04	0.00	0.05	0.01	0.05	0.00			
trans-1,2-dichloroethane	0.08	0.00	0.08	0.01	0.10	0.00	0.08	0.01	0.08	0.01			
	1.26	0.09	3.09	0.54	2.62	0.47	1.97	0.53	2.23	0.80			
	0.05	0.00	0.05	0.01	0.05	0.01	0.14	0.01	0.07	0.05			

dichloroethylene										
1,1-										
dichloroethane	0.33	0.08	0.65	0.18	0.82	0.34	0.41	0.13	0.55	0.22
cis-1,2-										
dichloroethylene	0.07	0.00	0.07	0.01	0.03	0.00	0.20	0.01	0.09	0.07
chloroform	0.17	0.02	0.57	0.16	0.53	0.18	0.18	0.04	0.36	0.22
carbon										
tetrachloride	0.12	0.01	0.18	0.02	0.17	0.03	0.18	0.02	0.16	0.03
1,2-										
dichloroethane	0.95	0.14	3.19	0.40	2.95	0.43	1.15	0.31	2.06	1.17
trichloroethylene	0.13	0.02	0.14	0.02	0.10	0.02	0.06	0.00	0.11	0.04
1,2-										
dichloropropane	0.57	0.21	1.48	0.53	0.96	0.23	0.14	0.05	0.79	0.57
bromodichlorom										
ethane	0.06	0.00	0.03	0.01	0.03	0.00	0.06	0.00	0.04	0.01
trans-1,3-										
dichloropropene	0.10	0.00	0.08	0.01	0.13	0.00	0.17	0.01	0.12	0.04
cis-1,3-										
dichloropropene	1.68	0.79	3.76	1.02	3.35	0.62	0.98	0.23	2.44	1.33
1,1,2-										
trichloroethane	0.06	0.01	0.12	0.04	0.11	0.07	0.05	0.05	0.09	0.03
tetrachloroethyle										
ne	0.06	0.00	0.09	0.02	0.08	0.02	0.06	0.01	0.07	0.01
1,2-										
dibromoethane	0.03	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.01
chlorobenzene	0.31	0.18	1.89	0.91	1.73	1.14	0.20	0.16	1.03	0.90
bromoform	0.02	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.00
1,1,2,2-										
tetrachloroethan										
e	0.94	0.30	3.43	0.97	3.16	0.70	0.73	0.30	2.06	1.43

1,3- dichlorobenzene	0.02	0.00	0.09	0.03	0.14	0.05	0.04	0.01	0.07	0.05
1,4 dichlorobenzene	0.11	0.01	0.65	0.20	0.40	0.05	0.09	0.01	0.31	0.27
benzyl chloride	0.12	0.02	0.10	0.05	0.13	0.07	0.24	0.23	0.15	0.06
1,2- dichlorobenzene	0.03	0.01	0.25	0.11	0.15	0.04	0.08	0.01	0.13	0.10
1,2,4- trichlorobenzene	0.04	0.00	0.17	0.04	0.25	0.01	0.14	0.02	0.15	0.09
hexachloro-1,3- butadiene	0.02	0.00	0.17	0.04	0.15	0.04	0.02	0.00	0.09	0.08
carbon disulfide	0.42	0.11	0.59	0.13	0.66	0.15	0.21	0.07	0.47	0.20
Acrolein	0.09	0.02	0.07	0.02	0.05	0.01	0.07	0.02	0.07	0.01
acetone	1.60	0.29	2.98	0.25	1.94	0.22	2.61	0.61	2.28	0.63
isopropanol	0.46	0.07	2.34	0.60	1.28	0.34	0.44	0.10	1.13	0.90
MTBE	0.37	0.11	0.66	0.23	0.35	0.11	0.35	0.13	0.43	0.15
vinyl acetate	0.17	0.04	0.33	0.09	0.42	0.18	0.26	0.08	0.30	0.11
MEK	0.69	0.06	1.14	0.10	0.73	0.09	0.77	0.43	0.84	0.21
ethyl acetate	1.06	0.17	1.56	0.25	1.43	0.18	1.34	0.95	1.35	0.21
tetrahydrofuran	0.41	0.56	0.08	0.11	0.43	0.45	0.24	0.03	0.29	0.16
methyl methacrylate	0.11	0.01	0.21	0.01	0.20	0.01	0.32	0.00	0.21	0.09
1,4-dioxane	0.05	0.00	0.07	0.01	0.09	0.00	0.26	0.01	0.12	0.10
4-methyl-2- pentanone	0.23	0.08	0.31	0.07	0.28	0.06	0.30	0.03	0.28	0.03
2-hexanone	0.15	0.00	0.23	0.01	0.28	0.01	0.29	0.02	0.23	0.07
<b>TVOC</b>	<b>38.81</b>	<b>10.21</b>	<b>83.05</b>	<b>20.07</b>	<b>77.51</b>	<b>16.77</b>	<b>39.62</b>	<b>13.12</b>	<b>59.75</b>	<b>28.57</b>



## 985 **S1. Source apportionment of VOCs**

Figure S1 shows the source profile of summertime VOCs obtained from the PMF model. The resolved factors were identified as biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, diesel vehicle exhaust, industrial production, paint solvent usage, and biogenic source. Factor 1 was characterized by high concentrations of ethane and ethylene. These compounds are tracers of incomplete combustion which emitted from vehicle exhaust and biomass/biofuel burning (An et al., 2017). Benzene, toluene, pentane, and decane concentrations were low in factor 1, therefore, it was identified as biomass/biofuel burning. Factor 2 was distinguished by a significant presence of LPG/NG VOCs propane, isobutene, and n-butane (Shao et al., 2016). So, factor 2 was identified as LPG/NG usage. Factor 3 was dominated by high concentrations of isopentane, n-pentane, and MTBE. Therefore, factor 3 was identified as gasoline evaporation (Song et al., 2018; Wang et al., 2016). Factor 4 possessed high concentrations of vehicle exhaust VOCs benzene and toluene (Song et al., 2018). Although these VOCs are also emitted by industrial processes, the contribution of benzene was several folds higher than toluene in this factor. Therefore, factor 4 was related to vehicle exhaust emission and it was assigned to gasoline vehicle exhaust (An et al., 2017). Factor 5 was characterized by high concentrations of acetylene, n-heptane, and decane. These are related to vehicle emission, especially diesel vehicle exhaust emission as diesel engine produce more acetylene than the gasoline engine does (Song et al., 2018; An et al., 2017). Therefore, factor 5 was attributed to diesel vehicle exhaust. Factor 6 was dominated by toluene and the sampling site was beside an industrial area. So, we identified this factor as industrial production. Due to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene, factor 7 was assigned to paint solvent usage sources (Li et al., 2018). Factor 8 was attributed to the biogenic source, which was mainly distinguished by a high concentration of isoprene (Song et al., 2018).

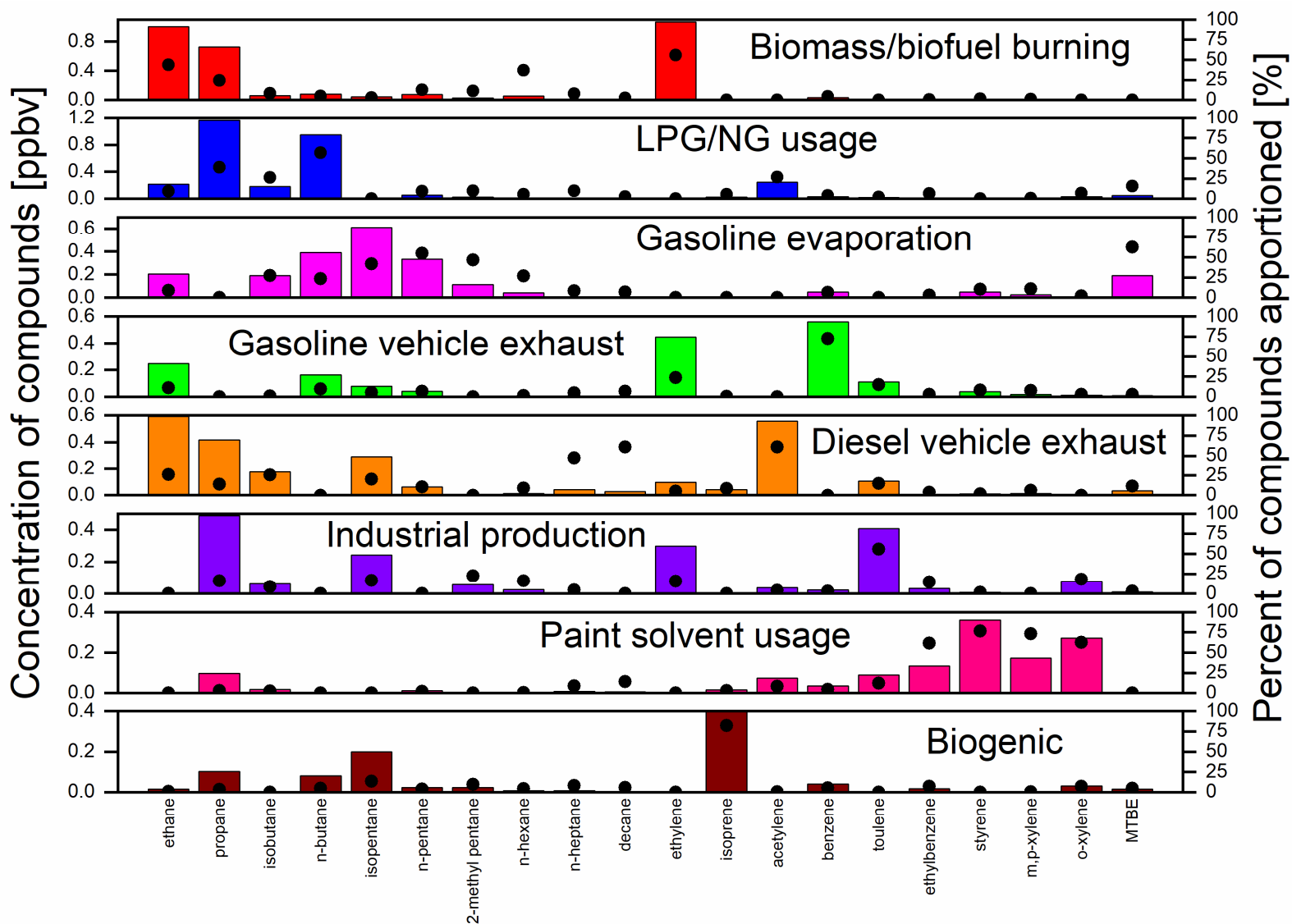
During autumn, the possible VOC sources were biomass/biofuel burning, multiple sources, gasoline vehicle exhaust, vehicle emission, LPG/NG usage, paint solvent usage and gasoline evaporation (Fig.S2). Factor 1 was represented by a high concentration of ethane and ethylene, so, it was identified as biomass/biofuel burning (An et al., 2017). Factor 2 was dominated by isoprene, n-heptane, decane, and acetylene. Among these compounds isoprene is mainly emitted by trees and rest of the compounds are related to diesel vehicle exhaust emission. Therefore, Factor 2 was identified as multiple sources. Factor 3 was identified as gasoline vehicle exhaust

due to high contribution of benzene and toluene. In factor 3, benzene was several folds higher than toluene. The 4<sup>th</sup> factor was mainly composed of vehicle emission related compounds 2-methyl pentane, n-hexane, n-heptane, n-pentane, and isopentane, therefore, identified as vehicle emission (Song et al., 2018). Factor 5 was assigned to LPG/NG usage as propane, isobutene, and n-butane were the main contributor to it (Shao et al., 2016). Factor 6 was characterized by a high concentration of o-xylene, m,p-xylene, ethylbenzene and styrene, which are typical tracer of paint solvent usage. Factor 7 was identified as gasoline evaporation, it was dominated by high concentrations of isopentane, n-pentane, and MTBE (Song et al., 2018).

During winter, the source factors were identified as gasoline vehicle exhaust, vehicle exhaust, gasoline evaporation, biomass/biofuel burning, multiple sources, LPG/NG usage, and paint solvent usage (Fig. S3). Factor 1 was assigned to gasoline vehicle exhaust; it was dominated by benzene and toluene and contribution of benzene was twice of toluene. Factor 2 was represented by a high concentration of isobutene, n-butane, acetylene, ethylene, ethane, n-heptane and decane. Isobutene and n-butane are related to LPG/NG usage, but, the contribution of propane was zero in factor 2. Acetylene, ethylene, and ethane emitted from combustion sources like vehicle exhaust and biomass burning. Decane and n-heptane are related to vehicle emission. By considering above information, factor 2 was identified as vehicle exhaust. Factor 3 was identified as gasoline evaporation and it was characterized by high concentrations of isopentane and n-pentane. Factor 4 was characterized by high contribution of ethylene and ethane; therefore, it was identified as biomass/biofuel burning. Factor 5 was characterized by high concentrations of isoprene, propane, n-hexane and n-heptane. Propane is related to LPG/NG usage, isoprene mainly emitted from trees (evergreen trees in winter), and n-hexane and n-heptane are related to vehicle emission. By considering above information, factor 5 was assigned to multiple sources. Factor 6 was dominated by high concentrations of propane. Therefore, it was identified as LPG/NG usage. Factor 7 was identified as paint solvent usage due to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene (Zhang et al., 2018; Song et al., 2020).

During spring, the possible VOC sources were biomass/biofuel burning, paint solvent usage, multiple sources, gasoline evaporation, gasoline vehicle exhaust, LPG/NG usage, and diesel vehicle exhaust (Fig. S4). Factors 1 was identified as a biomass/biofuel burning source for the high loading of ethylene and ethane and relatively lower contribution from the vehicle emission related compounds. Due to the high contribution of o-xylene, styrene, m,p-xylene, and

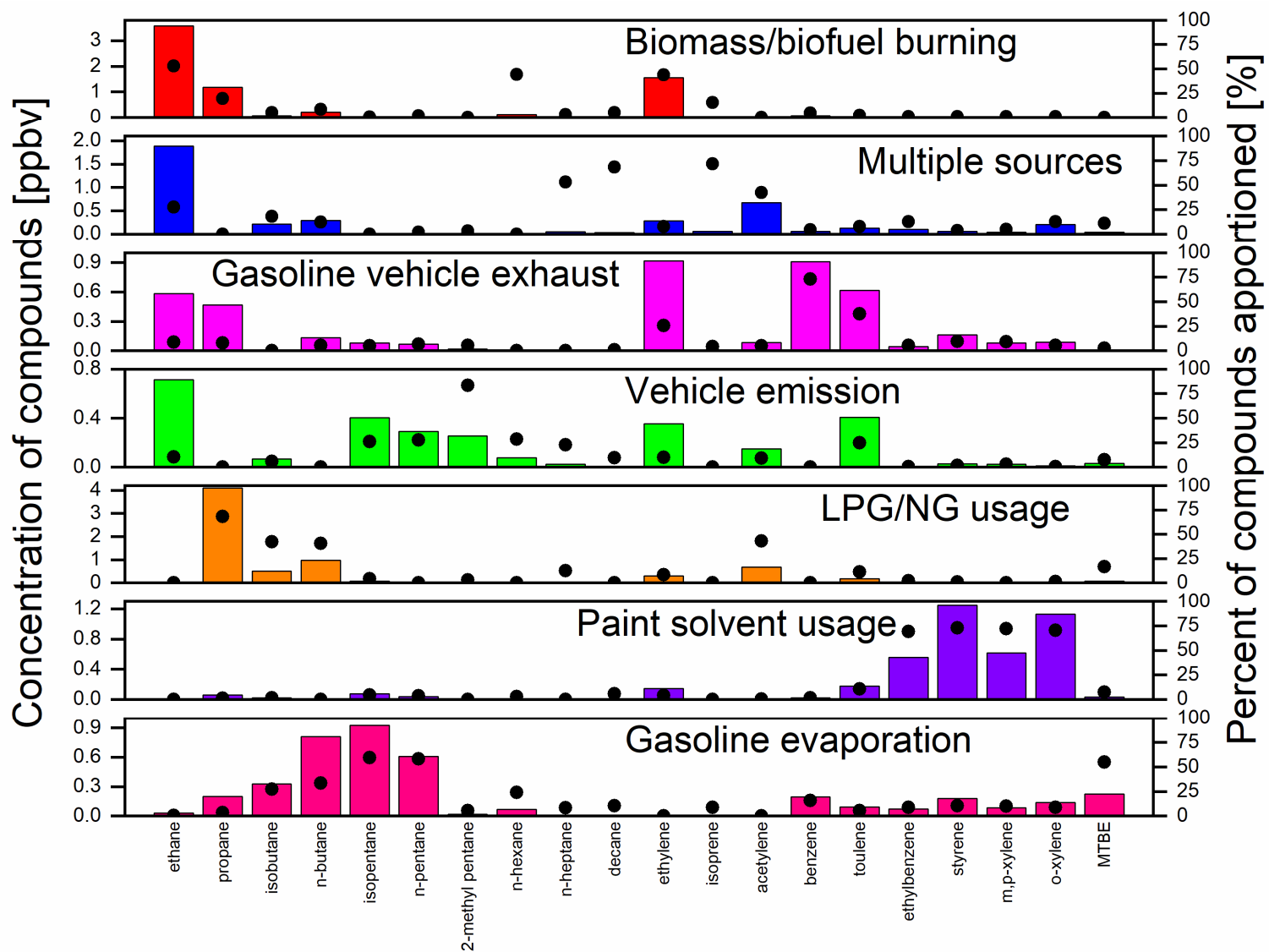
ethylbenzene, factor 2 was assigned to paint solvent usage sources (Li et al., 2018). Factor 3 had a high contribution of isoprene, n-hexane, n-heptane, decane, MTBE, toluene, ethylbenzene, and o-xylene. Therefore, factor 3 was identified as multiple sources. Factor 4 was represented by a high concentration of isopentane, n-pentane, and MTBE. Therefore, factor 4 was identified as gasoline evaporation. Factor 5 was represented by high concentrations of benzene, therefore, identified as gasoline vehicle exhaust. Factor 6 was assigned to LPG/NG usage due to the high contribution of propane, n-butane, and isobutane (Shao et al., 2016). Factor 7 was identified as diesel vehicle exhaust due to the high contribution of acetylene, n-heptane, and decane.



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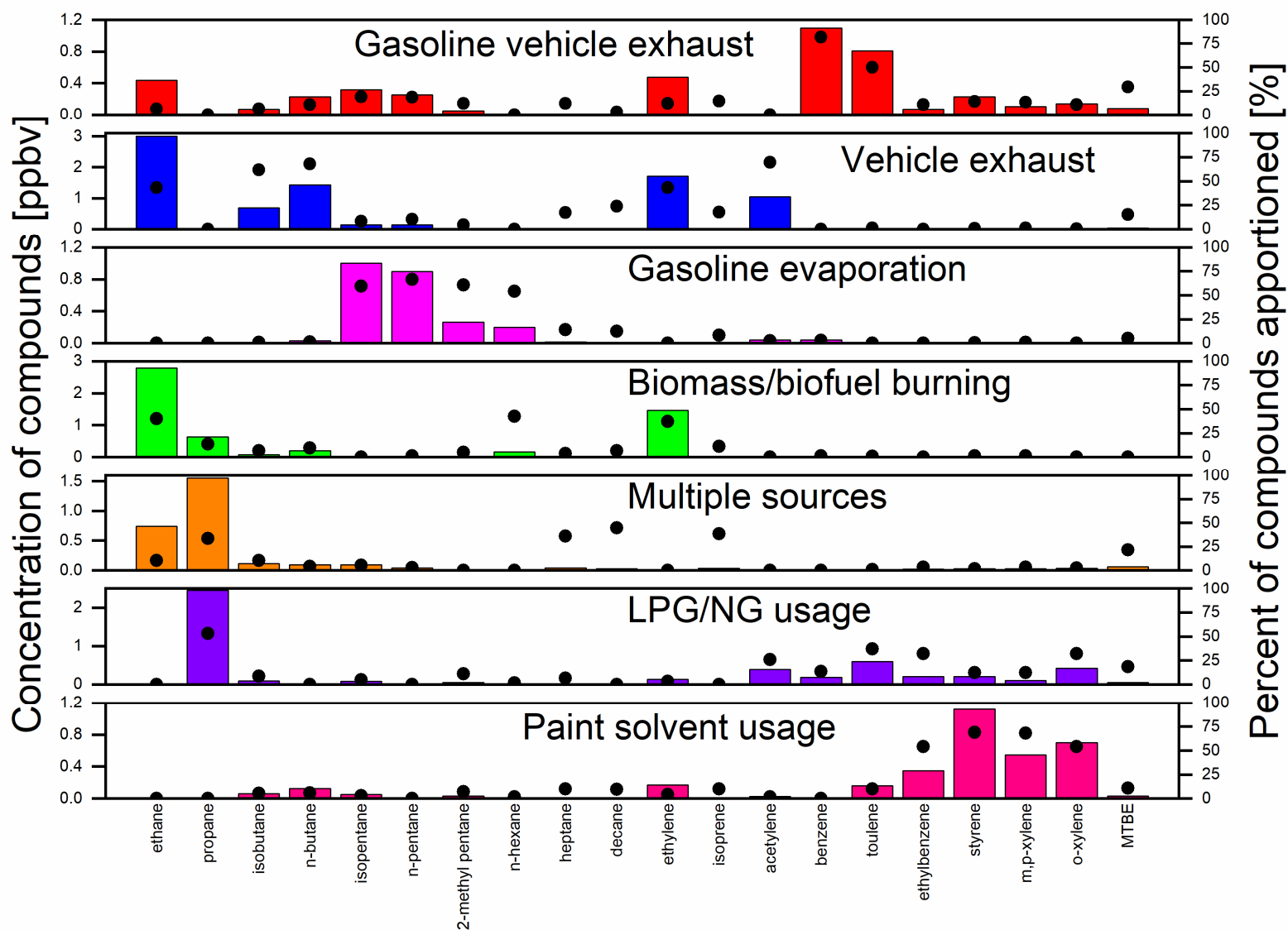
1056 **Figure S1: Source profile of VOCs during summer in Nanjing industrial area. Bars and dots represent the concentrations and**

1057 **percentages of the compounds, respectively.**



1058

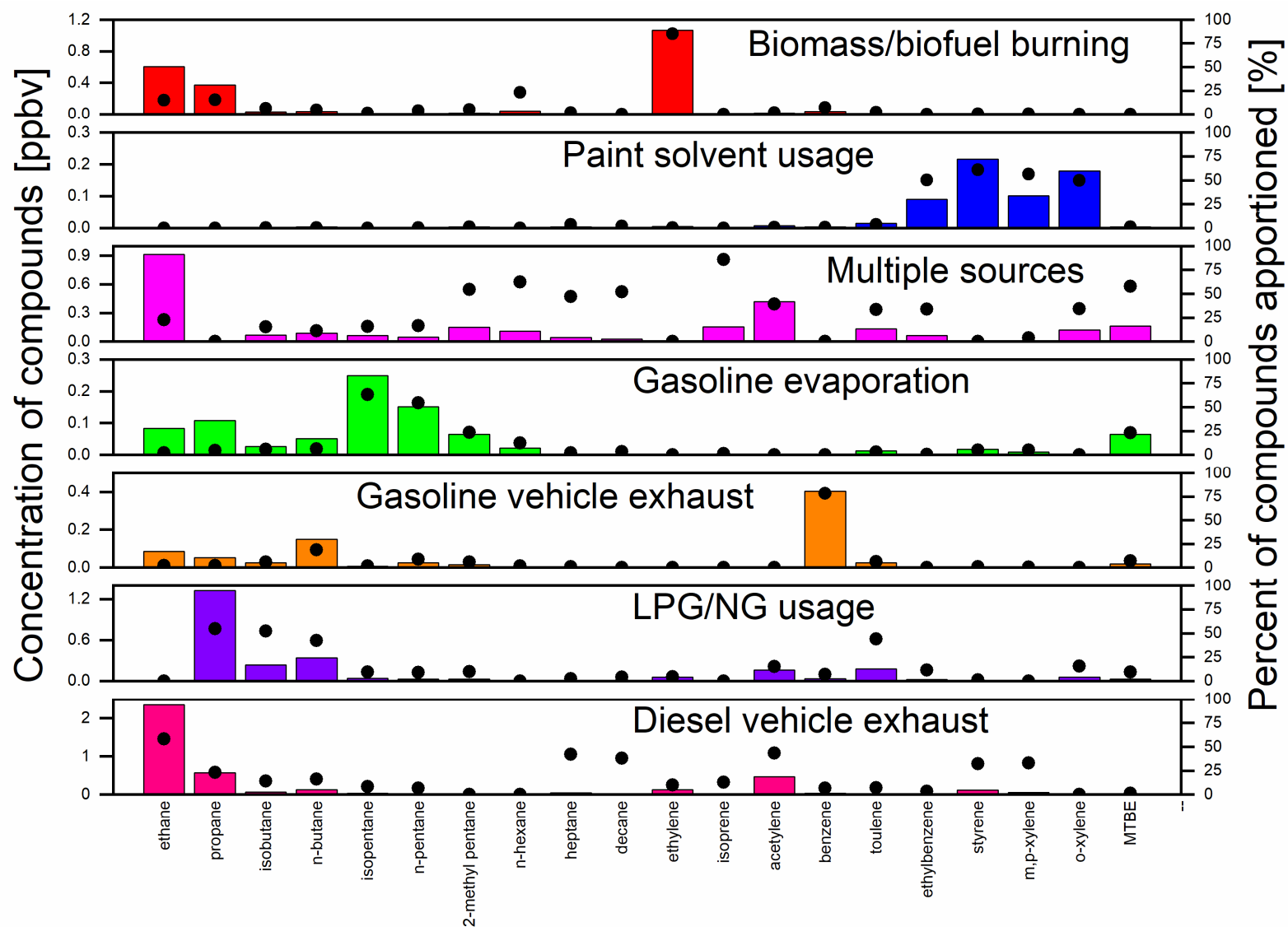
1059 **Figure S2: Source profile of VOCs during autumn in Nanjing industrial area. Bars and dots represent the concentrations and**  
 1060 **percentages of the compounds, respectively.**



1061

1062 **Figure S3: Source profile of VOCs during winter in Nanjing industrial area. Bars and dots represent the concentrations and**

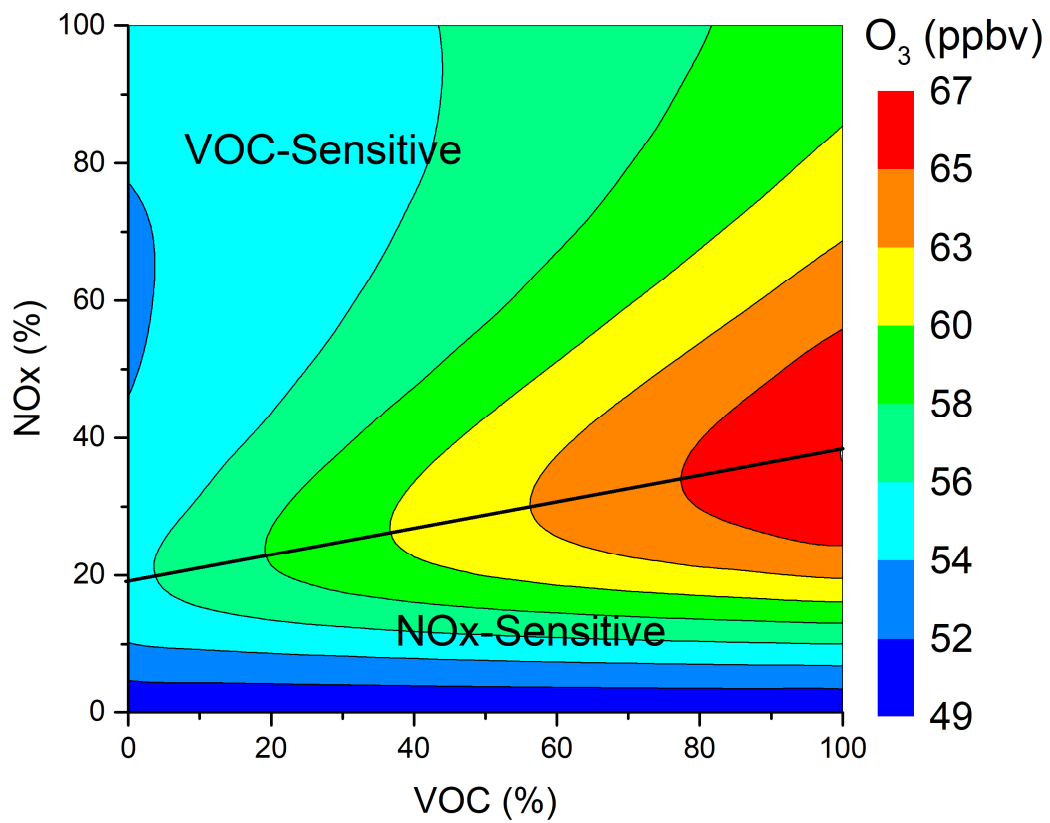
1063 **percentages of the compounds, respectively.**



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1065 **Figure S4: Source profile of VOCs during spring in Nanjing industrial area. Bars and dots represent the concentrations and**

1066 **percentages of the compounds, respectively.**



**Figure S5: O<sub>3</sub> isopleth diagram on a high O<sub>3</sub> episode day (July 29 2018) in Nanjing industrial area.**

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# Authors' response to referee 4

The authors are grateful to anonymous referee #4 for the insightful comments and suggestions. Here, we present the answers for each of the comments. The revised manuscript and supplement with tracked changes can be found at the end of the document.

5 **Approximately 100 speciated VOCs, measured by GC/FID/MS, are reported from a Nanjing industrial area in China from July 2018 – May 2020. The non-continuous measurement periods include field data from summer, autumn, winter, and spring. This measurement report focuses on the inclusion of select halocarbons and oxygenated VOCs to a “total” VOC (TVOC) measurement, which is then compared to past TVOC studies in Nanjing and other Chinese cities. The authors performed data analysis techniques**  
10 **including PMF, PSCF, and photochemical box modeling on this data set to assess potential VOC sources and the impact of these VOCs on local ozone production.**

### **General Comments**

15 **I note that the authors have already heavily revised their manuscript in response to previous Referee Comments (e.g. PMF results and discussion, exclusion of VOC ratio and ozone formation potential discussions) and this review is primarily based on the revised version.**

20 **The observations reported here, speciated and quantified VOC composition in Nanjing, would be a useful resource for the atmospheric research community. While the measurement techniques (described in Mozaffar et al. 2020, Atmospheric Research) employed for this study are appropriate and appear well done, some of the analysis and interpretations included in this measurement report could be refined. The following are some areas for concern that they authors might consider revising:**

25 **▪ Throughout the manuscript there is continuous discussion and comparison of VOC compositions measured in various cities from different studies. Here the authors compare observations of certain classes of VOCs by describing them as “%” (e.g. lines 75 – 91). I find this to not only be confusing, but also not a useful metric, as each study did not measure the same suite of VOCs. For example, comparing this studies % contribution of alkanes to the total VOC measurement to another studies is not useful if**  
30 **the other study was not measuring the same total VOC list. I would recommend that the authors revise the manuscript throughout. If they would like to directly compare their measurements to previous reports, they should do so on a concentration basis. Until this comparison is revised it is difficult to gauge how the measurements reported here compare to other areas.**

35 **Authors’ response: VOC concentrations are reported now instead of “%”.**

**▪ Along with the above comment, the use of the term “TVOCs” throughout this manuscript I find to be troubling. The TVOC measurement here is a sum of the suite of**

VOCs measured, but it is not a total VOC measurement. This term is especially frustrating in section 3.2, lines 242 – 263, where the authors compare their TVOC with that from other cities where entire groups of VOCs (e.g. halocarbons) were not included. The manuscript should be revised with care to make sure that any quantitative comparison with previous studies is “apples to apples” (even if that means that not all of the VOCs reported in this study are included in a specific comparison in the discussion).

40

45 Authors’ response: In the abstract, the term “TVOCs” is now defined. Hopefully, it will eliminate the confusion. In this kind of study, the term “TVOCs” is widely used to present the sum of the suite of VOCs measured.

The VOC species we presented in our manuscript does not exactly match with the previous studies discussed in the comparison section. That is why the “apples to apples” comparison of TVOCs with previous studies is not possible. Therefore, we deleted this TVOCs comparison part in the revised manuscript. However, we modified the TVOCs comparison part for the two previous studies performed in Nanjing. Except for halocarbons and OVOCs, only 4 VOC species concentrations are not presented in these studies compared to the current observation (Table S2). In the revised manuscript, the TVOCs concentration without halocarbons and OVOCs are compared between these studies.

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### Specific Comments

- **In section 2.4, which VOCs were used to model the impact of their reduction on ozone? The text (line 175) says 11 VOCs but does not list which ones or the authors’ reasoning for those choices.**

60

Authors’ response: 61 VOCs were constrained in the model. These constrained VOCs are listed in the revised Table S1. The rest of the measured VOCs were not constrained in the model as their reactions are not included in MCM. This information is now added in section 2.4. Actually, “11 NO<sub>x</sub> × 11 VOC concentrations” in line 175 represents something else. The model was run for 11 different concentration scenarios of the constrained VOCs and 11 different concentration scenarios of NO<sub>x</sub>.

65

- **In section 3.2, lines 224 – 228, the authors attribute a higher contribution of OVOCs in summer/spring to enhanced biogenic emissions. However, the concentration of the reported OVOCs (figure 2c) are fairly constant throughout the year (or even reduced in the summer). It appears the higher contribution of OVOCs in spring/summer is due to the reduction of other classes of VOCs (e.g. halocarbons).**

70

Authors’ response: Many thanks for the comment. These lines have been deleted in the revised manuscript.

- **The spring portion of the data set is from April 2020, could the authors provide comment on whether they view this measurement period to be representative of a**

75

**typical spring in Nanjing or not due to differences in daily operations due to the Covid pandemic.**

80 Authors' response: Actually, the spring portion of the data set is from April 15 to May 4 2020. The measurement period is representative of a typical spring in Nanjing; the temperature was around 20 °C (Figure 3). For your kind information, we could not do the measurement in spring 2019 due to the COVID pandemic.

- **The conclusion section should be re-written for clarity. The authors have numerous statements that are either redundant or grammatically incorrect.**

Authors' response: The conclusions section has been modified.

## 85 **Technical Corrections**

**Line 115: The authors should cite the supplemental from Mozaffar et al., 2020 here to give the reader a resource the GC/FID/MS technique, since the validity of the data included in the report relies on the quality of the analytical measurement**

Authors' response: Done, we cited it in the revised manuscript.

90 **Line 124: There are two Mozaffar et al., 2020 references in the list. They should be clarified as “a” and “b”**

Authors' response: Actually, there is one “Mozaffar et al., 2020” reference in the list. The other one is "Mozaffar & Zhang, 2020”.

95 **Line 149: I believe the notation for reaction rate constant with OH should be “kOH,i” generally using a capital “K” is for equilibrium constants.**

Authors' response: It is corrected in the revised manuscript and supplement.

**Line 217-218: Which citation are you referring to? There are two Nanjing studies included in Table S2.**

100 Authors' response: Citations have been added to the text now. Further information about location has also been added in Table S2.

**Figure 2: It would be helpful if the figure spacing was revised so that it is clearer that the TVOC and alkane data are on their own axis.**

Authors' response: Done, a revised figure has been added.

105 **Figure 3, Figure 4: It could help the comparison if all left and right axes were kept to the same range.**

Authors' response: The axes of Figure 3 have been fixed. Figure 4 has already been removed following the suggestion of Referee #2.

**Revised Figure 6: Keep color scheme consistent between pie graphs**

Authors' response: Done, the previous revised figure has been replaced by a modified one.

110 **Table S2: Missing concentration units (ppb)**

Authors' response: The unit has been added in the caption.

**Throughout: The manuscript should be edited for grammar, spelling errors, and redundant sentences.**

115 Authors' response: The manuscript has been checked thoroughly and edited for grammar, spelling errors, and redundant sentences.

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**Measurement report: High Contributions of Halocarbon and Aromatic Compounds to  
Emissions and Chemistry of Atmospheric VOCs in Industrial Area**

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**Abstract.** Volatile organic compounds (VOCs) are key components for tropospheric chemistry and air quality. We investigated ambient VOCs in an industrial area in Nanjing, China ~~from between~~ July 2018 ~~to~~ and May 2020. The ~~total~~ sum of the suite of measured VOCs (TVOCs) concentration was  $59.8 \pm 28.6$  ppbv during the investigation period. About twice TVOCs concentrations were observed in autumn ( $83 \pm 20$  ppbv) and winter ( $77.5 \pm 16.8$  ppbv) seasons compared to those in spring ( $39.6 \pm 13.1$  ppbv) and summer ( $38.8 \pm 10.2$  ppbv). ~~Unlike~~ In previous studies in Nanjing, oxygenated-VOCs (OVOCs) and halocarbons were not measured, ~~the observed TVOCs was about 1.5 and 3 times higher than those previously reported in the same study area and a nonindustrial suburban area in Nanjing, respectively~~ the current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2 folds higher than the one reported in the nonindustrial suburban area in Nanjing. Observed TVOCs concentrations were similar to those in metropolitan city Beijing and Shanghai, however, it was about 1.5–3 folds higher than those in Lanzhou, Wuhan, Tianjin, Ningbo, Chengdu, London, Los Angeles, and Tokyo. Due to the industrial influence, halocarbons ( $14.3 \pm 7.3$  ppbv, 24%) VOC-group was the second largest contributor to the TVOCs after alkanes ( $21 \pm 7$  ppbv, 35%), which is in contrast with the previous studies in Nanjing and



also in almost other regions in China. Relatively high proportions of ~~hale~~hydrocarbons and aromatics were observed in autumn (25.7 and 19.3%, respectively) and winter (25.8 and 17.6%, respectively) compared to those in summer (20.4 and 11.8%, respectively) and spring (20.3 and 13.6%, respectively). According to the potential source contribution function (PSCF), short-distance transports from the surrounding industrial areas and cities were the main reason for the high VOC concentration in the study area. According to positive matrix factorization (PMF) model results, ~~industry-related sources (23-47%) followed by~~ vehicle-related emissions (24.33-34.48%) contributed the major portion to the ambient VOC concentrations. ~~Whereas aromatics~~ Aromatics followed by alkenes were the top contributors to the loss rate of OH radicals ( $L_{OH}$ ) (37 and 32%, respectively), ~~alkenes followed by aromatics contributed most to the ozone formation potential (OFP) (39 and 28%, respectively). Besides, the aromatics VOC group was also the major contributor to the secondary organic aerosol potential (SOAP) (97%).~~ According to the empirical kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis ~~in assistance with a photochemical box model~~, the study area was in the VOC-sensitive regime for ozone ( $O_3$ ) formation during all the measurements seasons. ~~Therefore, mainly alkenes and aromatics emissions chiefly from industries and automobiles should be reduced to decrease the secondary air pollution formation in the study area.~~ Therefore, alkenes and aromatics emissions from automobiles need to be decreased to reduce the secondary air pollution formation in the study area.

## 1 Introduction

Air pollution characterized by severe ozone ( $O_3$ ) and haze pollution is a big problem in urban and industrial areas in China (He et al., 2019; Hui et al., 2018; Tan et al., 2018; Jia et al., 2016; Feng et al., 2016; Hui et al., 2019). In recent years,  $O_3$  concentration above the national standard, and severe haze events are frequently reported (He et al., 2019; Hui et al., 2019; Sheng et al., 2018; Feng et al., 2016; Tan et al., 2018; Jia et al., 2016). As a precursor of  $O_3$  and secondary organic aerosol (SOA), volatile organic compounds (VOCs) are largely responsible for the severe air pollution in China (Song et al., 2018; Hui et al., 2019; Hui et al., 2018; He et al., 2019). Unfortunately, anthropogenic VOC emissions have been increasing over the last two decades in China and it is expected to do so in the future (Mozaffar & Zhang, 2020, and references therein).

Atmospheric VOC has plenty of sources; it can be emitted from various anthropogenic and biogenic sources. Besides, it can also be formed in the atmosphere. Anthropogenic VOC sources mainly include industrial emission, vehicle exhaust, solvent usages, biomass burning, and fuel evaporation. On the other hand, vegetation is the main biogenic sources of VOC. In developed areas in China, vehicle exhaust and industrial emission are the ~~2~~two major VOC sources (He et al., 2019; Hui et al., 2018; Hui et al., 2019; Mo et al., 2017; Song et al., 2018; An et al., 2014; Mozaffar & Zhang, 2020). ~~Whereas~~ Vehicle-related sources are more dominant in the North China Plain (NCP), Central China (CC), and Pearl River Delta ~~region~~ (PRD) regions.; But industry-related sources are more influential in the Yangtze River Delta (YRD) area (Zhang et al., 2017; Meng et al., 2015; Sun et al., 2019; He et al., 2019; Zhang et al., 2018; An et al., 2017; Mozaffar & Zhang, 2020; Shao et al., 2016). Alkanes, Alkenes, aromatics, oxygenated-VOCs (OVOCs), and halocarbons are the most common VOC-groups in the atmosphere (Hui et al., 2019; Hung-Lung et al., 2007; Song et al., 2018; Tiwari et al., 2010; He et al., 2019; Na et al., 2001; Hui et al., 2018). VOC concentration and composition changes depending on seasons, for example, the contribution from biogenic and solvent utilization increases in summer, and contribution from combustion sources increases in winter (Mo et al., 2017; Song et al., 2018; An et al., 2014). The chemical reactivity of VOC depends on its chemical composition, for instance, alkenes and aromatics are generally more reactive than alkanes (Carter, 2010). ~~To understand the chemical reactivity and secondary product formation ability of VOCs,~~ An analysis of OH radical loss rate ( $L_{OH}$ ), ozone formation potential (OFP), and secondary organic aerosol potential (SOAP) are is commonly used to understand the chemical reactivity of VOCs (Song et al., 2018; He et al., 2019; Hui et al., 2018); Hui et al., 2019).

Industries are an important source of VOC, and different reactive and hazardous VOCs emissions from industries are already reported in different areas on earth (Zhang et al., 2018; Na et al., 2001; Hung-Lung et al., 2007; Yan et al. 2016; Tiwari et al., 2010; Shi et al., 2015; Zhang et al., 2018b). For instance, Zhang et al. (2018) reported a high concentration of alkanes ( $21.3 \pm 17.8 \text{ mg m}^{-3}$  out of the total  $23.1 \pm 24.5 \text{ mg m}^{-3}$  (82%)) and lifetime cancer risk of different aromatics and halocarbons in a petroleum refinery in Guangzhou, China. A high concentration of OVOCs ( $829.7 \pm 1076.7 \text{ ppbC}$  out of the total  $1317.3 \pm 1184.5 \text{ ppbC}$  (63%)) was observed in an industrial area in Ulsan, Korea (Na et al., 2001). Hung-Lung et al. (2007) mentioned a high concentration of aromatics ( $\sim 90 \text{ ppb}$  out of the total  $\sim 160 \text{ ppb}$ ) in an industrial area in Taiwan. A

high concentration of halocarbons (~~49%~~9590.2 mg m<sup>-3</sup> out of the total 19652 mg m<sup>-3</sup>) was observed in an iron smelt plant in Liaoning, China (Shi et al., 2015). Zhang et al. (2018) mentioned a high concentration of alkanes (~~42%~~39.4 ppbv out of the total 94.15 ppbv) and aromatics (~~20%~~18.9 ppbv out of the total 94.15 ppbv) in a petrochemical and other industries affected area in Shanghai, China. ~~High concentrations of aliphatic and aromatics were observed in a petrochemical industrial area in Yokohama, Japan (Tiwari et al., 2010).~~ Therefore, VOC composition varies ~~ed~~ among the industries/industrial areas in different regions. Mostly short-term investigations ~~were~~ are performed to characterize the VOCs in industry-affected areas. In the current study, we carried out a comprehensive investigation on VOC in an industrial area in Nanjing between July 2018 and May 2020. ~~Nanjing is located in the YRD region which is mainly affected by industrial emissions.~~ Several VOC investigations have already been performed in the Nanjing industrial area but OVOCs and halocarbons were not measured in those studies (An et al., 2017; An et al., 2014). However, OVOCs and halocarbons are already mentioned as one of the highest concentrated VOC -groups in other industrial regions (Na et al., 2001; Shi et al., 2015). In the current study area, a high concentration of alkanes (19.6 ppbv out of the total 43.5 ppbv 45%) and alkenes (11.1 ppbv out of the total 43.5 ppbv 25%) were observed in a previous investigation (An et al., 2014). Besides the incomplete VOC measurements, O<sub>3</sub> formation sensitivity to its precursors was not investigated properly using a photochemical box model in Nanjing. Moreover, source apportionment of VOCs was not conducted for different seasons of a year.

In the current study, we report the variations in concentrations and compositions of VOC during the observation period. We present the possible source areas and potential sources of VOC based on potential source contribution function (PSCF) and positive matrix factorization (PMF) model analysis. ~~We also present the contributions of different sources to ambient VOC during the measurement period.~~ We also report the chemical reactivity ~~and secondary product formation capacity~~ of the VOC using L<sub>OH</sub>, ~~OFP, and SOAP analysis~~. We also present the sensitivity analysis of O<sub>3</sub> formation using the empirical kinetic modelling approach (EKMA) and relative incremental reactivity (RIR) analysis. Therefore, this study provides valuable information to the scientific community and policymakers.

## 2 Material and Methods

### 2.1 Sampling Site Description, Gases Analysis, and Meteorology Data

Field measurements were carried out ~~at Nanjing University of Information Science and Technology (32.1°N, 118.4°E) for about one month in winter, spring, and summer and three months in autumn from between July 2018 to and May 2020 at Nanjing University of Information Science and Technology (32.1°N, 118.4°E), which is located in an industrial area in Nanjing, China.~~ The sampling site was on the rooftop of a building (~20 m). The sampling site is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high traffic roads, and residential areas. ~~A detailed description of the sampling site can be found elsewhere (Mozaffar et al., 2020).~~

We analysed ambient air VOCs using an online GC-FID/MS instrument (AC-GCMS 1000, Guangzhou Hexin Instrument Co., Ltd., China). FID detector analysed C2-C5 VOCs and MS analysed C6-C12 VOCs. The instrument analysed one sample at every hour. During the investigation period, we inspected and calibrated the instrument regularly to ensure the accuracy of the data (Mozaffar et al., 2020). We monitored the O<sub>3</sub> concentrations using a 49i O<sub>3</sub> analyser (Thermo Fisher Scientific Inc., USA); NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations were measured using a 42i NO-NO<sub>2</sub>-NO<sub>x</sub> analyser (Thermo Fisher Scientific Inc., USA); SO<sub>2</sub> concentrations were followed using a 43i SO<sub>2</sub> analyser (Thermo Fisher Scientific Inc., USA); and CO concentrations were measured using a 48i CO analyser (Thermo Fisher Scientific Inc., USA). We also measured temperature and relative humidity, wind speed, wind direction, and solar radiation by HMP155 (Vaisala, Finland), 010C (Met One Instruments, Inc., USA), 020CC (Met One Instruments, Inc., USA), and CNR4 (Kipp & Zonen, The Netherlands) analysers, respectively. A detailed description of the instrumentation, sampling procedure, analysis, quality control, and calibration procedure can be found elsewhere (Mozaffar et al., 2020).

### 2.2 Positive Matrix Factorization (PMF) model and Potential Source Contribution Function (PSCF)

We used the positive matrix factorization (PMF) model (US Environmental Protection Agency, USEPA, version 5.0) for the source apportionments of VOCs. A detailed description of the model can be found elsewhere (Hui et al., 2019; Song, ~~Tan, Feng, Qu, Liu,~~ et al., 2018). ~~In this study, w~~We used 620 potential VOC tracers (Fig. S1 - S4) in the PMF model ~~to analyse the VOC~~

~~sources for different seasons.~~ The error fraction was set to 20% for the sample data uncertainty estimation. We explored the PMF factor number from 4-8 to determine the optimal number of sources. Finally, we decided to choose an 7 to 8-factor solution ( ~~$Q_{\text{true}}/Q_{\text{robust}} = 1.0$~~ ) for different seasons as  $Q_{\text{true}}/Q_{\text{robust}}$  was  $\sim 1.0$ ,  $Q_{\text{true}}/Q_{\text{expected}}$  was ranging from 0.99-1.45 (Hui et al., 2019), and strong correlations (0.7-0.8) were observed between the concentrations extracted from the model and the observed concentrations of each compound (He et al., 2019).

We used the potential source contribution function (PSCF) to locate possible source areas of VOCs for different seasons during the investigation period. We used Zefir analysis software to do the PSCF analysis and the Hysplit4 model to cluster the backward trajectories (Petit et al., 2017). Backward trajectories in the sampling site were estimated using the National Centers for Environmental Prediction data ~~Backward trajectories in the sampling site were estimated using the data provided by the National Centers for Environmental Prediction~~ (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1>). We estimated 24-72 hr backward trajectories 24 times a day arriving at 500 m above the ground surface using the hysplit4 model. For the PSCF analysis, we divided the geographic region covered by the back trajectories into an array of  $0.1^\circ \times 0.1^\circ$  grid cells and used the mean TVOCs concentration as the VOC reference value. More details about the PSCF analysis can be found in previous studies (Chen et al., 2018).

### **2.3 OH radical loss rate ( $L_{\text{OH}}$ ), ~~Ozone formation potential (OFP), and Secondary organic aerosol potential (SOAP)~~**

To evaluate the daytime photochemistry of VOCs, we estimated their OH radical loss rate ( $L_{\text{OH}}$ ). The following equation was used to estimate the  $L_{\text{OH}}$  ( $\text{s}^{-1}$ ) (Zhang et al., 2020).

$$L_{\text{OH}} = [\text{VOC}]_i \times k_{\text{OH},i} \quad (1)$$

Where  $[\text{VOC}]_i$  is the concentration of VOC species  $i$  ( $\text{molecule cm}^{-3}$ ),  $k_{\text{OH},i}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is the reaction rate constant of  $i$  VOC with OH radical. The  $k_{\text{OH}}$  values for the VOCs are collected from Carter (2010) (Table S1).

~~The Ozone formation potential (OFP) of the VOCs is their maximum contribution to the  $\text{O}_3$  formation (Hui et al., 2018a). The OFP (ppbv) of the VOCs was estimated using the following equation:~~

$$OFP = [VOC]_i \times MIR_i$$

(2)

Where  $MIR_i$  is the maximum incremental reactivity of the  $i$  VOC. The MIR values for the VOCs are also collected from Carter (2010) (Table S1).

The contribution of VOCs to the formation of secondary organic aerosol is estimated by secondary organic aerosol potential (SOAP) (Song et al., 2018). We estimated the SOAP (ppbv) of VOCs using the following equation.

$$SOAP = [VOC]_i \times SOAP_i^p$$

(3)

Where  $SOAP_i^p$  is the SOA formation potential of the  $i$  VOC on a mass basis relative to toluene (Derwent et al., 2010). In this study, the  $SOAP_i^p$  factors of the VOCs are collected from Derwent et al. (2010) (Table S1).

## 2.4 Empirical Kinetic Modelling Approach (EKMA) and Relative Incremental Reactivity (RIR)

The empirical kinetic modelling approach (EKMA) is a well-known procedure to develop the  $O_3$  formation reduction strategy by testing the relationship between ambient  $O_3$  and its precursors (He et al., 2019; Hui et al., 2018; Vermeuel et al., 2019; Tan et al., 2018). In this study, we used the Framework for 0-D Atmospheric Model (FOAM v 3.2, Wolfe et al., 2016), a photochemical box model run by Master Chemical Mechanism (MCM) v3.2 chemistry (Jenkin et al., 1997; 2003, 2015; Saunders et al., 2003), to get the data for the EKMA isopleth. The FOAM-MCM box model can simulate 16940 reactions of 5733 chemical species. The box model was run using the VOCs and gas concentrations and the meteorological data as input. 61 VOCs were constrained in the model as the rest of the observed VOC species reactions are not included yet in MCM. These constrained VOCs are listed in Table S1. To generate the  $O_3$  isopleth from the model simulated data, a total of 121 reduction scenarios (11  $NO_x$   $\times$  11 VOC concentrations) were simulated and the maximum  $O_3$  produced in-at each model scenario was saved.

The relative incremental reactivity (RIR, Cardelino & Chameides, 1995) is also used to test the  $O_3$  formation sensitivity of its precursors. ~~The  $O_3$  formation sensitivity to its precursors' concentrations can also be assessed by the relative incremental.~~ We also utilized the FOAM-MCM box model data to estimate the RIR. The RIR is simply defined as the percentage change

in O<sub>3</sub> formation per percentage change in precursor's concentration. In this study, we reduced the precursor's concentration by 10% for the RIR estimation. The RIR was estimated using the following equation.

$$RIR(X) = \frac{[P_{O_3}(X) - P_{O_3}(X - \Delta X)] / P_{O_3}(X)}{[\Delta X] / [X]}$$

(4)

Where [X] is the observed concentration of a precursor X, [ΔX] is the changes in the concentration of X. P<sub>O<sub>3</sub></sub>(X) and P<sub>O<sub>3</sub></sub>(X - ΔX) are the simulated net O<sub>3</sub> production ~~with using~~ the observed and ~~the~~ reduced concentration of the precursor X, respectively.

### 3 Results and discussion

#### 3.1 Overview of the metrological conditions and air pollutants concentrations

The time series of the hourly ~~inorganic air pollutants, meteorological parameters, and TVOC concentrations data~~ are shown in Fig. 1. The discontinuity of the time series data is due to the failure of the instruments and COVID-19 lockdowns. The data measured between July and August 2018 are termed summertime data. Similarly, data collected between September and November 2018 are autumntime data, December 2018 and January 2019 are wintertime data, and April and May 2020 are springtime data. ~~The measured data from July to August 2018, September to November 2018, December 2018 to January 2019, and April to May 2020 are termed as summer, autumn, winter, and springtime data, respectively.~~ Overall, the observed temperature and solar radiation gradually decreased from summer to winter and increased back to the summertime level in spring. The temperature ranged between -5.7 and 41.4 °C during the measurement period. The relative humidity values varied from 18 to 100%; ~~and~~ high values were generally observed in winter and autumn. During the observation period, wind speed ranged between 0.1 and 7.5 ms<sup>-1</sup>. Wind prevailed at the sampling site from many directions during the measurement periods; more details about the wind direction will be discussed in Sect.3.3.2. The O<sub>3</sub> and NO<sub>x</sub> concentrations varied from 2 to 160 ppbv and 0.4 to 90 ppbv, respectively. Whereas high O<sub>3</sub> concentrations (>80 ppbv) were observed in summer and spring, high NO<sub>x</sub> concentrations were measured in winter and at the end of autumn. The CO and SO<sub>2</sub> concentrations ranged from 83 to 3398 ppbv and 0.5 to 21 ppbv, respectively. Generally, high

concentrations of CO and SO<sub>2</sub> were observed in winter and spring. The measured NO and NO<sub>2</sub> concentrations varied from 0.4 to 51 ppbv and 1 to 79 ppbv, respectively. In general, ~~the~~ high NO and NO<sub>2</sub> concentrations were observed in autumn and winter. The TVOCs concentrations estimated with all the measured VOCs varied between 9 and 393 ppbv during the observation period and the high values were measured in autumn and winter. More details about the abovementioned parameters will be discussed in the following section.

### 3.2 Concentration and composition of VOCs

In total, 100 VOCs were observed in Nanjing industrial area, including 27 alkanes, 11 alkenes, ~~1~~ one alkyne, 17 aromatics, 31 halocarbons, 12 OVOCs, and ~~1~~ one other (carbon disulfide) (Table S2). Ethane (5.8±2.5 ppbv), propane (4.2±1.5 ppbv), and ethylene (3±1.6 ppbv) were the most abundant VOCs in the study area during the observation period. However, we observed season-wise variations in the order of abundant VOC species (Table S2). For instance, acetone was the 3<sup>rd</sup> highest concentrated VOC in spring. The abovementioned 4 VOC species are also frequently mentioned as the most abundant VOCs in different regions in China (Deng et al., 2019; He et al., 2019; J. Li et al., 2018; Ma et al., 2019). We compared the individual VOC concentrations with the available data presented in recent investigations. The individual VOC concentrations in the current observation were similar to those reported in the previous investigations in the same study area (An et al., 2017), however, they were almost twice of those found in a nonindustrial suburban area in Nanjing (Wu et al., 2020) (Table S2). Some of the differences -may be due to the differences in the observation period. The reported yearly concentrations (Wu et al., 2020) were probably estimated over continuous measurement data for a year. However, in the current observation, the measurements were not continuously performed during all the days of a year. The autumn time individual VOC concentrations ~~in the current observation~~ were about 1.4 fold lower than those measured in Beijing during October-November (Li et al., 2015). The wintertime individual VOC concentrations were also about 1.4 fold lower than those measured in and Shanghai during November-January (Zhang et al., 2018). ~~but~~ But, the yearly individual VOC concentrations in the current observation were similar to those measured in Guangzhou from June to May (Zou et al., 2015). During the observation period, the concentrations of different VOC-groups were in the order of alkanes (21±7 ppbv, 35%)> halocarbons (14.3±7.3 ppbv, 24%)> aromatics (9.9±5.8 ppbv, 17%)> OVOCs (7.5±1.9 ppbv, 13%)> alkenes (5±1.9 ppbv,



8%)> alkynes ( $1.4 \pm 0.3$  ppbv, 2%)> others ( $0.5 \pm 0.2$  ppbv, 1%). ~~However, we noticed relatively higher proportions of OVOCs (14% and 18%) than the aromatics (12% and 14%) in summer and spring (Fig. 2c & f). The relatively higher contribution of OVOCs in summer and spring could be related to the biogenic emissions (e.g. acetone, MEK from trees). Indeed, the relative contribution of acetone and MEK to the TVOCs were higher in summer and spring than those in autumn and winter (Table S2). Huang et al. (2019) reported that the industries, biogenic emissions, and secondary formation are the main source of OVOCs in southern China.~~ Relatively high proportions of ~~he~~hydrocarbons and aromatics were observed in autumn (25.7 and 19.3%, respectively) and winter (25.8 and 17.6%, respectively) compared to those measured in summer (20.4 and 11.8%, respectively) and spring (20.3 and 13.6%, respectively) (Fig. 2f). ~~The high proportions of he~~hydrocarbons and aromatics in autumn and winter ~~It~~ could be related to the burning of biomass and fossil fuel for additional heating. Similar to the observation in the current study, the alkane is generally the most abundant VOC group in China (Mozaffar & Zhang, 2020). The relatively high contribution ~~from of~~ halocarbons to the TVOCs could be related to the industrial emissions in the study area. ~~In previous studies in an iron smelt plant in Liaoning, China, a high concentration of halocarbons (49%) was observed (Shi et al., 2015).~~ However, halocarbons and OVOCs were not measured in previous investigations in the same study area (An et al., 2014; An et al., 2017; Shao et al., 2016) and also in another suburban area in Nanjing (Wu et al., 2020). Either aromatics or alkenes was mentioned as the second most abundant VOC ~~group~~ in those studies in Nanjing, which is the 3<sup>rd</sup> and 5<sup>th</sup> most abundant VOC group in the current investigation. ~~In Shanghai, a nearby city, alkanes (42%) and alkenes (26%) were two major VOC groups (Zhang et al., 2018).~~ The TVOCs concentration estimated with all the measured VOCs was  $59.8 \pm 28.6$  ppbv over the whole observation period, and relatively higher TVOCs concentrations were measured in autumn ( $83 \pm 20$  ppbv) and winter ( $77.5 \pm 16.8$  ppbv) compared to those observed in spring ( $39.6 \pm 13.1$  ppbv) and summer ( $38.8 \pm 10.2$  ppbv). The TVOCs concentration without halocarbons were  $45.4 \pm 20.4$ ,  $61.7 \pm 14.6$ ,  $57.4 \pm 11.8$ ,  $31.6 \pm 10.9$ , and  $30.9 \pm 8.2$  ppbv during the whole observation period, autumn, winter, spring and summer, respectively. ~~About 1.5 times higher TVOCs concentration was observed relative to the previous investigation in the same study area (An et al., 2014; An et al., 2017). Besides, we also found 3-times higher TVOCs concentration compared to the one in a nonindustrial suburban area in Nanjing (Wu et al., 2020).~~ As mentioned before, Hhalocarbons and OVOCs were not measured

440 reported in the previous investigations in Nanjing (An et al., 2017; Wu et al., 2020). The current TVOCs concentration without halocarbons and OVOCs was similar to the previous investigation in the same study area, however, 2-folds higher than the one reported in the nonindustrial suburban area in Nanjing. ~~those previous studies in Nanjing, it could be one of the reasons for the relatively high TVOCs concentration in the current study.~~ Observed autumn and wintertime TVOCs concentrations were similar to those measured in urban Beijing (86.2 ppbv in autumn) and Shanghai (94.1 ppbv in winter) (Li et al., 2015; Zhang et al., 2018). Similarly, observed summertime TVOCs concentration was similar to those found in urban Xi'an (42.6 ppbv), 445 Wuhan (43.9 ppbv) (Zeng et al., 2018; Sun et al., 2019). (Hui et al., 2018b) However, yearly TVOCs concentration was 1.5-3 folds higher than those in Lanzhou, Wuhan, Tianjin, Ningbo, Chengdu, London, Los Angeles, and Tokyo (Jia et al., 2016; Hui et al., 2018; B. Liu et al., 2016a; Mo et al., 2017; Song et al., 2018; von Schneidemesser et al., 2010; Warneke et al., 2012; Hoshi et al., 2008). The diurnal variation of the TVOCs, alkenes, aromatics, halocarbons, 450 OVOCs, and alkanes concentrations showed a double-hump structure (Fig. 2a, b, d, & e). This double-hump pattern indicates the contribution of traffic emission during the rush-hours in the morning and evening. The lowest concentration of the TVOCs and different VOC-groups reached 12:00-16:00. Oppositely, the highest concentration of O<sub>3</sub> was reached at-in that period (Fig. 3). The lowest O<sub>3</sub> concentrations were observed in winter which was consistent with the 455 solar radiations.

### 3.3 Sources of VOCs

#### 3.3.1 Specific Ratios

460 The use of the toluene/benzene (T/B) ratio is one of the simplest ways to preliminary analyse the VOC sources. If the T/B ratio is < 2, the study area is mainly affected by vehicle emissions (Hui et al., 2018, 2019). If the T/B ratio is > 2, the study area is influenced by other sources (e.g. industry, solvent utilization) beside vehicle emissions (Kumar et al., 2018; Niu et al., 2012; Li et al., 2019). Moreover, the T/B ratios are ranged between 0.2-0.6 in coal and biomass burning affected areas (Wang et al., 2009; Akagi et al., 2011). The diurnal variations in T/B ratios during different seasons are depicted in Fig. 4 (a, b, c, & d). The mean values of T/B ratios were ranged 465 between 0.9-2 (1.4±0.3), 1.3-2 (1.7±0.2), 1.1-1.6 (1.4±0.1), and 1.4-2.7 (1.9±0.3) during summer, autumn, winter, and spring, respectively. As the mean values of T/B ratios were around

2, the study area could be mainly affected by vehicle emissions. The double hump pattern in the diurnal variations in T/B ratios also indicates that the rush-hour traffic had a significant influence on the VOCs concentrations in the study area. Besides, the 75<sup>th</sup> percentiles of T/B ratios were above 2 most of the investigation periods, therefore, the study area could also be influenced by industrial emissions.

Figure 4 (e, f, g, & h) shows the ratios of different alkanes and aromatics to acetylene. Acetylene is a tracer of combustion sources, the ratios of different alkanes and aromatics to acetylene are used to comprehend the contribution of other sources to combustion sources. The mean ratios of propane, n-butane, and i-butane to acetylene were around 2.0-4.0, 0.7-1.6, and 0.4-0.8, respectively during all the seasons, which were smaller than those (11.5, 1.8, and 2.6, respectively) observed in Guangzhou city centre, which was affected by liquefied petroleum gas (LPG) emissions (Zhang et al., 2013). Therefore, LPG usages probably contributed a little fraction to the alkanes in the study area. The mean ratios of benzene, toluene, C8 aromatics, and C9 aromatics to acetylene were around 0.3-1.0, 0.4-1.1, 0.2-0.6, and 0.1, respectively during all the seasons. The observed ratios of benzene and toluene to acetylene were much higher than those found in Jianfeng Mountains in Hainan (0.2 and 0.1, respectively) but comparable to those measured in urban Guangzhou (0.4 and 0.4-1, respectively) (Tang et al., 2007). Besides, the observed ratios of C8 aromatics and C9 aromatics to acetylene were comparable to traffic emission influenced urban Guangzhou (0.68 and 0.2, respectively) and Wuhan (0.5 and 0.2, respectively) (Zhang et al., 2013; Hui et al., 2018). Therefore, vehicle exhaust probably contributed significantly to the aromatics in the study area.

### 3.3.2 Potential Source Contribution Function (PSCF)

Besides the local sources, both the long and short distance transports of air mass could bring VOCs to the study area. Figure 5 shows the wind cluster and PSCF analysis results for different seasons. During summer, the major air masses were short-distance transports from the southwest (40.44%) direction and two long-distance types of transport from southeast (39.31 and 25%) directions. A minor air mass (21%) was transported from the east direction. High PSCF values were in the nearby southwest, and southeast, and east directions; therefore, VOC pollution in the study area was mainly affected by the short-distance transport from the south and east directions. During autumn, the dominant air masses were short-distance transport from the northeast

~~northwest (5935%) and long-distance transport from the northwest (3034%) directions.~~ However, according to the PSCF analysis, VOC pollution was mainly influenced by the short distance transport from the south ~~and east~~ directions. During winter, short-distance transports from the ~~northeast (46%) and~~ northwest (~~3752%~~) directions ~~were~~ was the major incoming air masses to the study area. According to the PSCF values, the short-distance air masses from the south and ~~east north directions were~~ mainly transported VOC to the receptor site. During spring, air mass was mainly transported from the ~~southwestern north (4950%) and eastern southwest (3032%) directions.~~ A minor long-distance air mass was transported from the northwest (18%) direction. Atmospheric VOCs to the study area were mainly transported by these ~~two~~ air masses mostly from the nearby areas. Overall, the high PSCF values were concentrated around the measurement site, therefore, short distance transports from the surrounding areas and cities were the main reason for the high VOC concentration. The above conclusion perfectly makes sense as the sampling site is surrounded by different chemical and petrochemical industries, steel plants, gas stations, high traffic roads, and residential areas.

### 3.3.3 PMF Model Analysis

~~Differences were observed among the source profiles of VOCs obtained for different seasons (Sect. S1). For instance, the biogenic source was identified in summer, biomass burning source was distinguished in autumn, and LPG/NG usage source was found in winter and spring. However, industry and vehicle related VOC sources were identified during all the measurement seasons. According to PMF model results, aromatics were emitted from solvent usages, vehicle, and industry related sources. Besides, industry and combustion processes were the main sources of halocarbons and OVOCs. Moreover, alkanes and alkenes were emitted from vehicle exhaust and fuel usage sources.~~

~~Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, industry related sources contributed to the major portion of the ambient VOC concentrations followed by vehicle emission. Industrial emission accounted for about 32%, 47%, 45%, and 23% in summer, autumn, winter, and spring, respectively. The contributions of vehicle emission were about 34%, 26%, 24%, and 27% in summer, autumn, winter, and spring, respectively. The contribution of vehicle emission remained similar during the 4 seasons,~~

however, the contribution of the industrial emission increased in autumn and winter. Previous investigations performed in Beijing, Tianjin, Wuhan, Chengdu, and Shuozhou also found that the industry and vehicle are the two most important VOC sources (Zhang et al. 2017; Liu et al. 2016; Hui et al. 2018; Song et al. 2018) Jia et al., 2016). Besides these two sources, solvent usage (11%, 10%, 10%, and 4%, respectively) and gasoline evaporation (17%, 10%, NA, 6%, respectively) were two important VOC sources during those 4 seasons. Moreover, source contribution from the biogenic source in summer (7%), biomass burning in autumn (7%), LPG/NG usage in winter (11%) and spring (18%), and multiple sources in winter (10%) and spring (23%) was observed.

According to the PMF model analysis, five VOC sources were common during all the measurement seasons. They were biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, and paint solvent usage (Sect. S1). The biogenic source was distinguished only in summer. Figure 6 shows the relative contributions of different sources to ambient VOCs during different seasons. Overall, vehicle-related sources contributed the most to the ambient VOC concentrations. The total contributions of vehicle-related emissions were about 39%, 33%, 48%, and 42% in summer, autumn, winter, and spring, respectively. The contributions of biomass/biofuel burning sources were about 19%, 21%, 17%, and 16.4% in summer, autumn, winter, and spring, respectively. Besides these two sources, LPG/NG usage (18%, 21%, 16%, and 18%, respectively) and paint solvent usage (8%, 12%, 11%, 5%, respectively) were two other important VOC sources during those four seasons.

### 3.4 Chemical reactivity ( $L_{OH}$ ) and contribution to $O_3$ and SOA formation

The estimated loss rates of OH radical ( $L_{OH}$ ) with VOCs were about 2-fold high in autumn ( $13.7 \text{ s}^{-1}$ ) and winter ( $13.5 \text{ s}^{-1}$ ) compared to those in summer ( $7 \text{ s}^{-1}$ ) and spring ( $7.5 \text{ s}^{-1}$ ) (Fig. 7 a). The relatively high  $L_{OH}$  values in autumn and winter were due to the relatively high VOC concentrations in these seasons (Fig.2). The average  $L_{OH}$  value was  $10.4 \pm 3.6 \text{ s}^{-1}$  over the four seasons. It was in a similar range with the values determined in Guangzhou ( $10.9 \text{ s}^{-1}$ ), Chongqing ( $10 \text{ s}^{-1}$ ), Xian ( $1.6\text{-}16.2 \text{ s}^{-1}$ ), and Tokyo ( $7.7\text{-}13.4 \text{ s}^{-1}$ ), however, higher than the values estimated in Shanghai ( $2.9\text{-}5 \text{ s}^{-1}$ ,  $6.2 \text{ s}^{-1}$ ) and Beijing ( $7 \text{ s}^{-1}$ ) (Tan et al., 2019; Zhu et al., 2019; Yoshino et al., 2012; Song et al., 2020). While alkene was the highest contributor to the  $L_{OH}$  in summer ( $3 \text{ s}^{-1}$ , 43%) and spring ( $2.6 \text{ s}^{-1}$ , 35%), aromatic was the maximum contributor in autumn ( $6.9 \text{ s}^{-1}$ ,

50%) and winter ( $5.9 \text{ s}^{-1}$ , 44%) (Fig. 7 a & d). An increase in the OH loss rate by OVOCs was observed in spring (17%) compared to the other seasons (10, 8, and 9% in summer, autumn, and winter, respectively). Over the four seasons, the contribution of VOC-groups to  $L_{\text{OH}}$  exhibited the following trend: aromatics > alkenes > alkanes > OVOCs > halocarbons. Similar to the current study, aromatic is also mentioned as the maximum contributors to  $L_{\text{OH}}$  in different regions in China, however, the alkene is generally reported as the top contributor to  $L_{\text{OH}}$  (Zhang et al., 2020; Zhao et al., 2020; Hui et al., 2018; Song et al., 2020). Figure 7 also shows the top 10 VOCs contributing to  $L_{\text{OH}}$  for different seasons. Whereas isoprene was the highest contributor to  $L_{\text{OH}}$  in summer, it was styrene ~~was the largest contributor~~ in autumn and winter. On the other hand, naphthalene was the main contributor to  $L_{\text{OH}}$  in spring. Overall, styrene, naphthalene, ethylene, and isoprene were the main contributor to  $L_{\text{OH}}$  ~~in the study area~~. In previous studies in China, these compounds are also mentioned as one of the highest contributors to  $L_{\text{OH}}$  (Zhao et al., 2020; Hui et al., 2018; Song et al., 2020).

~~The estimated  $\text{O}_3$  formation potential (OFP) of VOCs were about 2-times high in autumn (170.8 ppbv) and winter (175.4 ppbv) relative to those in summer (86.2 ppbv) and spring (82.8 ppbv) (Fig. 8 a). The average OFP value was  $128.8 \pm 51.2$  ppbv during the measurement period. The springtime OFP was similar to the one estimated in Beijing (80 ppbv) (Li et al., 2015). The summertime OFP was about 1.5 times higher than the one in Xi'an (Song et al., 2020), but, about 1.4-2 folds lower than those found in Shanghai (Liu et al., 2019). The average OFP was about 1.5 times higher than the one in Wuhan (Hui et al., 2018). Whereas alkene was the major contributor to OFP in summer (37.4 ppbv, 43%), winter (72.8 ppbv, 41%), and spring (31.6 ppbv, 38%), aromatics contributed the most to OFP in autumn (62.7 ppbv, 37%) (Fig. 12 a & d). During the measurement period, the contribution of VOC-groups to OFP showed the following trend: alkenes > aromatics > alkanes > OVOCs > halocarbons. The alkene is also mentioned as the top contributor to OFP in Nanjing and the same observation is commonly found in China (An et al., 2014; Hui et al., 2018; Song et al., 2018; Song et al., 2020). The top 10 VOCs contributing to OFP for different seasons are also shown in Fig. 8 (b, c, e, & f). Ethylene was the major contributor to OFP during all the season. Followed by ethylene, cis-1,3-dichloropropene was the main contributor to OFP from summer to winter. In spring, propylene was the second most contributors to OFP. Overall, different alkenes were the highest contributor to OFP in the study area. Alkenes are also mentioned as the top contributor to OFP in the previous investigations in~~

Nanjing (An et al., 2014). Therefore, the reduction of these alkenes emissions in the study area could be one of the ways to reduce ambient O<sub>3</sub> concentration.

The secondary organic aerosol potentials (SOAP) were about 3 times higher in autumn (1422 ppbv) and winter (1269 ppbv) than those in summer (466 ppbv) and spring (398 ppbv) (Fig. 9a). The average SOAP was 889±531 ppbv during the measurement period. The average SOAP was about 2-3 times higher than those estimated in Wuhan and Beijing (Hui et al., 2019; Li et al., 2020). Aromatics was the main contributor to SOAP during all the seasons (95-97%) (Fig. 9 a & d) which was consistent with the observations in Chengdu (Song et al., 2018), Beijing (Li et al., 2020), and Wuhan (Hui et al., 2019). During the measurement period, the contribution of VOC-groups to SOAP exhibited the following trend: aromatics > alkanes > alkenes > OVOCs. Styrene, cumene, toluene, benzene, and o-xylene were the major contributor to SOAP during all the season (Fig. 9 b, c, e, & f). Therefore, the reduction of these aromatics emissions in the study area could be one of the ways to reduce ambient SOA concentration.

### 3.5 Sensitivity analysis of O<sub>3</sub> formation

Figure 10 shows the EKMA isopleth diagrams of O<sub>3</sub> for different seasons. In all the diagrams, VOC and NO<sub>x</sub> = 100 % is the base case. The ridgeline divided the diagrams into two regimes, VOC-sensitive (above) the line and NO<sub>x</sub>-sensitive (below) the line regimes. For all the seasons, the study area fell above the ridgeline. Moreover, a decrease in O<sub>3</sub> production was noticed decreased with the decrease in VOC concentration. Therefore, the study area was in the VOC-sensitive regime for O<sub>3</sub> formation during all the seasons. As a case study, O<sub>3</sub> formation sensitivity to its precursors was tested on a high O<sub>3</sub> concentration day (July 29 2018, maximum 126 ppbv). During the high O<sub>3</sub> episode, the study area was also in the VOC-sensitive regime for O<sub>3</sub> formation (Fig. S5). We also employed the RIR analysis to evaluate the O<sub>3</sub> production sensitivity to VOC, NO<sub>x</sub>, and CO concentrations (Fig. 11). The RIR value of VOC was the highest during all the seasons. It indicates that the O<sub>3</sub> production was more sensitive to the reduction of VOC concentration. This finding is consistent with the above results in the EKMA isopleth diagrams (Fig. 10). Except for the spring, the RIR values of CO were very small relative to those for the VOC. It indicates that the CO concentrations were relatively less important for the O<sub>3</sub> formation during those seasons. The RIR values for NO<sub>x</sub> were negative during all the seasons, implying that the O<sub>3</sub> formation was in the NO<sub>x</sub>-titration regime in the

study area. From the above analysis, it is evident that a reduction of VOC concentration in the study area will be the most efficient way to reduce the O<sub>3</sub> formation. The previous two studies performed in Nanjing also concluded the same finding based on VOC/NO<sub>x</sub> ratios and RIR analysis (An et al., 2015; Xu et al., 2017). Our findings are also consistent with the previous studies performed in other regions in China (Tan et al., 2018a; He et al., 2019; Feng et al., 2019; Ma et al., 2019). However, NO<sub>x</sub>-sensitive regions for O<sub>3</sub> formation are also found in China (Tan et al., 2018; Jia et al., 2016).

#### 4 Conclusions

~~Industries are an important anthropogenic source of VOCs. VOC plays a major role in tropospheric chemistry and air quality.~~ Nanjing is one of the biggest industrial cities in China. We performed a long term investigation of ambient VOCs ~~in an industrial area~~ in Nanjing. ~~Compare to the previous investigation in the current study area similar TVOCs concentrations were observed. However, about 2-folds high TVOCs concentrations were observed compared to the one previously reported in a nonindustrial suburban area in Nanjing. About 1.5 and 3-folds high TVOCs concentrations were observed compared to those previously reported in the same study area and a nonindustrial suburban area in Nanjing, respectively. The relatively high TVOCs was due to halocarbons and OVOCs concentrations were not measured in those previous studies in Nanjing. Therefore, halocarbons and OVOCs were an important part of the TVOCs in Nanjing, and industrial emissions had a large influence on VOC concentration in the study area. Observed TVOCs concentration was also about 1.5-3 folds higher than those reported in other cities in China and the world, but, similar to those measured in urban Beijing and Shanghai. This high VOC concentration in the study area needs to be reduced to decrease O<sub>3</sub> concentration and improve the local air quality.~~ TVOCs concentrations were about 2-times high in autumn and winter compared to those observed in summer and spring. Generally, haze pollutions frequently happen in autumn and winter, therefore, VOC concentration reduction in these seasons is an important step to reduce haze pollutions in the study area. Halocarbon was the 2<sup>nd</sup> largest contributor to the TVOCs following alkanes, it indicates the impact of industrial emissions on the local air. ~~After alkane, halocarbon was the 2<sup>nd</sup> largest contributor to the TVOCs, indicating a high influence of industrial emissions. Generally, alkenes/aromatics/OVOCs are the 2<sup>nd</sup> largest contributor to the TVOCs in China, therefore, industries in Nanjing emitted a high amount of~~



~~halocarbons into the atmosphere.~~ As halocarbons are carcinogenic, their emissions ~~should need~~ to be reduced. ~~The short distance transports from the surrounding areas and cities were the main reason for high VOC concentration.~~ PSCF analysis indicated that ~~the short distance transports from the surrounding areas and cities were the main reason for high VOC concentration in the study area.~~ Hence, local emissions ~~should need to~~ should need to be reduced ~~to decrease the haze and O<sub>3</sub> pollution in the study area.~~ Industries- Vehicle-related emissions were the major VOC sources in the study area ~~followed by vehicles~~, thus, emission reduction from ~~these two~~ these two sources should get more priority. Aromatics and alkenes ~~accounted for most~~ were the major contributors of to the L<sub>OH</sub>, ~~OF<sub>P</sub>, and SOAP~~, thus, these 2 ~~kinds of~~ VOC groups should get more priority in emission reduction policies and strategies. During all the seasons, the study area was in the VOC-sensitive regime for O<sub>3</sub> formation. Therefore, VOCs ~~especially aromatics and alkenes~~ emission reduction is the most effective way to decrease the local O<sub>3</sub> formation.

#### **Data availability**

All the data presented in this article can be accessed through <https://osf.io/bm6cs/>.

#### **Author contribution**

YLZ designed and supervised the project; MYF, FX, YCL, FC, and AM conducted the measurements; AM analysed the data and prepared the manuscript. All authors contributed in discussion to improve the article.

#### **Competing interests**

The authors declare that they have no conflict of interest.

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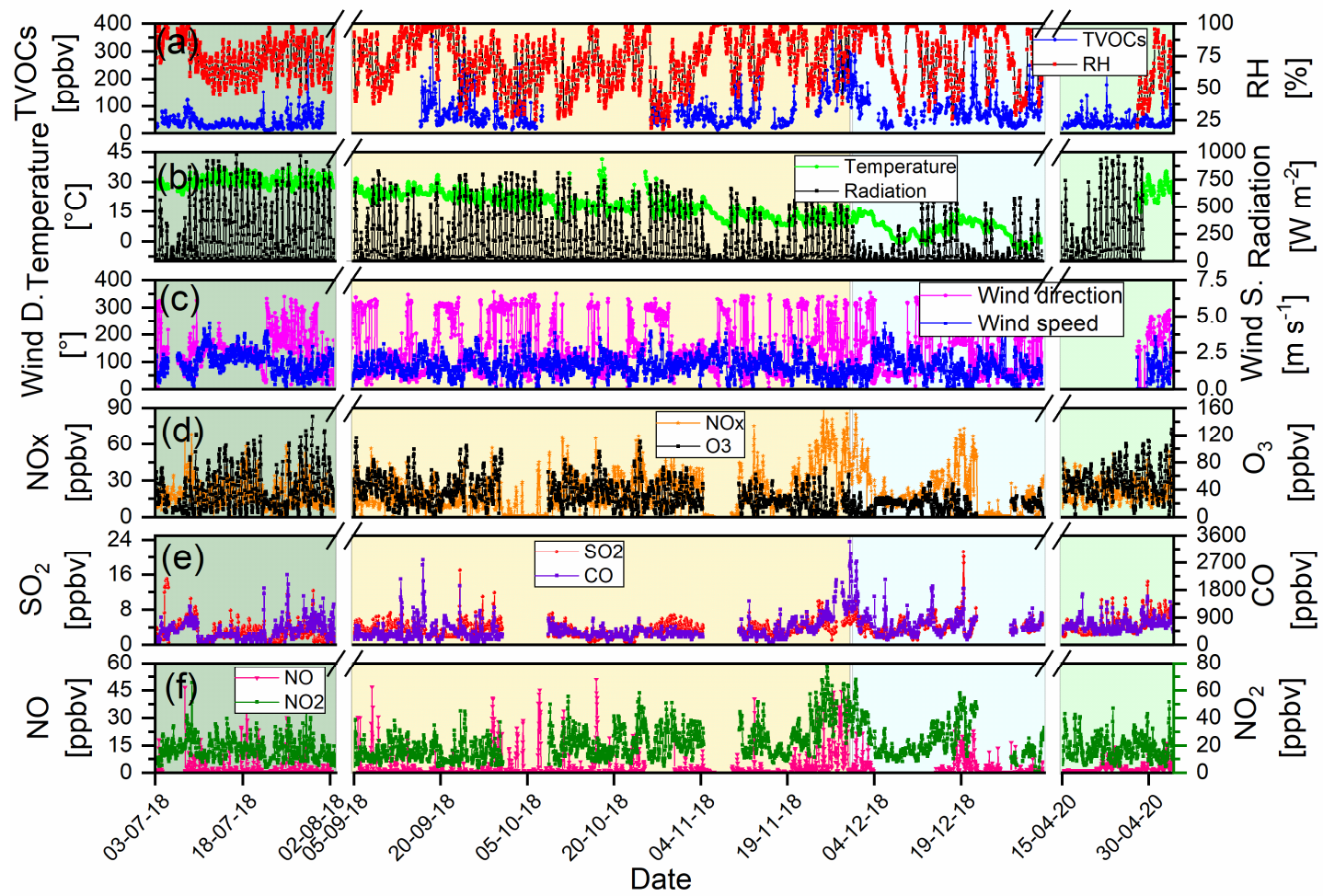
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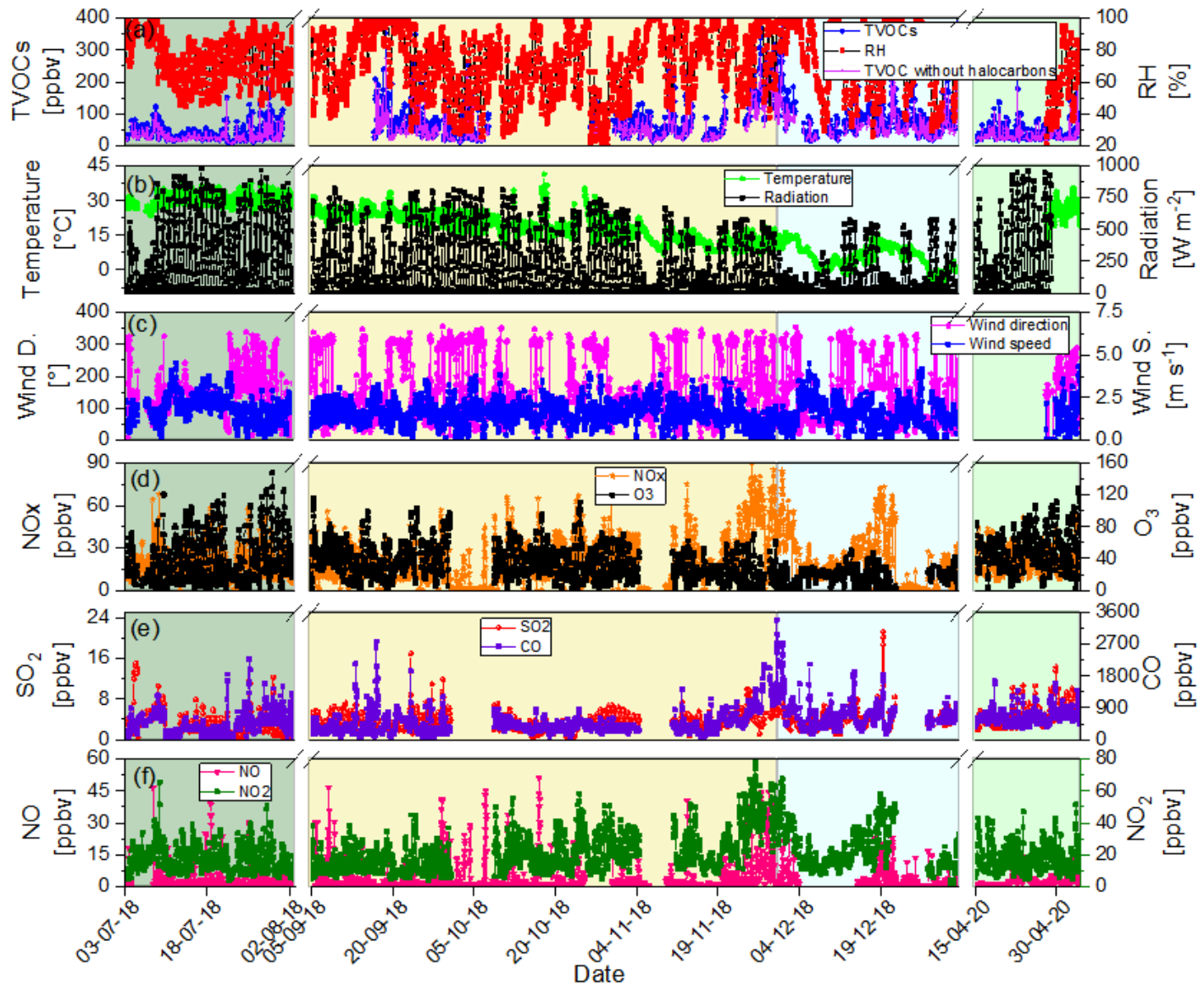
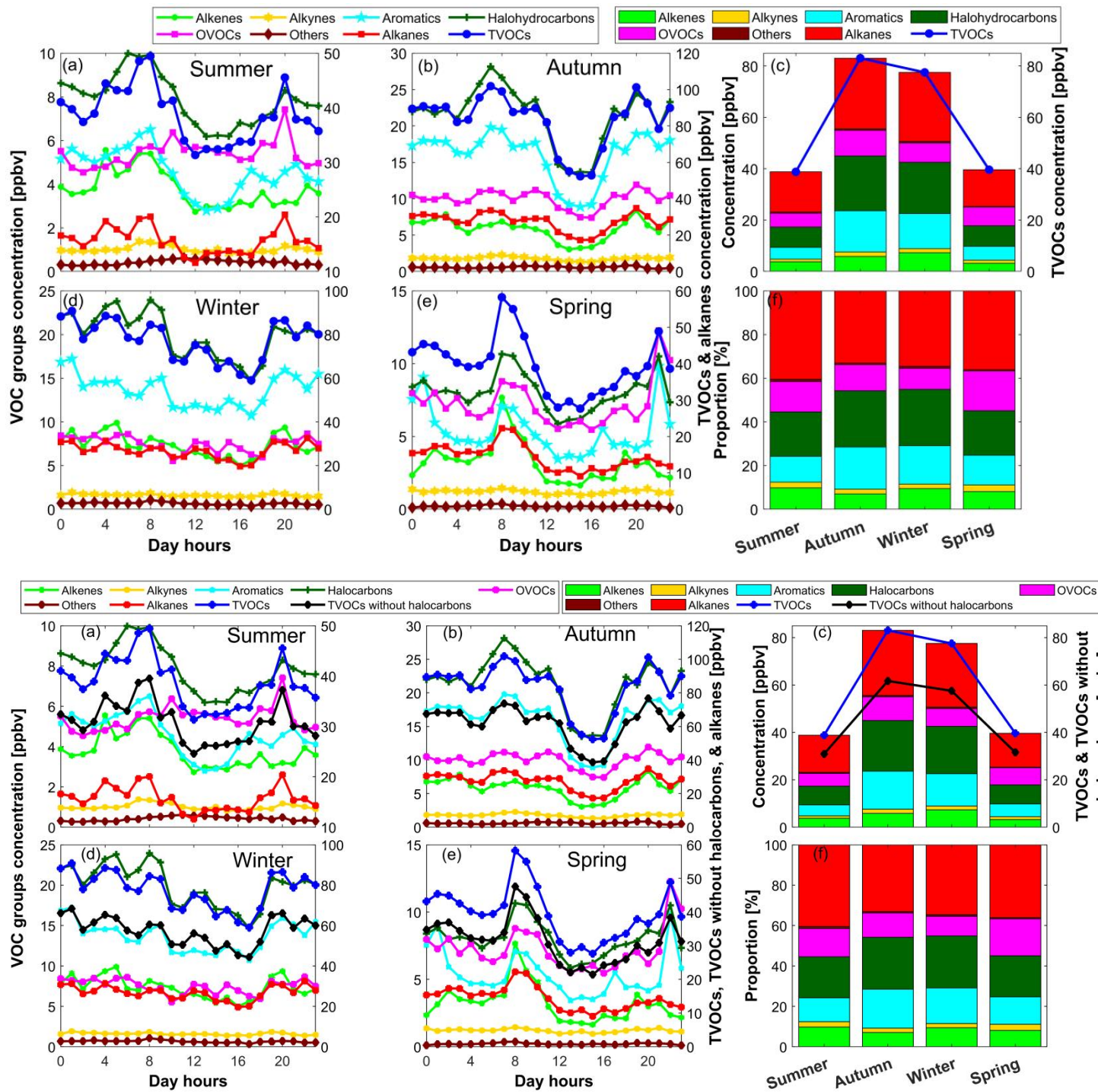


Figure 1: Time series of hourly meteorological parameters, inorganic air pollutants, ~~and~~ TVOCs, and TVOCs without halocarbons concentrations during the observation period at Nanjing. The green, yellow, cyan, and light-green shaded areas indicate summer, autumn, winter, and spring seasons, respectively. The discontinuity of the measured data is due to the instruments failure.

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Figure 2: Diurnal variations in TVOCs and different VOC-groups, TVOCs, TVOCs without halocarbons concentrations in different seasons (a, b, d, & e) and seasonal variations in average concentrations and proportion of different VOC-groups, TVOCs, TVOCs without halocarbons (c & f).

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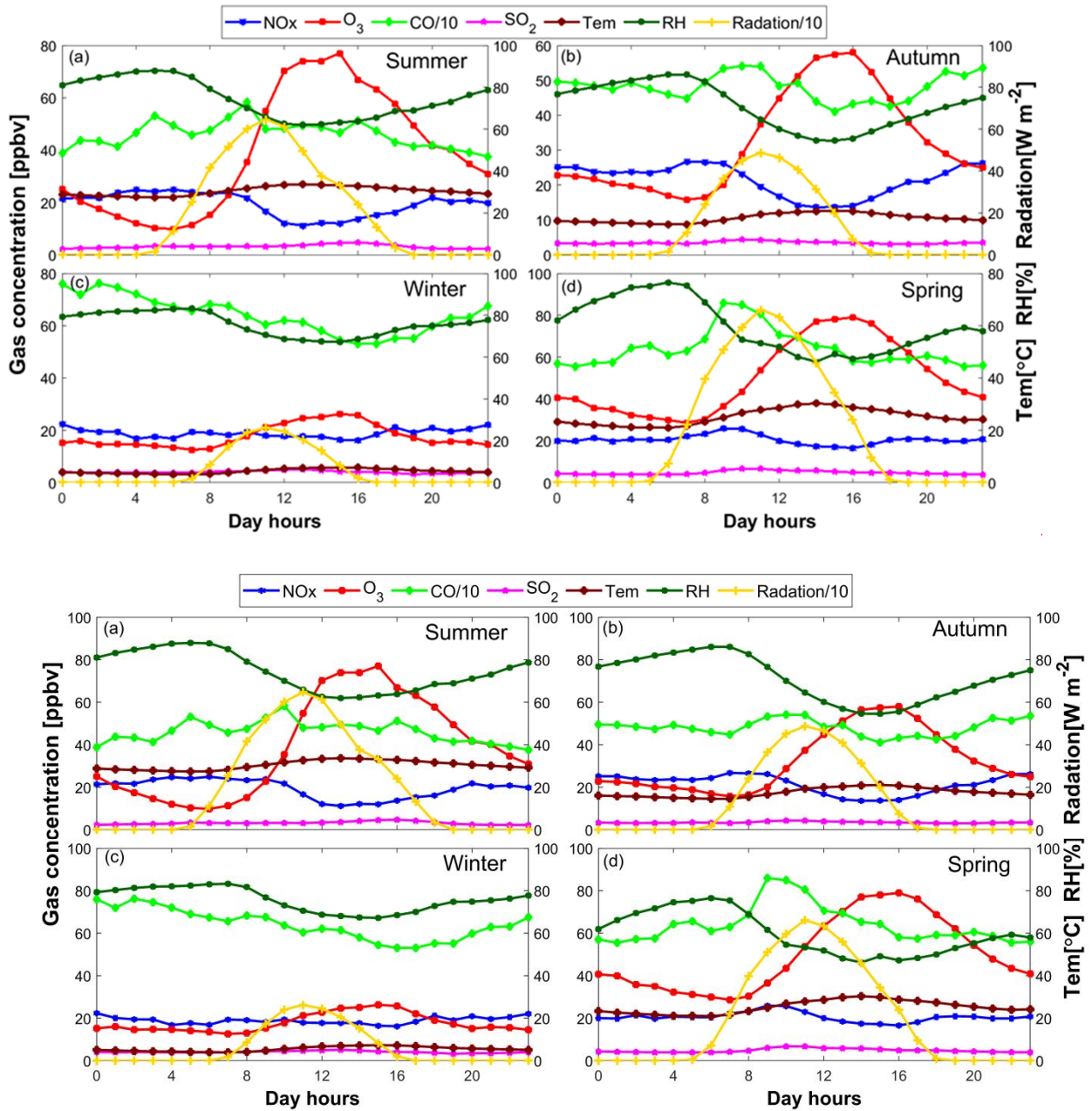
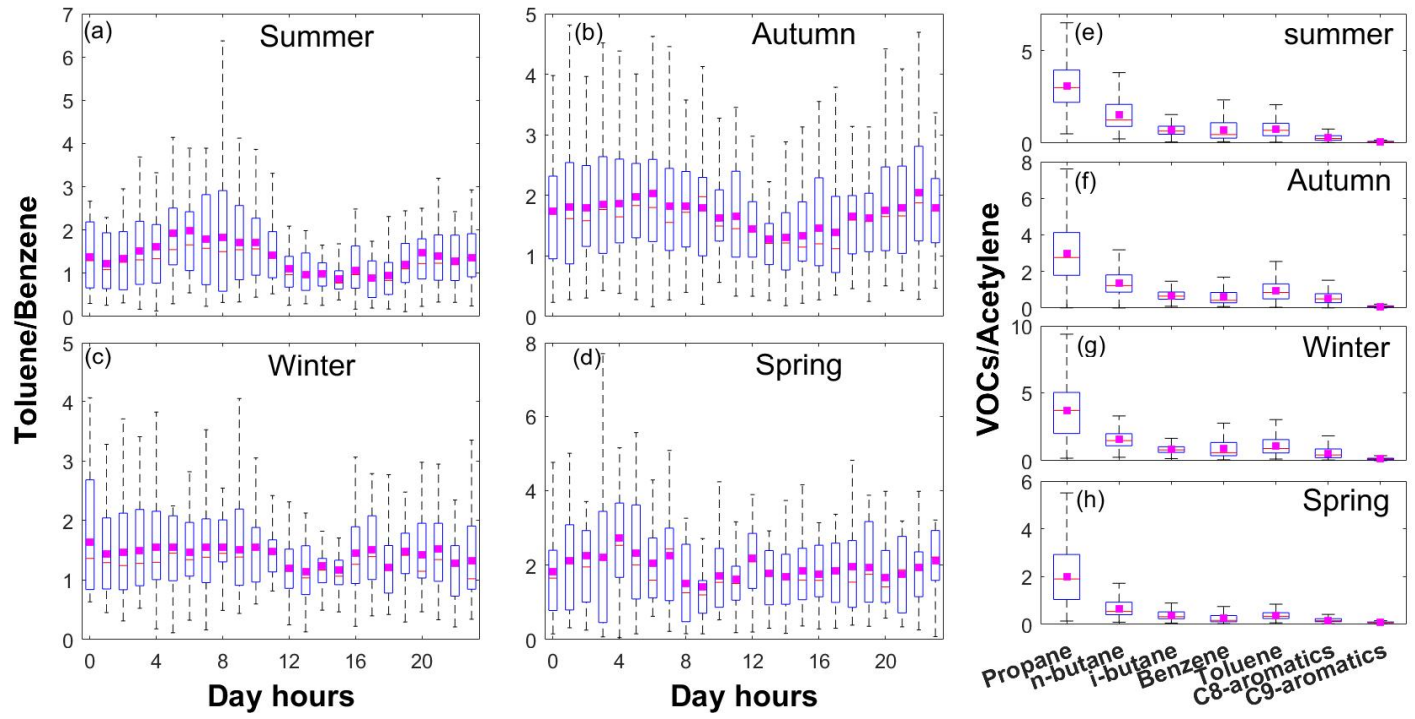


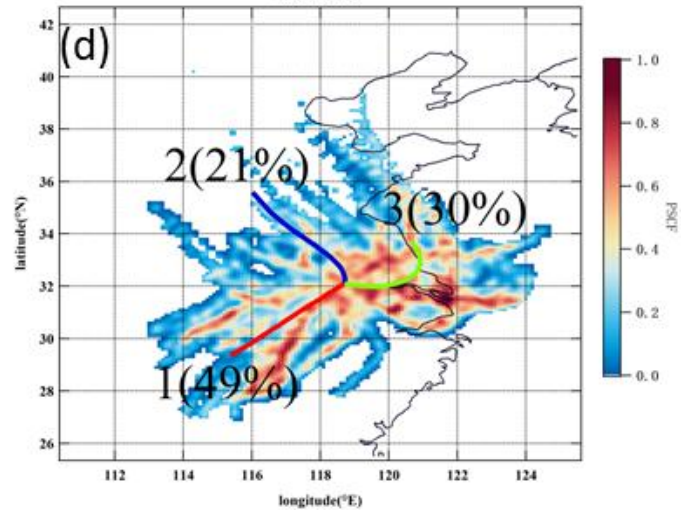
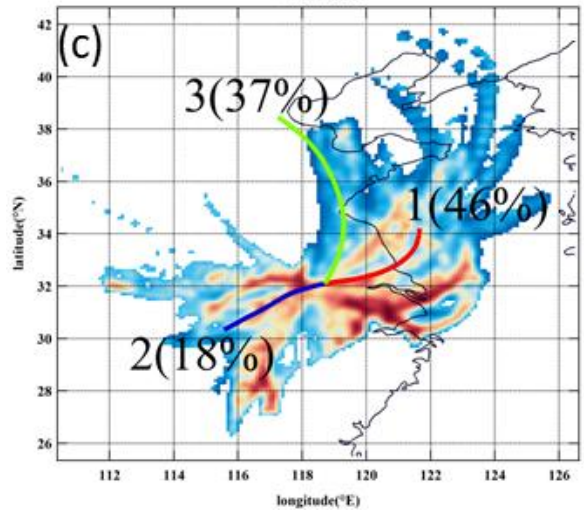
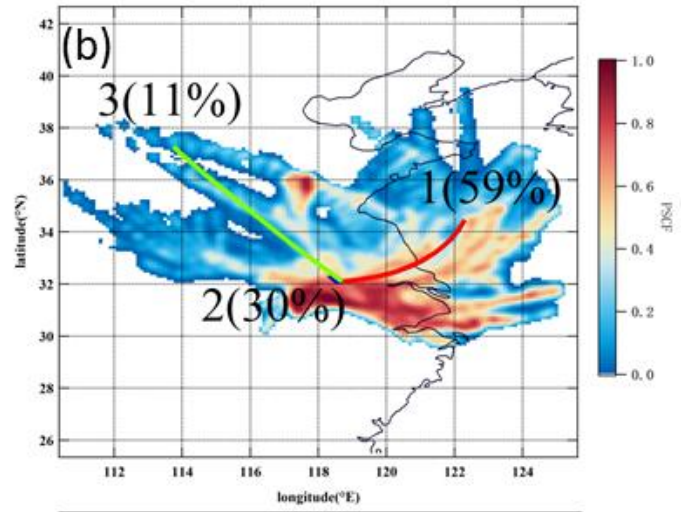
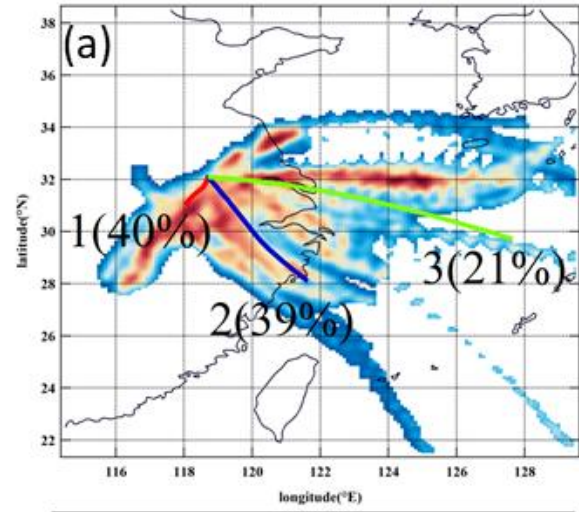
Figure 3: Diurnal variations in weather conditions and NO<sub>x</sub>, O<sub>3</sub>, CO, and SO<sub>2</sub> concentrations in different seasons. Note that the plotted CO concentrations and solar radiation values are reduced by 10-folds for a better visualization.

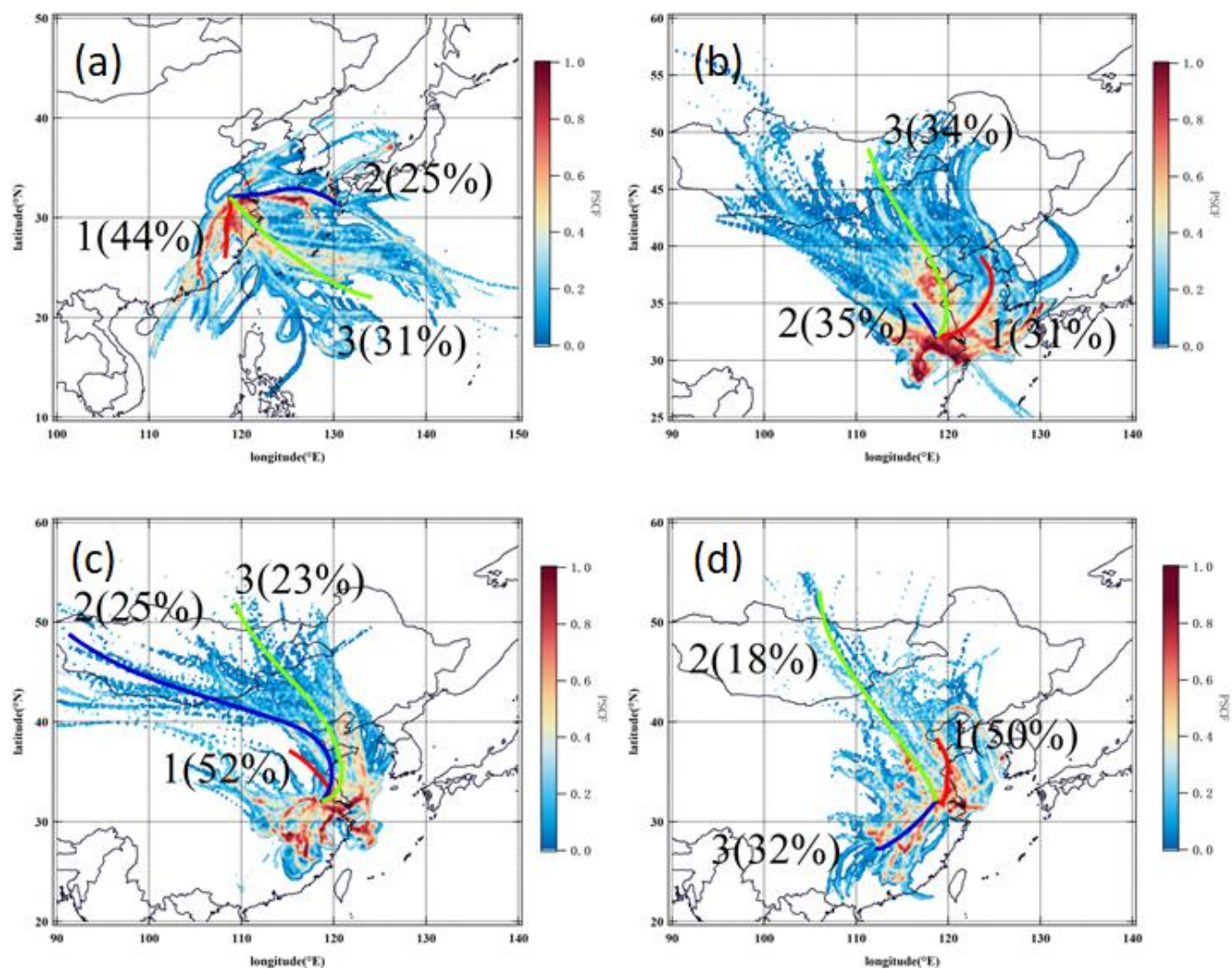
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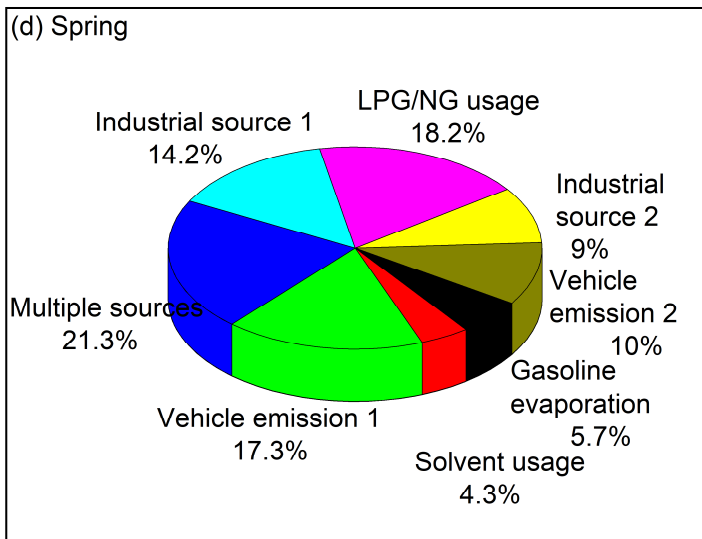
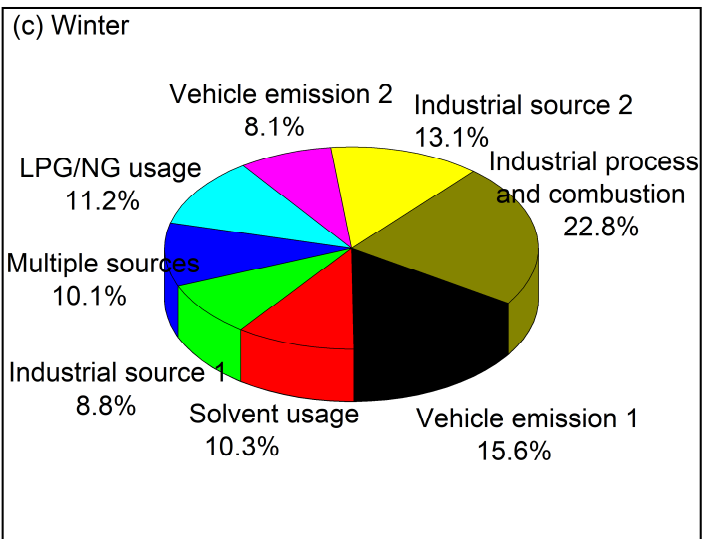
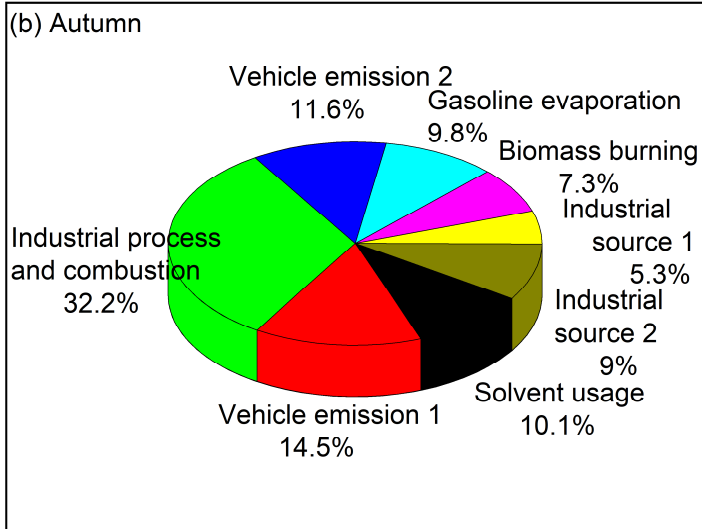
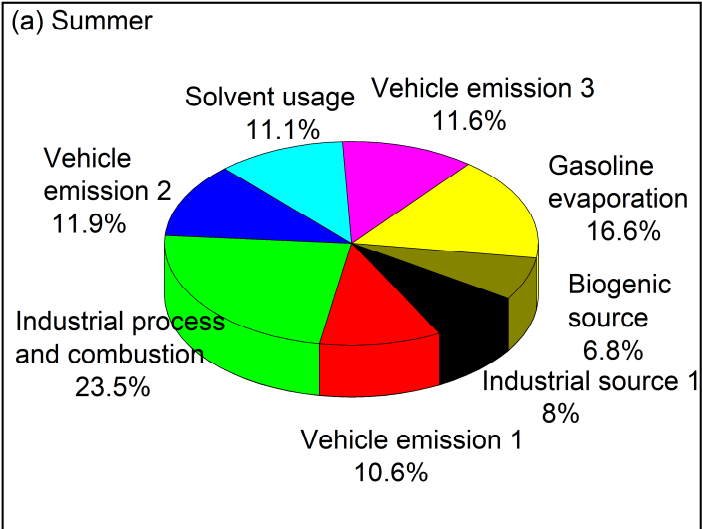
**Figure 4: Diurnal variations in toluene/benzene ratios (a, b, c, & d) and in the ratios of different VOCs to acetylene in different seasons (e, f, g, & h). The pink-colored squares in the box-plots represent the average values.**

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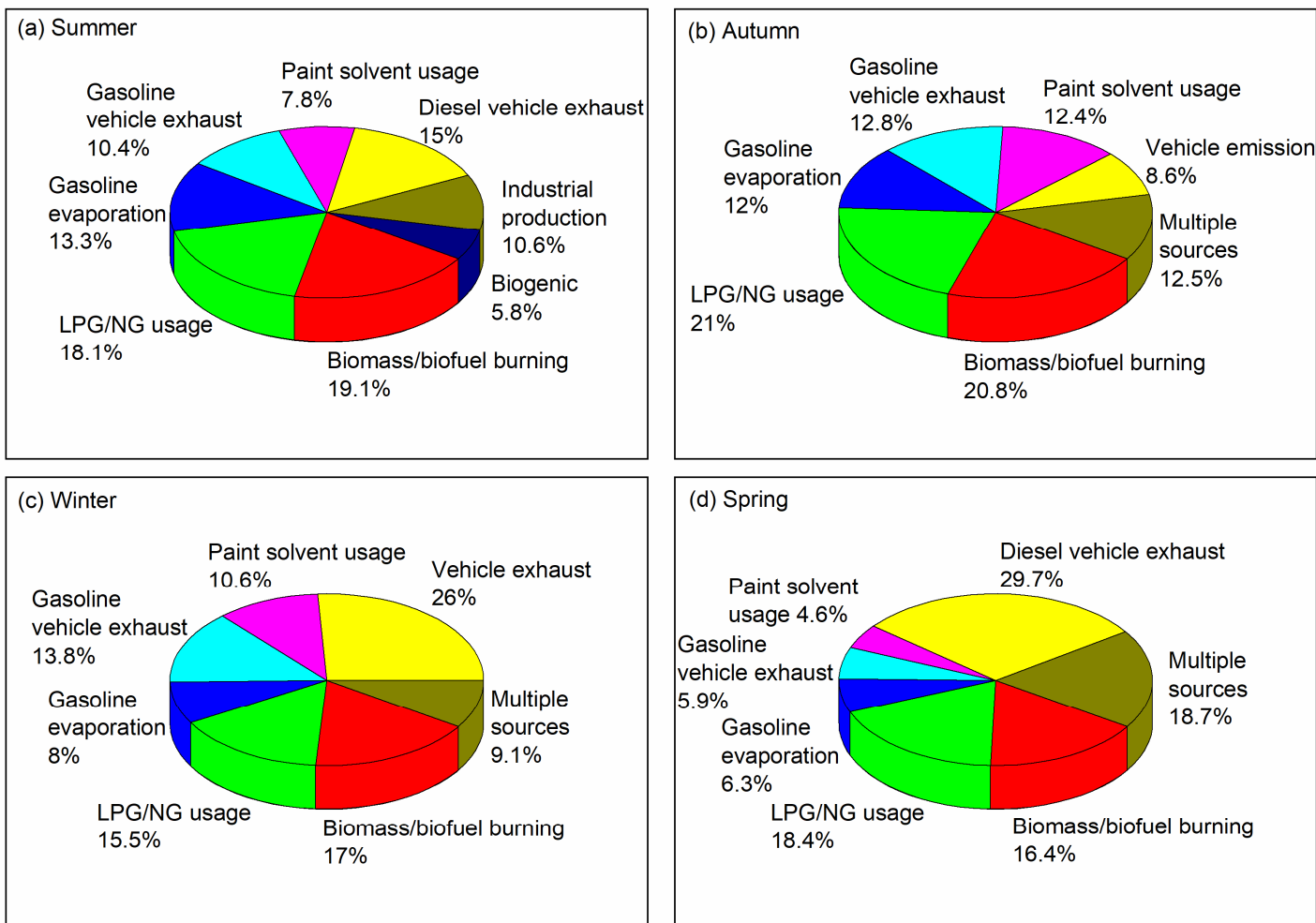




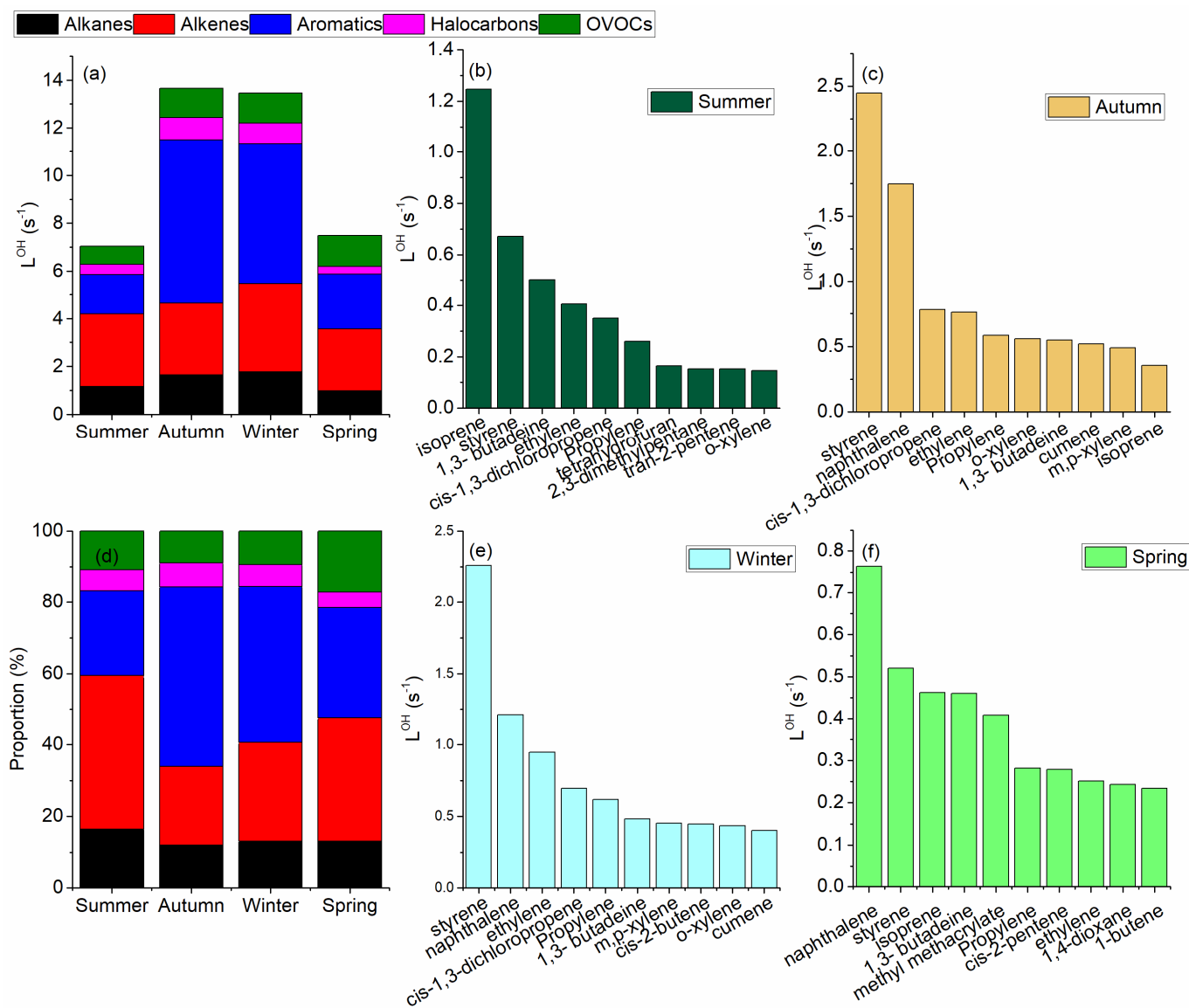
910 | **Figure 5: Wind cluster and PSCF analysis during (a) summer (b) autumn, (c) winter, and (d) spring based on the 24-72 hours backward air mass trajectories from the study area.**



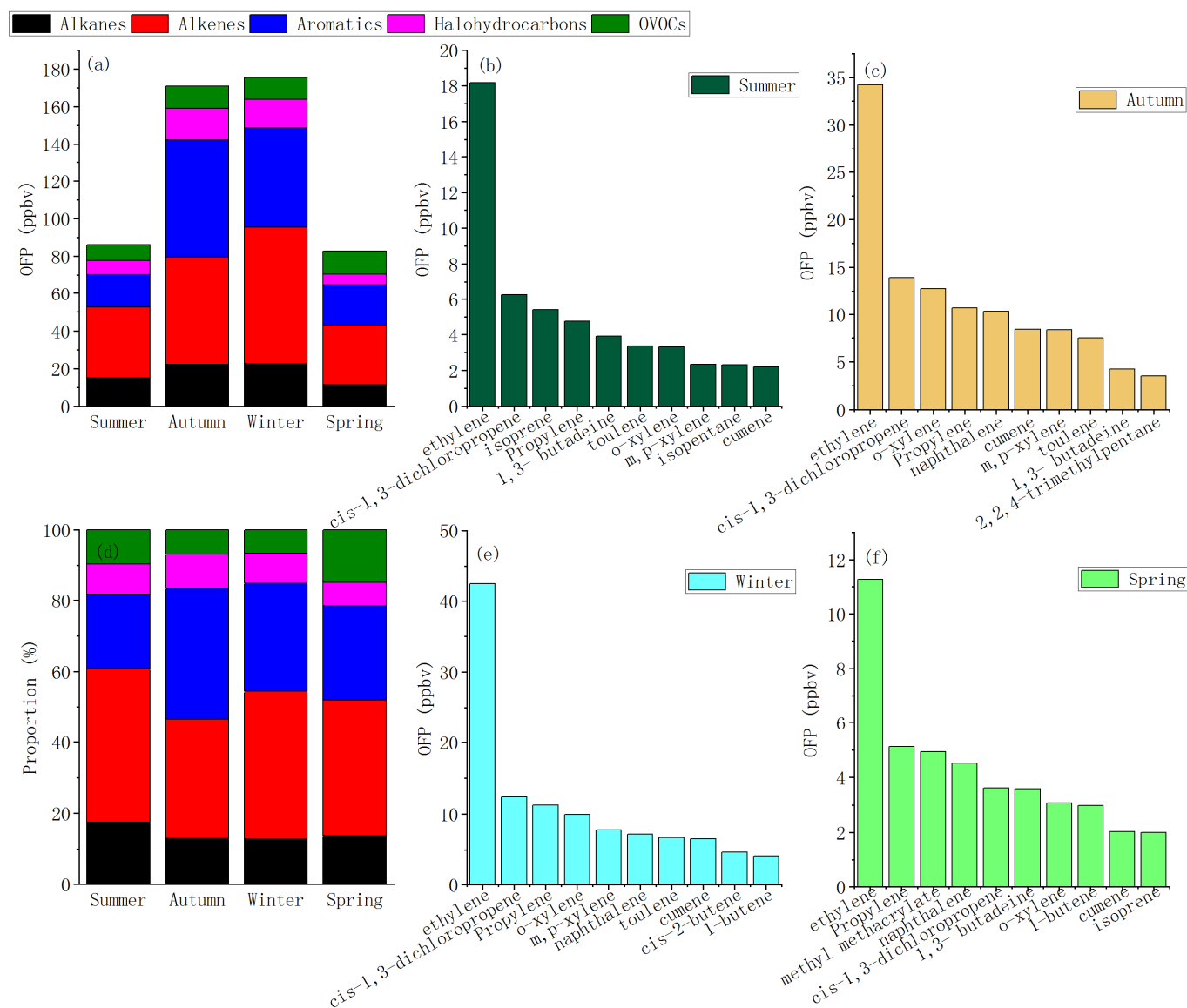




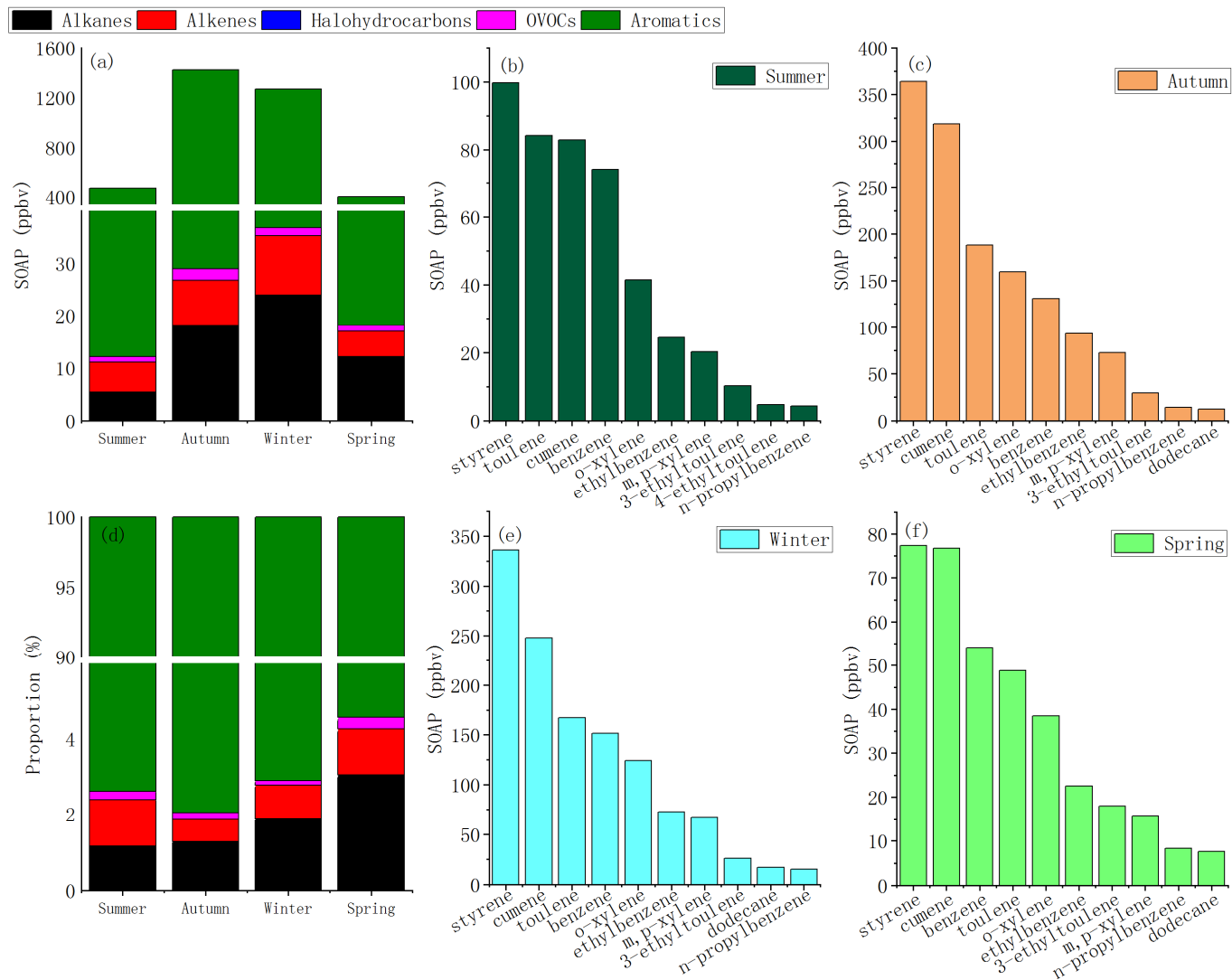
**Figure 6: relative contributions of different sources to ambient VOCs in Nanjing industrial area during different seasons**



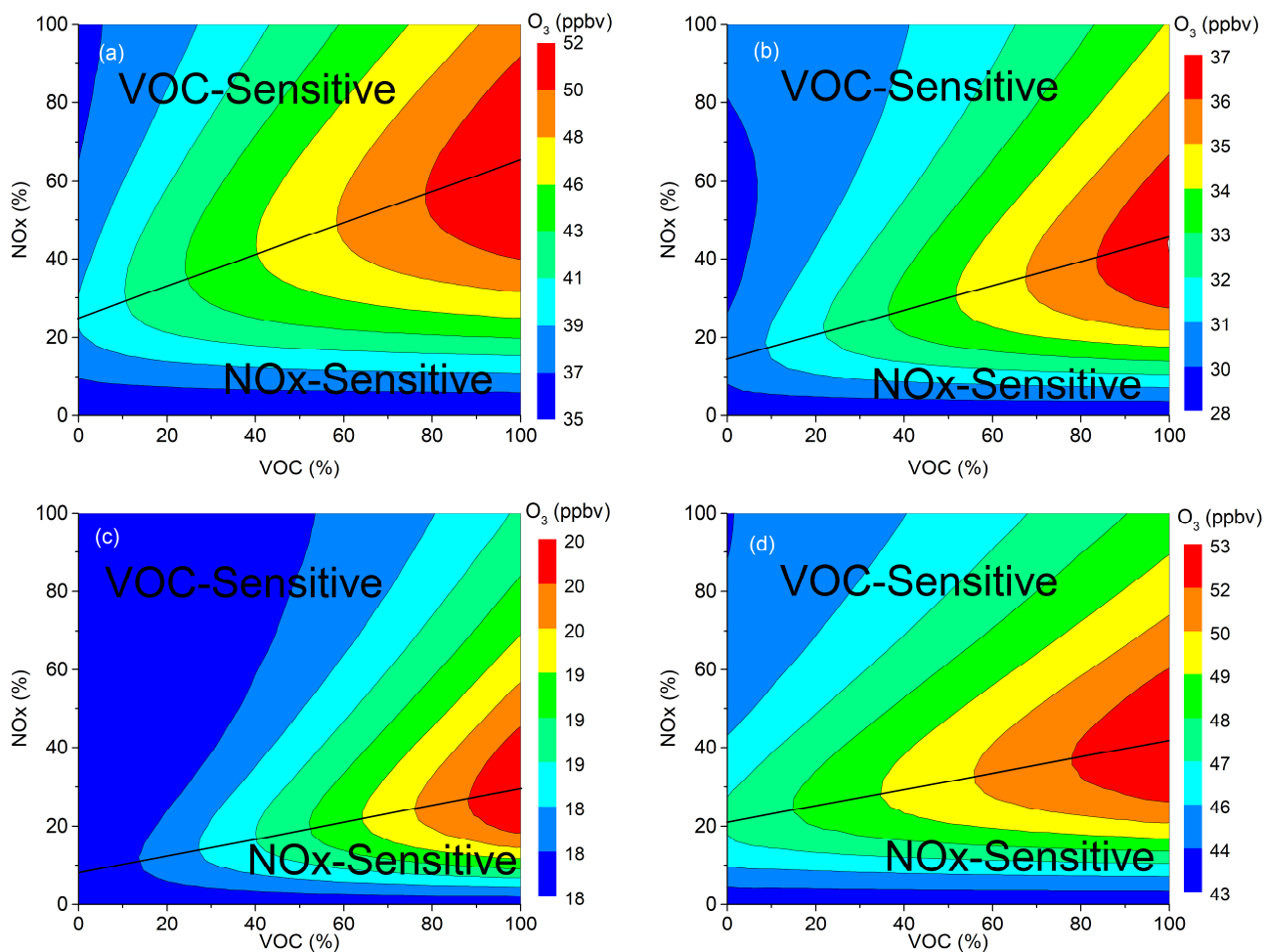
**Figure 7: Contribution to OH loss rates of different VOC-groups and the top 10 VOC species in different seasons**



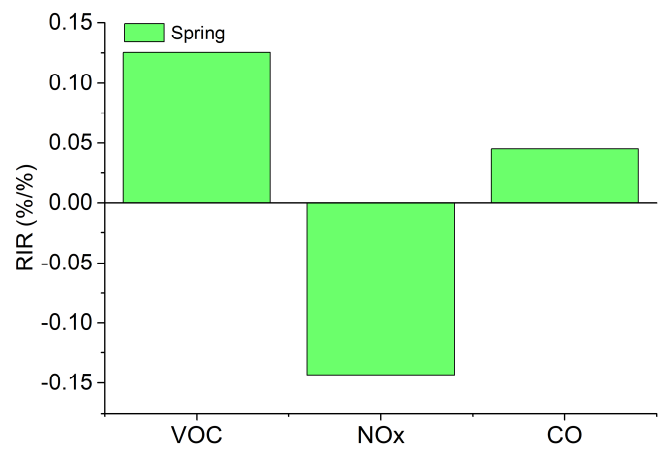
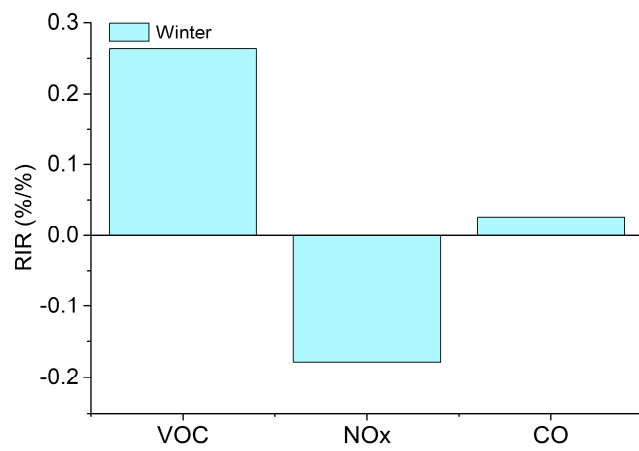
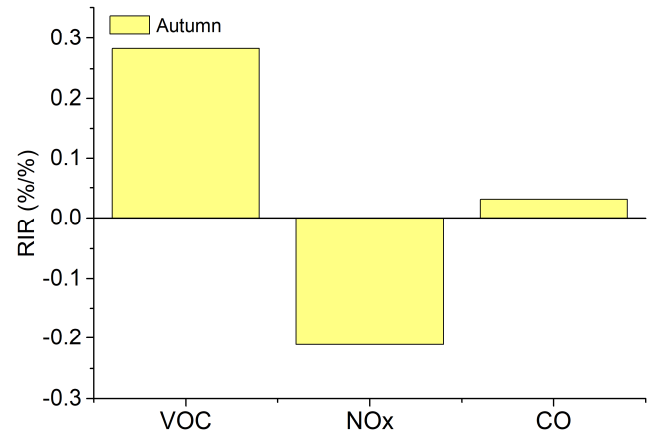
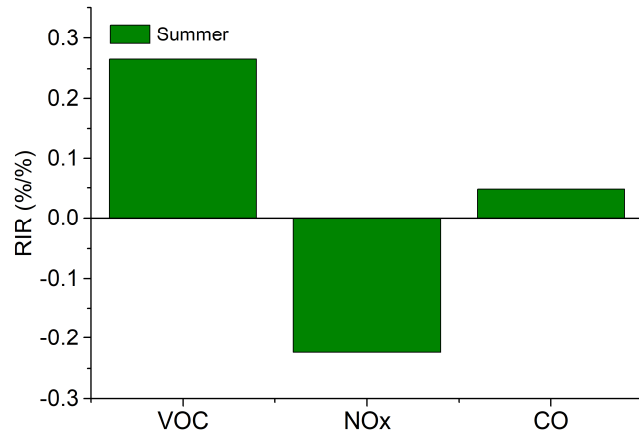
**Figure 8: Contribution to ozone formation potential of different VOC-groups and the top 10 VOC-species in different seasons**



**Figure 9: Contribution to secondary organic aerosol formation potential of different VOC groups and the top-10 VOC species in different seasons**



930 **Figure 10: O<sub>3</sub> isopleth diagram for (a) summer (b) autumn, (c) winter, and (d) spring based on percentage changes in VOCs and NO<sub>x</sub> concentrations in Nanjing and corresponding modelled O<sub>3</sub> production.**



935 **Figure 11: The RIR values of the VOC, NOx, and CO for the different seasons in**  
**Nanjing**

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950 **Measurement report: High Contributions of Halocarbon and Aromatic Compounds to  
Atmospheric VOCs in Industrial Area**

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965 **Table S1: OH reaction rate constant ( $k_{OH}$ ) of VOCs and list of VOCs constrained in the  
F0AM model**

Compounds	$k_{OH}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (Carter, 2010)	Constrained in F0AM model
Ethane	2.54E-13	Yes
propane	1.11E-12	Yes
isobutane	2.14E-12	Yes
n-butane	2.38E-12	Yes
isopentane	3.60E-12	Yes
n-pentane	3.84E-12	Yes
2,2 dimethylbutane	2.27E-12	
2,3 dimethyl butane	5.79E-12	
2-methyl pentane	5.20E-12	Yes
cyclopentane	5.02E-12	
3-methylpentane	5.20E-12	
n-hexane	5.25E-12	Yes
2,4-dimethylpentane	4.77E-12	
methylcyclopentane	5.68E-12	
isoheptane	6.81E-12	Yes

cyclohexane	7.02E-12	
2,3-dimethylpentane	7.15E-12	
3-methylhexane	7.17E-12	Yes
2,2,4-trimethylpentane	3.38E-12	
heptane	6.81E-12	Yes
methylcyclohexane	9.64E-12	
2-methylheptane	8.31E-12	
n-octane	8.16E-12	Yes
n-nonane	9.75E-12	Yes
Decane	1.10E-11	Yes
n-hendecane	1.23E-11	Yes
dodecane	1.32E-11	Yes
ethylene	8.15E-12	Yes
Propylene	2.60E-11	Yes
trans-2-butene	6.32E-11	Yes
cis-2-butene	5.58E-11	
1-butene	3.11E-11	Yes
1,3- butadiene	6.59E-11	
1-pentene	3.14E-11	Yes
trans-2-pentene	6.70E-11	
isoprene	9.96E-11	Yes
cis-2-pentene	6.50E-11	Yes
1-hexene	3.70E-11	Yes
acetylene	7.56E-13	Yes
benzene	1.22E-12	Yes
toluene	5.58E-12	Yes
ethylbenzene	7.00E-12	Yes
m,p-xylene	2.31E-11	Yes
o-xylene	1.36E-11	Yes
Styrene	5.80E-11	Yes
Cumene	6.30E-12	Yes
n-propylbenzene	5.80E-12	Yes
3-ethyltoluene	1.86E-11	Yes
4-ethyltoluene	1.18E-11	Yes
Mesitylene	5.67E-11	Yes
2-ethyltoluene	1.19E-11	Yes
1,2,4-trimethylbenzene	3.25E-11	Yes
1,2,3-trimethylbenzene	3.27E-11	Yes
1,3-diethylbenzene	2.55E-11	
1,4-diethylbenzene	1.64E-11	Yes
Naphthalene	2.30E-11	



Chloromethane	4.48E-14	Yes
vinyl chloride	6.90E-12	Yes
methyl bromide	4.12E-14	
Chloroethene	0	Yes
trichlorofloromethane	0	
Vinylidene chloride	0	
1,1,2-Trichlor-1,2,2-trifluorethan	0	
Dichloromethane	1.45E-13	Yes
trans-1,2-dichloroethylene	0	
1,1-dichloroethane	2.60E-13	Yes
cis-1,2-dichloroethylene	0	
Chloroform	1.06E-13	Yes
carbon tetrachloride	0	
1,2-dichloroethane	2.53E-13	Yes
Trichloroethylene	2.34E-12	Yes
1,2-dichloropropane	4.50E-13	Yes
bromodichloromethane	0	
trans-1,3-dichloropropene	1.44E-11	
cis-1,3-dichloropropene	8.45E-12	
1,1,2-trichloroethane	2.00E-13	Yes
tetrachloroethylene	0	Yes
1,2-dibromoethane	2.27E-13	Yes
Chlorobenzene	7.70E-13	
Bromoform	0	
1,1,2,2-tetrachloroethane	0	Yes
1,3-dichlorobenzene	5.55E-13	
1,4 dichlorobebezne	5.55E-13	
benzyl chloride	0	
1,2-dichlorobenzene	5.55E-13	
1,2,4-trichlorobenzene	0	
hexachloro-1,3-butadiene	0	
carbon disulfide	2.76E-12	
Acrolein	1.99E-11	Yes
Acetone	1.91E-13	Yes
Isopropanol	5.09E-12	Yes
MTBE	0	Yes
vinyl acetate	3.16E-11	
MEK	1.20E-12	Yes
ethyl acetate	1.60E-12	Yes
Tetrahydrofuran	1.61E-11	
methyl methacrylate	5.25E-11	

1,4-dioxane	3.83E-11	
4-methyl-2-pentanone	1.27E-11	Yes
2-hexanone	9.10E-12	Yes

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967 **Table S2: VOC concentrations (ppbv) measured in the industrial area in Nanjing. VOC concentrations (ppbv) observed in**  
 968 **previous studies in Nanjing are also listed.**

Compounds	Current study										(An et al., 2017), Nanjing (industrial suburban)	(Wu et al., 2020), Nanjing (nonindustrial suburban)	
	Summer		Autumn		Winter		Spring		Yearly		Summer	Winter	Yearly
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Mean	Mean
ethane	2.81	0.58	8.06	1.77	7.66	1.39	4.76	1.25	5.82	2.49	2.76	7.66	2.89
propane	3.12	0.63	6.09	1.21	4.92	0.91	2.73	0.92	4.22	1.57	1.70	4.51	3.29
isobutane	0.75	0.16	1.25	0.26	1.16	0.15	0.48	0.14	0.91	0.36	1.04	2.25	0.9
n-butane	1.75	0.39	2.61	0.63	2.32	0.26	0.87	0.29	1.89	0.76	1.09	2.35	1.53
isopentane	1.59	0.29	1.56	0.47	1.63	0.31	0.42	0.19	1.30	0.59	0.86	1.13	1.26
n-pentane	0.66	0.17	1.06	0.29	1.36	0.25	0.31	0.10	0.85	0.46	0.50	0.86	0.78
2,2 dimethylbutane	0.08	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.28	0.03	0.04
2,3 dimethyl butane	0.13	0.03	0.18	0.03	0.11	0.00	0.20	0.02	0.16	0.04	0.12	0.35	0.04
2-methyl pentane	0.26	0.08	0.32	0.10	0.44	0.11	0.29	0.06	0.33	0.08	0.25	0.41	0.16
cyclopentane	0.15	0.03	0.10	0.02	0.08	0.01	0.22	0.03	0.14	0.06	0.08	0.12	0.08
3-methylpentane	0.25	0.06	0.38	0.09	0.37	0.12	0.25	0.08	0.31	0.07	0.22	0.31	0.26
n-hexane	0.17	0.04	0.33	0.09	0.41	0.17	0.21	0.06	0.28	0.11	0.41	0.48	0.47
2,4-	0.06	0.00	0.06	0.01	0.06	0.00	0.13	0.01	0.08	0.03	0.05	0.08	0.01

dimethylpentane													
methylcyclopentane	0.12	0.03	0.16	0.04	0.14	0.04	0.13	0.03	0.14	0.02	0.08	0.13	0.26
isoheptane	0.13	0.04	0.12	0.04	0.11	0.04	0.16	0.03	0.13	0.02			
cyclohexane	0.44	0.29	0.37	0.15	0.43	0.31	0.21	0.13	0.36	0.10	0.41	0.60	0.15
2,3-dimethylpentane	0.86	0.59	0.73	0.30	0.85	0.63	0.42	0.25	0.72	0.21	0.11	0.20	0.02
3-methylhexane	0.10	0.02	0.12	0.03	0.09	0.02	0.14	0.02	0.11	0.02	0.04	0.05	0.08
2,2,4-trimethylpentane	1.59	0.37	2.81	0.82	3.26	0.78	1.16	0.74	2.21	0.99	0.03	0.02	0.03
heptane	0.10	0.01	0.12	0.02	0.12	0.01	0.10	0.01	0.11	0.01	1.92	0.2	0.11
methylcyclohexane	0.18	0.02	0.18	0.04	0.19	0.03	0.16	0.03	0.18	0.01	0.08	0.12	0.08
2-methylheptane	0.08	0.00	0.08	0.01	0.08	0.00	0.17	0.01	0.10	0.04	0.01	0.05	0.02
n-octane	0.09	0.01	0.08	0.01	0.09	0.01	0.20	0.01	0.11	0.06	0.19	0.21	0.05
n-nonane	0.06	0.00	0.08	0.02	0.08	0.02	0.07	0.00	0.07	0.01	0.03	0.05	0.03
decane	0.05	0.00	0.06	0.01	0.06	0.01	0.05	0.00	0.06	0.01	0.05	0.06	0.04
n-hendecane	0.04	0.01	0.16	0.01	0.22	0.01	0.17	0.01	0.15	0.07	0.06	0.09	0.02
dodecane	0.08	0.00	0.36	0.02	0.50	0.01	0.22	0.02	0.29	0.18	0.07	0.13	0.03
ethylene	2.02	0.58	3.80	0.89	4.71	1.09	1.25	0.71	2.95	1.59	3.08	6.62	1.21
Propylene	0.41	0.34	0.91	0.46	0.97	0.31	0.44	0.58	0.68	0.30	0.98	2.09	0.70
trans-2-butene	0.02	0.00	0.06	0.02	0.23	0.01	0.03	0.01	0.09	0.10	0.07	0.14	0.07
cis-2-butene	0.07	0.00	0.16	0.03	0.33	0.03	0.09	0.01	0.16	0.12	0.06	0.10	0.05

1-butene	0.07	0.00	0.10	0.02	0.43	0.02	0.31	0.13	0.22	0.17	0.18	0.23	0.15
1,3- butadiene	0.31	0.07	0.34	0.05	0.30	0.03	0.28	0.00	0.31	0.02			
1-pentene	0.16	0.03	0.14	0.03	0.08	0.03	0.10	0.03	0.12	0.04	0.04	0.05	0.04
tran-2-pentene	0.09	0.03	0.06	0.02	0.05	0.01	0.09	0.02	0.07	0.02	0.03	0.04	0.03
isoprene	0.51	0.37	0.15	0.06	0.09	0.02	0.19	0.02	0.23	0.19	0.58	0.07	0.18
cis-pentene	0.07	0.02	0.06	0.01	0.07	0.01	0.17	0.02	0.09	0.05	0.03	0.02	0.02
1-hexene	0.05	0.03	0.06	0.02	0.06	0.03	0.24	0.01	0.10	0.09	0.03	0.02	0.01
acetylene	1.02	0.15	1.77	0.24	1.59	0.15	1.20	0.13	1.40	0.35	2.63	6.46	
benzene	0.80	0.19	1.41	0.41	1.63	0.39	0.58	0.37	1.10	0.50	1.86	3.21	0.82
toulene	0.84	0.40	1.88	0.51	1.67	0.31	0.49	0.12	1.22	0.66	1.47	3.20	1.07
ethylbenzene	0.22	0.05	0.83	0.21	0.65	0.15	0.20	0.10	0.48	0.32	1.27	1.79	0.43
m,p-xylene	0.24	0.07	0.86	0.24	0.80	0.17	0.19	0.07	0.52	0.36	0.46	0.59	0.67
o-xylene	0.43	0.09	1.67	0.42	1.30	0.29	0.40	0.21	0.95	0.63	0.28	0.39	0.21
styrene	0.47	0.15	1.71	0.49	1.58	0.35	0.36	0.15	1.03	0.71	0.17	0.30	0.12
cumene	0.87	0.19	3.34	0.84	2.60	0.59	0.80	0.41	1.90	1.27			
n-propylbenzene	0.04	0.01	0.13	0.02	0.14	0.01	0.08	0.11	0.10	0.05	0.09	0.08	0.03
3-ethyltoulene	0.10	0.02	0.29	0.06	0.26	0.05	0.18	0.21	0.21	0.09	0.05	0.05	0.03
4-ethyltoulene	0.07	0.00	0.08	0.01	0.08	0.01	0.10	0.06	0.08	0.01	0.19	0.29	0.03
mesitylene	0.03	0.00	0.06	0.02	0.08	0.03	0.04	0.00	0.05	0.02			
2-ethyltoulene	0.04	0.01	0.07	0.02	0.07	0.02	0.06	0.07	0.06	0.02	0.51	0.08	
1,2,4-trimethylbenzen	0.06	0.01	0.06	0.02	0.08	0.03	0.13	0.11	0.08	0.03	0.33	0.42	0.09

e													
1,2,3-trimethylbenzene											0.05	0.05	0.05
e	0.08	0.01	0.20	0.03	0.22	0.01	0.10	0.01	0.15	0.07			
1,3-diethylbenzene	0.09	0.00	0.18	0.02	0.17	0.01	0.16	0.01	0.15	0.04	0.03	0.05	0.01
1,4-diethylbenzene	0.09	0.00	0.17	0.02	0.20	0.01	0.17	0.01	0.16	0.05	0.04	0.10	0.04
naphthalene	0.13	0.02	3.09	0.98	2.14	0.22	1.35	0.29	1.68	1.25			
chloromethane	0.16	0.02	0.56	0.08	1.21	0.33	0.15	0.01	0.52	0.50			
vinyl chloride	0.05	0.00	0.07	0.02	0.09	0.02	0.16	0.01	0.09	0.05			
methyl bromide	0.04	0.00	0.05	0.01	0.04	0.01	0.03	0.00	0.04	0.01			
chloroethene	0.08	0.01	0.08	0.02	0.10	0.03	0.05	0.01	0.08	0.02			
trichlorofluoromethane	0.23	0.01	0.18	0.01	0.30	0.02	0.21	0.04	0.23	0.05			
Vinylidene chloride	0.05	0.01	0.05	0.01	0.04	0.00	0.05	0.01	0.05	0.00			
1,1,2-Trichloro-1,2,2-trifluoroethane	0.08	0.00	0.08	0.01	0.10	0.00	0.08	0.01	0.08	0.01			
dichloromethane	1.26	0.09	3.09	0.54	2.62	0.47	1.97	0.53	2.23	0.80			
trans-1,2-dichloroethylene	0.05	0.00	0.05	0.01	0.05	0.01	0.14	0.01	0.07	0.05			
1,1-dichloroethane	0.33	0.08	0.65	0.18	0.82	0.34	0.41	0.13	0.55	0.22			

cis-1,2-dichloroethylene	0.07	0.00	0.07	0.01	0.03	0.00	0.20	0.01	0.09	0.07
chloroform	0.17	0.02	0.57	0.16	0.53	0.18	0.18	0.04	0.36	0.22
carbon tetrachloride	0.12	0.01	0.18	0.02	0.17	0.03	0.18	0.02	0.16	0.03
1,2-dichloroethane	0.95	0.14	3.19	0.40	2.95	0.43	1.15	0.31	2.06	1.17
trichloroethylene	0.13	0.02	0.14	0.02	0.10	0.02	0.06	0.00	0.11	0.04
1,2-dichloropropane	0.57	0.21	1.48	0.53	0.96	0.23	0.14	0.05	0.79	0.57
bromodichloroethane	0.06	0.00	0.03	0.01	0.03	0.00	0.06	0.00	0.04	0.01
trans-1,3-dichloropropene	0.10	0.00	0.08	0.01	0.13	0.00	0.17	0.01	0.12	0.04
cis-1,3-dichloropropene	1.68	0.79	3.76	1.02	3.35	0.62	0.98	0.23	2.44	1.33
1,1,2-trichloroethane	0.06	0.01	0.12	0.04	0.11	0.07	0.05	0.05	0.09	0.03
tetrachloroethane	0.06	0.00	0.09	0.02	0.08	0.02	0.06	0.01	0.07	0.01
1,2-dibromoethane	0.03	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.01
chlorobenzene	0.31	0.18	1.89	0.91	1.73	1.14	0.20	0.16	1.03	0.90
bromoform	0.02	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.00
1,1,2,2-tetrachloroethane	0.94	0.30	3.43	0.97	3.16	0.70	0.73	0.30	2.06	1.43

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1,3- dichlorobenzene	0.02	0.00	0.09	0.03	0.14	0.05	0.04	0.01	0.07	0.05
1,4 dichlorobenzene	0.11	0.01	0.65	0.20	0.40	0.05	0.09	0.01	0.31	0.27
benzyl chloride	0.12	0.02	0.10	0.05	0.13	0.07	0.24	0.23	0.15	0.06
1,2- dichlorobenzene	0.03	0.01	0.25	0.11	0.15	0.04	0.08	0.01	0.13	0.10
1,2,4- trichlorobenzene	0.04	0.00	0.17	0.04	0.25	0.01	0.14	0.02	0.15	0.09
hexachloro-1,3- butadiene	0.02	0.00	0.17	0.04	0.15	0.04	0.02	0.00	0.09	0.08
carbon disulfide	0.42	0.11	0.59	0.13	0.66	0.15	0.21	0.07	0.47	0.20
Acrolein	0.09	0.02	0.07	0.02	0.05	0.01	0.07	0.02	0.07	0.01
acetone	1.60	0.29	2.98	0.25	1.94	0.22	2.61	0.61	2.28	0.63
isopropanol	0.46	0.07	2.34	0.60	1.28	0.34	0.44	0.10	1.13	0.90
MTBE	0.37	0.11	0.66	0.23	0.35	0.11	0.35	0.13	0.43	0.15
vinyl acetate	0.17	0.04	0.33	0.09	0.42	0.18	0.26	0.08	0.30	0.11
MEK	0.69	0.06	1.14	0.10	0.73	0.09	0.77	0.43	0.84	0.21
ethyl acetate	1.06	0.17	1.56	0.25	1.43	0.18	1.34	0.95	1.35	0.21
tetrahydrofuran	0.41	0.56	0.08	0.11	0.43	0.45	0.24	0.03	0.29	0.16
methyl methacrylate	0.11	0.01	0.21	0.01	0.20	0.01	0.32	0.00	0.21	0.09
1,4-dioxane	0.05	0.00	0.07	0.01	0.09	0.00	0.26	0.01	0.12	0.10



4-methyl-2-pentanone	0.23	0.08	0.31	0.07	0.28	0.06	0.30	0.03	0.28	0.03
2-hexanone	0.15	0.00	0.23	0.01	0.28	0.01	0.29	0.02	0.23	0.07
<b>TVOC</b>	<b>38.81</b>	<b>10.21</b>	<b>83.05</b>	<b>20.07</b>	<b>77.51</b>	<b>16.77</b>	<b>39.62</b>	<b>13.12</b>	<b>59.75</b>	<b>28.57</b>

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## S1. Source apportionment of VOCs

970 Figure S1 shows the source profile of summertime VOCs. The resolved factors were identified as biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, diesel vehicle exhaust, industrial production, paint solvent usage, and biogenic source. Factor 1 was characterized by high concentrations of ethane and ethylene. These compounds are tracers of incomplete combustion emitted from vehicle exhaust and biomass/biofuel burning (An et al., 975 2017). Benzene, toluene, pentane, and decane concentrations were low in factor 1, therefore, it was identified as biomass/biofuel burning. Factor 2 was distinguished by a significant presence of LPG/NG VOCs propane, isobutene, and n-butane (Shao et al., 2016). So, factor 2 was identified as LPG/NG usage. Factor 3 was dominated by high concentrations of isopentane, n-pentane, and MTBE. Therefore, factor 3 was identified as gasoline evaporation (Song et al., 980 2018; Wang et al., 2016). Factor 4 possessed high concentrations of vehicle exhaust VOCs benzene and toluene (Song et al., 2018). These VOCs are also emitted by industrial processes. But the contribution of benzene was several folds higher than toluene. Therefore, factor 4 was related to vehicle exhaust emission and it was assigned to gasoline vehicle exhaust (An et al., 2017). Factor 5 was characterized by high concentrations of acetylene, n-heptane, and decane. 985 These are related to vehicle emissions. As diesel engines produce more acetylene than gasoline engines (Song et al., 2018; An et al., 2017), factor 5 was attributed to diesel vehicle exhaust. Factor 6 was dominated by toluene and the sampling site was beside an industrial area. So, we identified this factor as industrial production. Due to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene, factor 7 was assigned to paint solvent usage sources (Li et al., 990 2018). Factor 8 was attributed to the biogenic source, which was mainly distinguished by a high concentration of isoprene (Song et al., 2018).

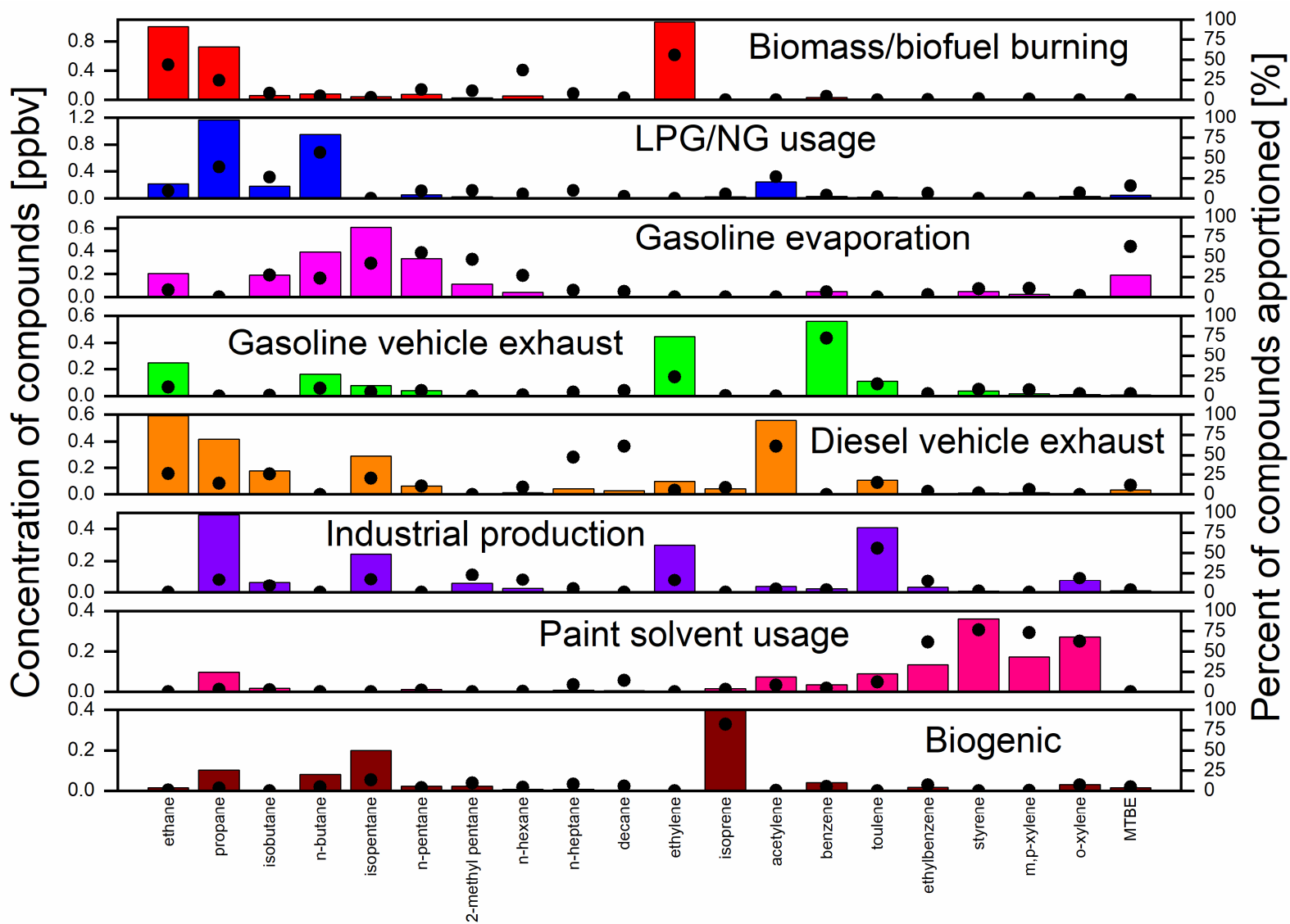
During autumn, the possible VOC sources were biomass/biofuel burning, multiple sources, gasoline vehicle exhaust, vehicle emission, LPG/NG usage, paint solvent usage and gasoline evaporation (Fig.S2). Factor 1 was represented by a high concentration of ethane and ethylene, 995 so, it was identified as a biomass/biofuel burning source (An et al., 2017). Factor 2 was dominated by isoprene, n-heptane, decane, and acetylene. Among these compounds, isoprene is mainly emitted by trees and the rest of the compounds are related to diesel vehicle exhaust emission. Therefore, Factor 2 was identified as multiple sources. Factor 3 was identified as

gasoline vehicle exhaust due to the high contribution of benzene and toluene. In factor 3,  
1000 benzene was several folds higher than toluene. The 4<sup>th</sup> factor was mainly composed of vehicle  
emission-related compounds 2-methyl pentane, n-hexane, n-heptane, n-pentane, and isopentane,  
therefore, identified as vehicle emission (Song et al., 2018). Factor 5 was assigned to LPG/NG  
usage as propane, isobutene, and n-butane were the main contributors (Shao et al., 2016). Factor  
6 was characterized by a high concentration of o-xylene, m,p-xylene, ethylbenzene and styrene,  
1005 which are typical tracers of paint solvent usage sources. Factor 7 was identified as gasoline  
evaporation, it was dominated by high concentrations of isopentane, n-pentane, and MTBE  
(Song et al., 2018).

During winter, the source factors were gasoline vehicle exhaust, vehicle exhaust, gasoline  
evaporation, biomass/biofuel burning, multiple sources, LPG/NG usage, and paint solvent usage  
1010 (Fig. S3). Factor 1 was assigned to gasoline vehicle exhaust. It was dominated by benzene and  
toluene; the contribution of benzene was twice of toluene. Factor 2 was characterized by  
isobutene, n-butane, acetylene, ethylene, ethane, n-heptane and decane. Isobutene and n-butane  
are related to LPG/NG usage. But, the contribution of propane was zero in factor 2. Acetylene,  
ethylene, and ethane are emitted from combustion sources like vehicle exhaust and biomass  
1015 burning. Decane and n-heptane are also related to vehicle emissions. By considering the above  
information, factor 2 was identified as vehicle exhaust. Factor 3 was characterized by high  
concentrations of isopentane and n-pentane, therefore, identified as a gasoline evaporation  
source. Factor 4 was characterized by a high contribution of ethylene and ethane; therefore,  
identified as a biomass/biofuel burning source. Factor 5 was characterized by high  
1020 concentrations of isoprene, propane, n-hexane and n-heptane. Propane is related to LPG/NG  
usage, isoprene is mainly emitted from trees (evergreen trees in winter), and n-hexane and n-  
heptane are related to vehicle emission. By considering the above information, factor 5 was  
assigned to multiple sources. Factor 6 was dominated by high concentrations of propane.  
Therefore, it was identified as LPG/NG usage. Factor 7 was identified as paint solvent usage due  
1025 to the high contribution of o-xylene, m,p-xylene, ethylbenzene and styrene (Zhang et al., 2018;  
Song et al., 2020).

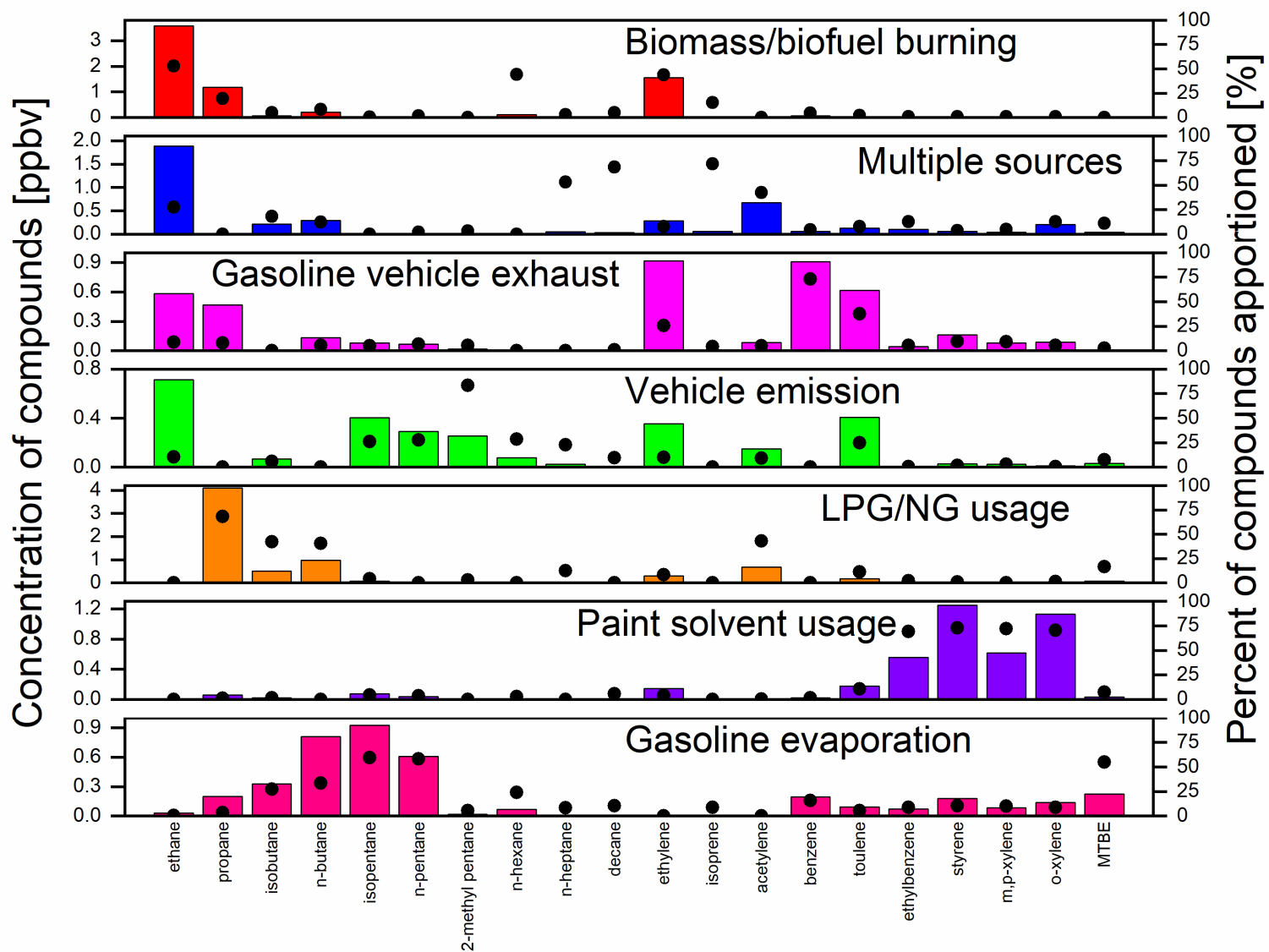
During spring, the possible VOC sources were biomass/biofuel burning, paint solvent usage,  
multiple sources, gasoline evaporation, gasoline vehicle exhaust, LPG/NG usage, and diesel

vehicle exhaust (Fig. S4). Factors 1 was identified as a biomass/biofuel burning source for the  
1030 high loading of ethylene and ethane and relatively lower contribution from the vehicle emission-  
related compounds. Due to the high contribution of o-xylene, styrene, m,p-xylene, and  
ethylbenzene, factor 2 was assigned to paint solvent usage sources (Li et al., 2018). Factor 3 had  
a high contribution of isoprene, n-hexane, n-heptane, decane, MTBE, toluene, ethylbenzene, and  
o-xylene. Therefore, factor 3 was identified as multiple sources. Factor 4 was represented by a  
1035 high concentration of isopentane, n-pentane, and MTBE. Therefore, factor 4 was identified as  
gasoline evaporation. Factor 5 was represented by high concentrations of benzene, therefore,  
identified as gasoline vehicle exhaust. Factor 6 was assigned to LPG/NG usage due to the high  
contribution of propane, n-butane, and isobutane (Shao et al., 2016). Factor 7 was identified as  
diesel vehicle exhaust due to the high contribution of acetylene, n-heptane, and decane.



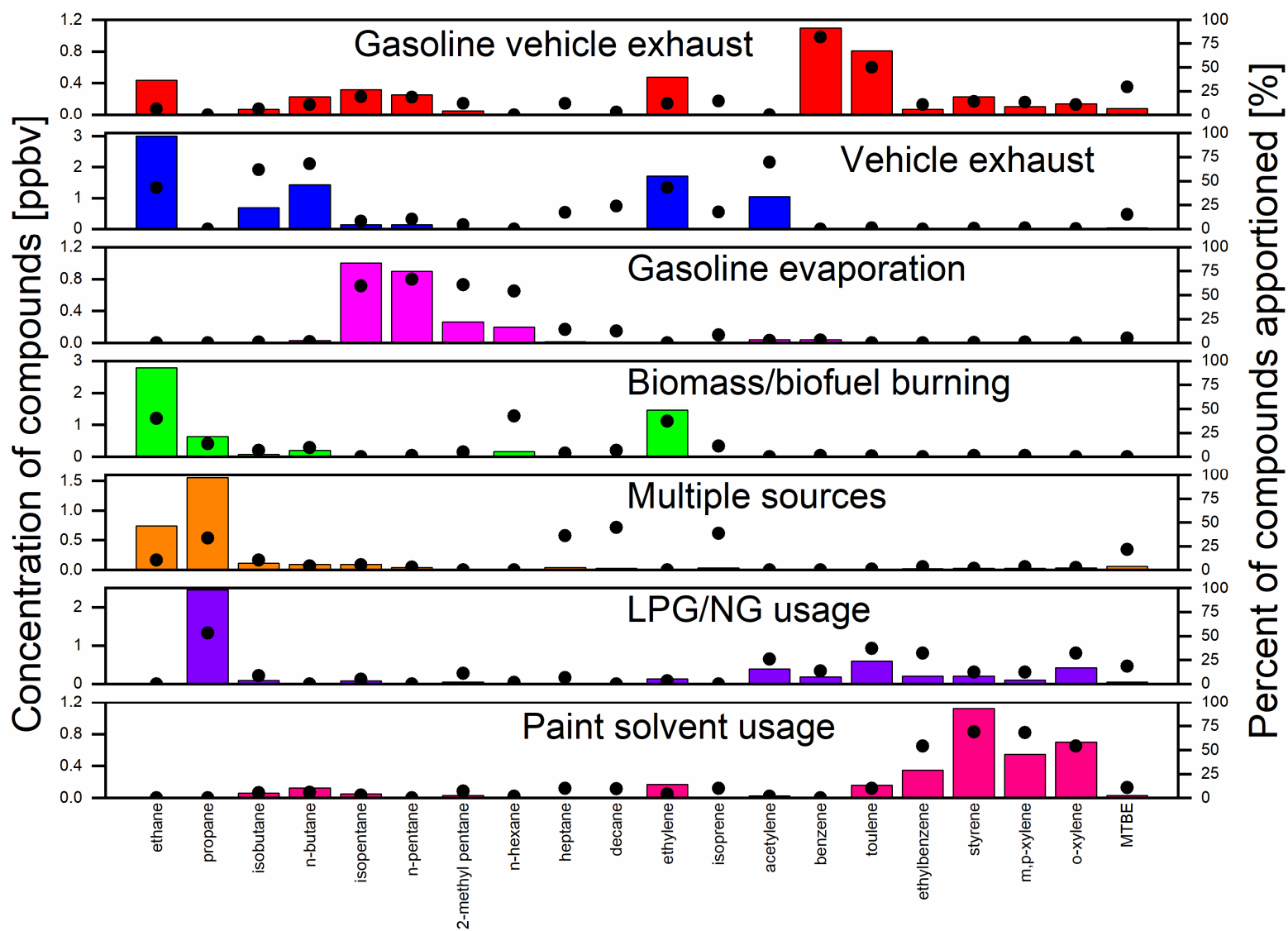
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1041 **Figure S1: Source profile of VOCs during summer in Nanjing industrial area. Bars and dots represent the concentrations and**  
 1042 **percentages of the compounds, respectively.**



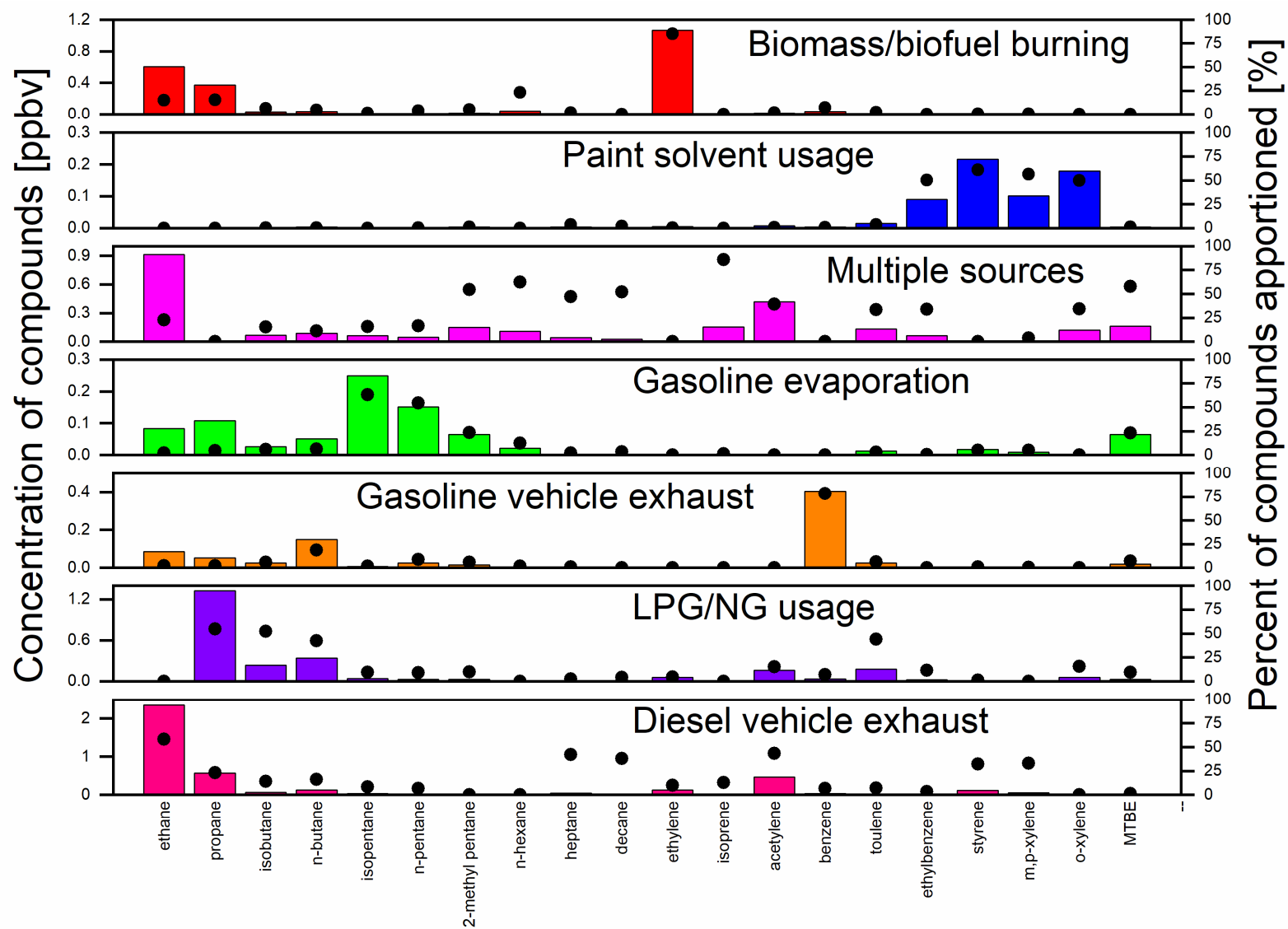
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1044 **Figure S2: Source profile of VOCs during autumn in Nanjing industrial area. Bars and dots represent the concentrations and**  
 1045 **percentages of the compounds, respectively.**



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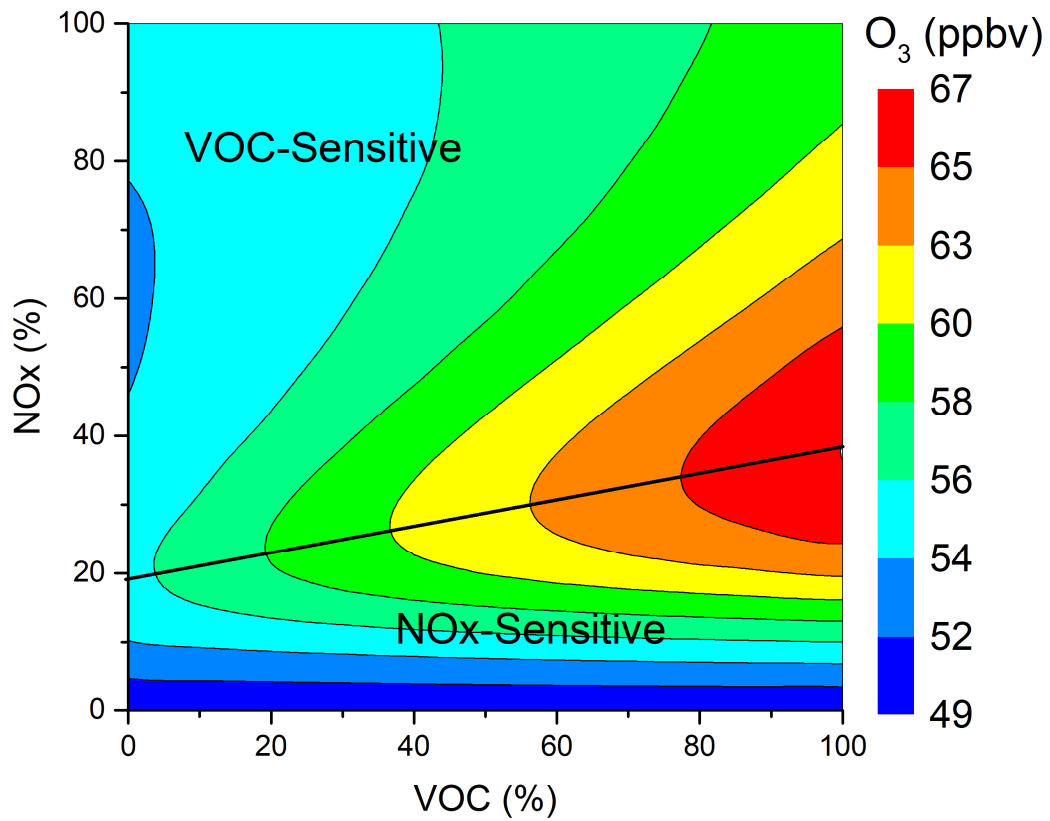
1047 **Figure S3: Source profile of VOCs during winter in Nanjing industrial area. Bars and dots represent the concentrations and**  
 1048 **percentages of the compounds, respectively.**



1049

1050 **Figure S4: Source profile of VOCs during spring in Nanjing industrial area. Bars and dots represent the concentrations and**  
 1051 **percentages of the compounds, respectively.**





**Figure S5: O<sub>3</sub> isopleth diagram on a high O<sub>3</sub> episode day (July 29 2018) in Nanjing industrial area.**

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