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.

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 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

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.

The observations reported here, speciated and quantified VOC composition in Nanjing, wuold 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:

- **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 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 comparision is revised it is difficult to gauge how the measurements reported here compare to other areas.**

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).

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 perform in Nanjing. Except for halocarbons and OVOCs, only 4 VOC species concentrations are not presented in these studies compare to the current observation (Table S2). In the revised manuscript, the TVOCs concentration without halocarbons and OVOCs are compared between these studies.

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.**

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 NOx × 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 NOx.

- **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).**

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**

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

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.

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.

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".

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.

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.

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.

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.

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

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

Ahsan Mozaffar [1,2,3], Yan-Lin Zhang [1,2,3*], Yu-Chi Lin[1,2,3], Feng Xie [1,2,3], Mei-Yi Fan [1,2,3], and Fang Cao [1,2,3]

[1]Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[2]Key Laboratory Meteorological Disaster; Ministry of Education & Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disaster, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[3]Jiangsu Provincial Key Laboratory of Agricultural Meteorology, College of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China.

Correspondence to: Yan-Lin Zhang (dryanlinzhang@outlook.com)

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 totalsum of the suite of measured 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 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±7.3 ppbv, 24%) VOC-group was the second largest contributor to the TVOCs after alkanes (21±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 ha~~e~~lo~~hydro~~carbons 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~~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 source~~s~~ 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~~ V~~v~~ehicle-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 change~~s~~ 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,~~ A~~a~~nalysis 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±17.8 mg m^{-3} out of the total 23.1±24.5 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±1076.7 ppbC out of the total 1317.3±1184.5 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 (~90 ppb out of the total ~160 ppb) in an industrial area in Taiwan. A high concentration of halocarbons (~~49%~~9590.2 mg m^{-3} out of the total 19652 mg m^{-3}) 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 varie~~d~~s 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_3 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_{OH}~~, OFP, and SOAP analysis~~. We also present the sensitivity analysis of O_3 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_3 concentrations using a 49i O_3 analyser (Thermo Fisher Scientific Inc., USA).~~,~~ NO, NO_2 and NOx concentrations were measured using a 42i NO-NO_2-NOx analyser (Thermo Fisher Scientific Inc., USA)~~,~~. SO_2 concentrations were followed using a 43i SO_2 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 ~~6~~20 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 a~~n~~ 7 to 8-factor solution ~~(Q_{true}/Q_{robust} = ~1.0)~~for different seasons as Q_{true}/Q_{robust} was ~1.0, $Q_{true}/Q_{expected}$ 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° × 0. 1° 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_{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_{OH}). The following equation was used to estimate the L_{OH} (s^{-1}) (Zhang et al., 2020).

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

Where $[VOC]_i$ is the concentration of VOC species i (molecule cm^{-3}), $k_{OH,i}$ (cm^3 $molecule^{-1}$ s^{-1}) is the reaction rate constant of i VOC with OH radical. The k_{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 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^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 (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 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 NOx × 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_3 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. $P_{O3}(X)$ and $P_{O3}(X-\Delta X)$ are the simulated net O_3 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^{-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 NOx 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 NOx 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~~ 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 3rd 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 investigation~~s~~ 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±0.3 ppbv, 2%)> others (0.5±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 h~~e~~alo~~hydro~~carbons 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 helohydrocarbons 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 3rd and 5th 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±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 observed 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, ~~H~~halocarbons and OVOCs were not ~~measured~~

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), 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, 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_3 was reached ~~at~~ in that period (Fig. 3). The lowest O_3 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 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^{th} 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 south~~west~~ (~~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 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 (~~59~~35%) and long-distance transport from the northwest~~west~~ (~~30~~34%) directions. However, according to the PSCF analysis, VOC pollution was mainly influenced by the short distance transport from the south ~~and east~~ direction~~s~~. During winter, short-distance transport~~s~~ from the ~~northeast (46%) and~~ northwest (~~37~~52%) direction~~s~~ ~~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 (~~49~~50%) and ~~eastern~~ southwest (~~30~~32%) 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 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 th~~o~~ese seasons (Fig.2). The average L_{OH} value was 10.4±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 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_{OH} exhibited the following trend: aromatics > alkenes > alkanes > OVOCs > halocarbons. Similar to the current study, aromatic is also mentioned as the maximum contributor~~s~~ to L_{OH} in different regions in China, however, the alkene is generally reported as the top contributor to L_{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_{OH} for different seasons. Whereas isoprene was the highest contributor to L_{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_{OH} in spring. Overall, styrene, naphthalene, ethylene, and isoprene were the main contributor to L_{OH} ~~in the study area~~. In previous studies in China, these compounds are also mentioned as one of the highest contributors to L_{OH} (Zhao et al., 2020; Hui et al., 2018; Song et al., 2020).

~~The estimated 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±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_3 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_3 formation

Figure 10 shows the EKMA isopleth diagrams of O_3 for different seasons. In all the diagrams, VOC and NOx = 100 % is the base case. The ridgeline divided the diagrams into two regimes, VOC-sensitive ~~(~~above~~)~~ the line and NOx-sensitive ~~(~~below~~)~~ the line~~regimes~~. For all the seasons, the study area fell above the ridgeline. Moreover, ~~a decrease in~~ O_3 production ~~was noticed~~decreased with the decrease in VOC concentration. Therefore, the study area was in the VOC-sensitive regime for O_3 formation during all the seasons. As a case study, O_3 formation sensitivity to its precursors was tested on a high O_3 concentration day (July 29 2018, maximum 126 ppbv). During the high O_3 episode, the study area was also in the VOC-sensitive regime for O_3 formation (Fig. S5). We also employed the RIR analysis to evaluate the O_3 production sensitivity to VOC, NOx, and CO concentrations (Fig. 11). The RIR value of VOC was the highest during all the seasons. It indicates that the O_3 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_3 formation during those seasons. The RIR values for NOx were negative during all the seasons, implying that the O_3 formation was in the NOx-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_3 formation. The previous two studies performed in Nanjing also concluded the same finding based on VOC/NOx 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, NOx-sensitive regions for O_3 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_3 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 2nd largest contributor to the TVOCs following alkanes, it indicates the impact of industrial emissions on the local air.~~After alkane, halocarbon was the 2^{nd} largest contributor to the TVOCs, indicating a high influence of industrial emissions. Generally, alkenes/aromatics/OVOCs are the 2^{nd} 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 be reduced~~ to decrease the haze and O_3 pollution in the study area~~. ~~Industries~~ Vehicle-related emissions were the major VOC source~~s~~ in the study area~~ followed by vehicles~~, thus, emission reduction from this~~ese two~~ source~~s~~ should get more priority. Aromatics and alkenes ~~accounted for most~~were the major contributors ~~of~~ to the L_{OH}, ~~OFP, 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_3 formation. Therefore, VOCs ~~especially aromatics and alkenes~~ emission reduction is the most effective way to decrease the local O_3 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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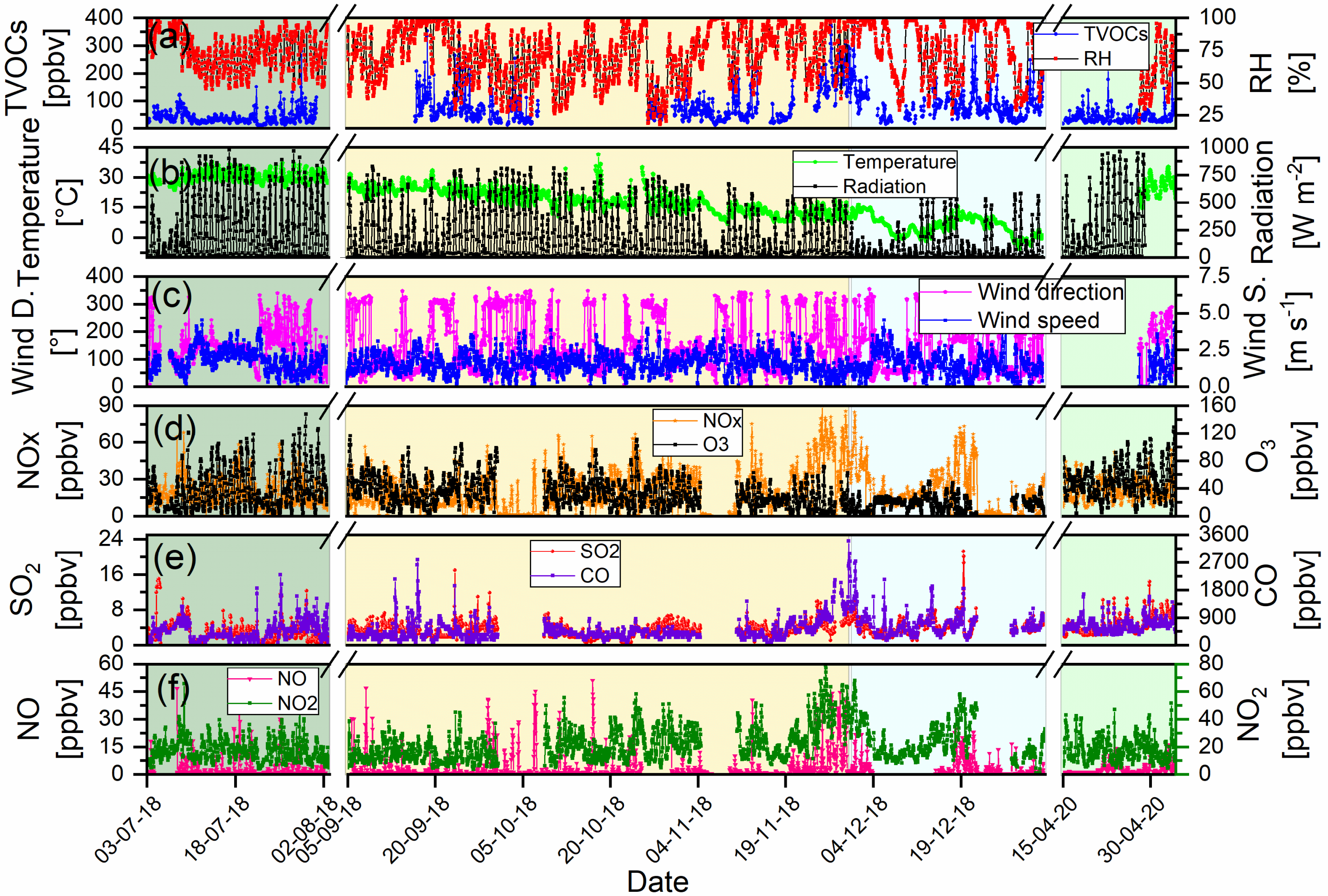

TVOCs [ppbv]
RH [%]
TVOCs
RH
Temperature [°C]
Radiation [W m-2]
Temperature
Radiation
Wind D. [°]
Wind S. [m s-1]
Wind direction
Wind speed
NOx [ppbv]
O3 [ppbv]
NOx
O3
SO2 [ppbv]
CO [ppbv]
SO2
CO
NO [ppbv]
NO2 [ppbv]
NO
NO2
03-07-18
18-07-18
02-08-18
05-09-18
20-09-18
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04-11-18
19-11-18
04-12-18
19-12-18
15-04-20
30-04-20
Date

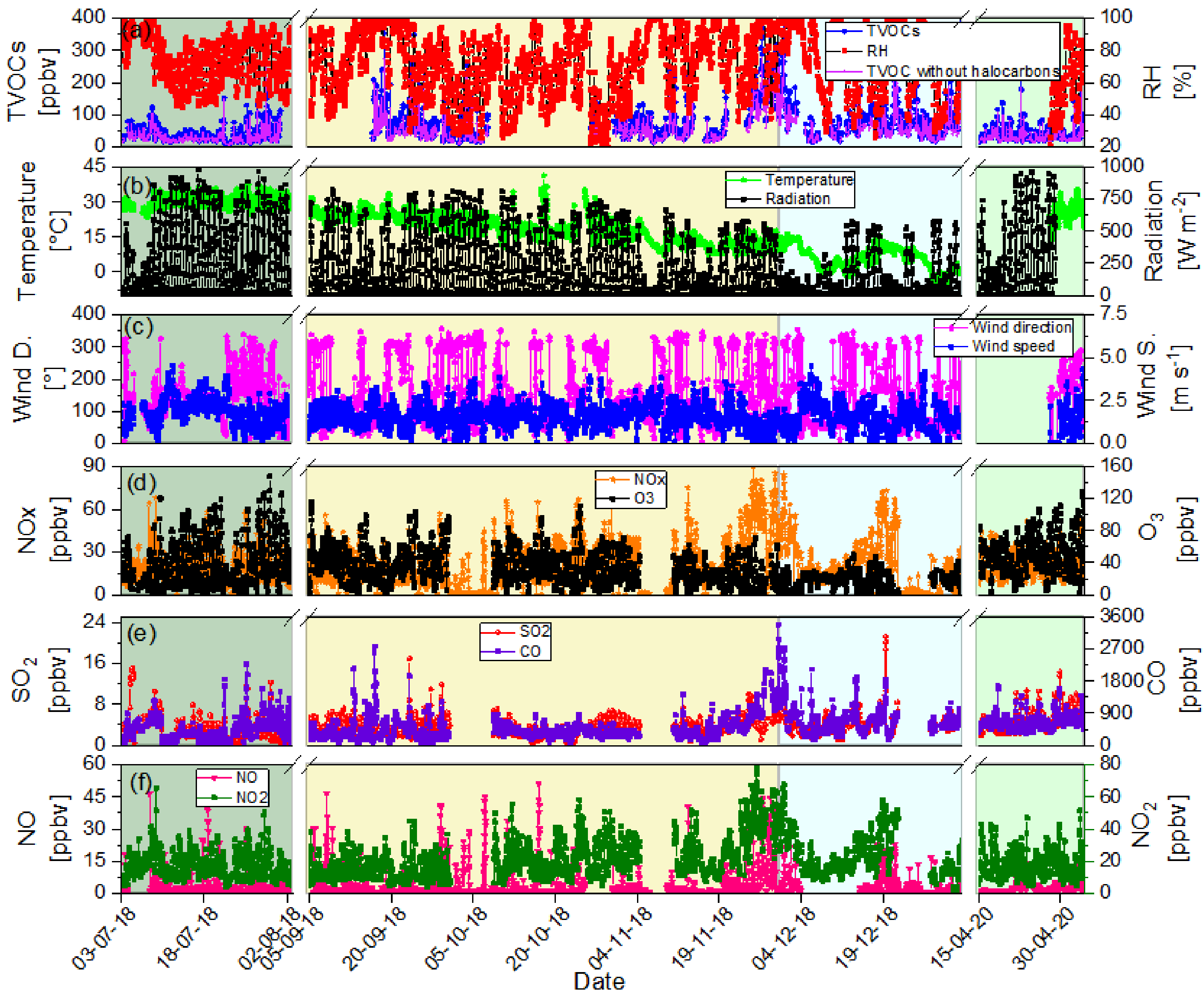
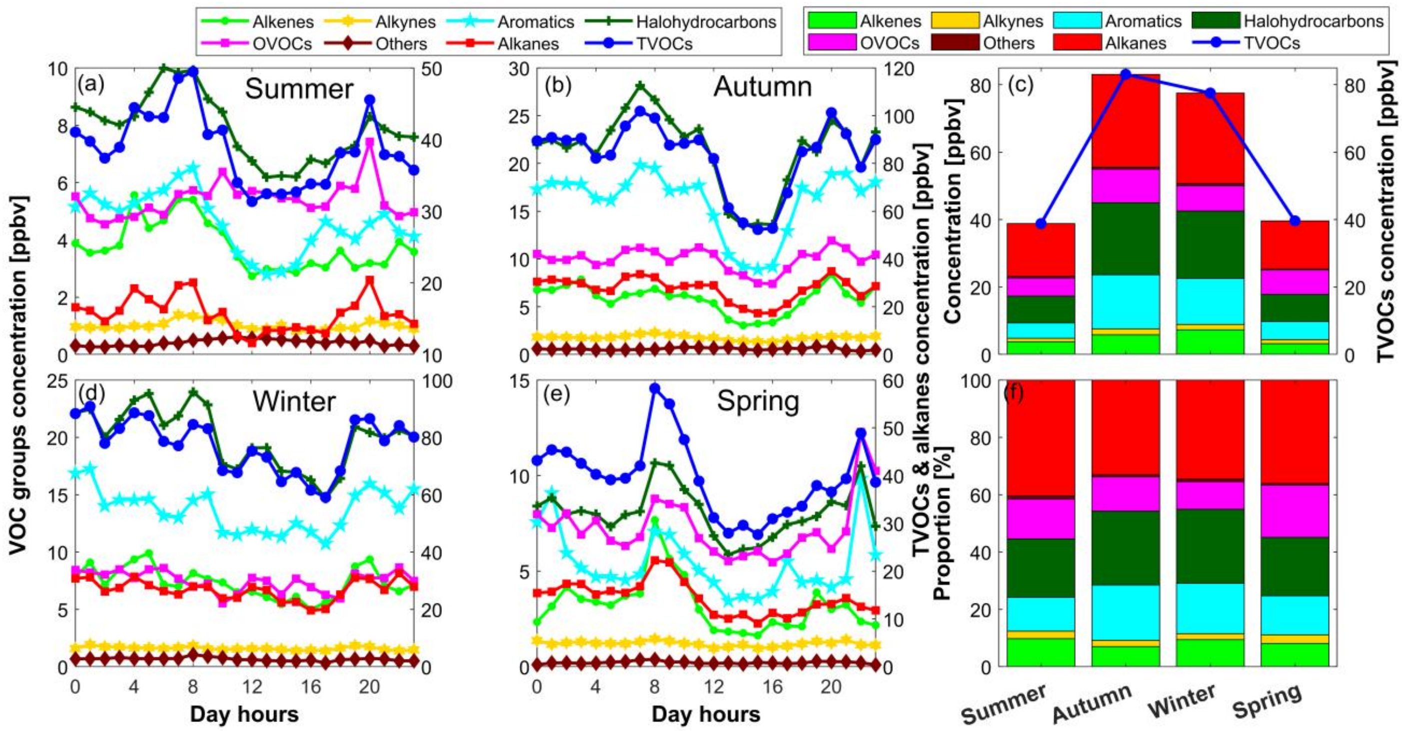


Figure 1: Time series of hourly meteorological parameters, inorganic air pollutants, ~~and~~ TVOCs, and TVOCs without halocarbons concentrations during the observation period at Nanjing. The green, yellow, cyan, and light-green shaded areas indicate summer, autumn, winter, and spring seasons, respectively.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



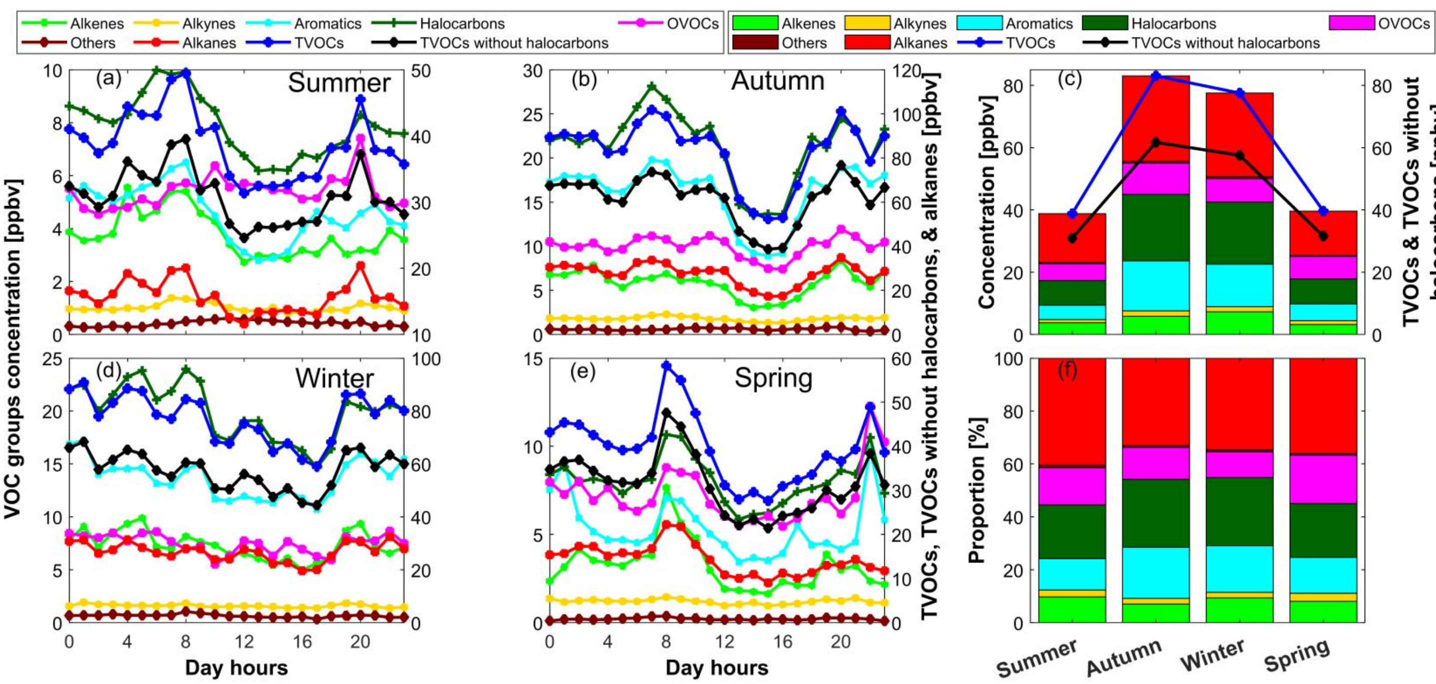
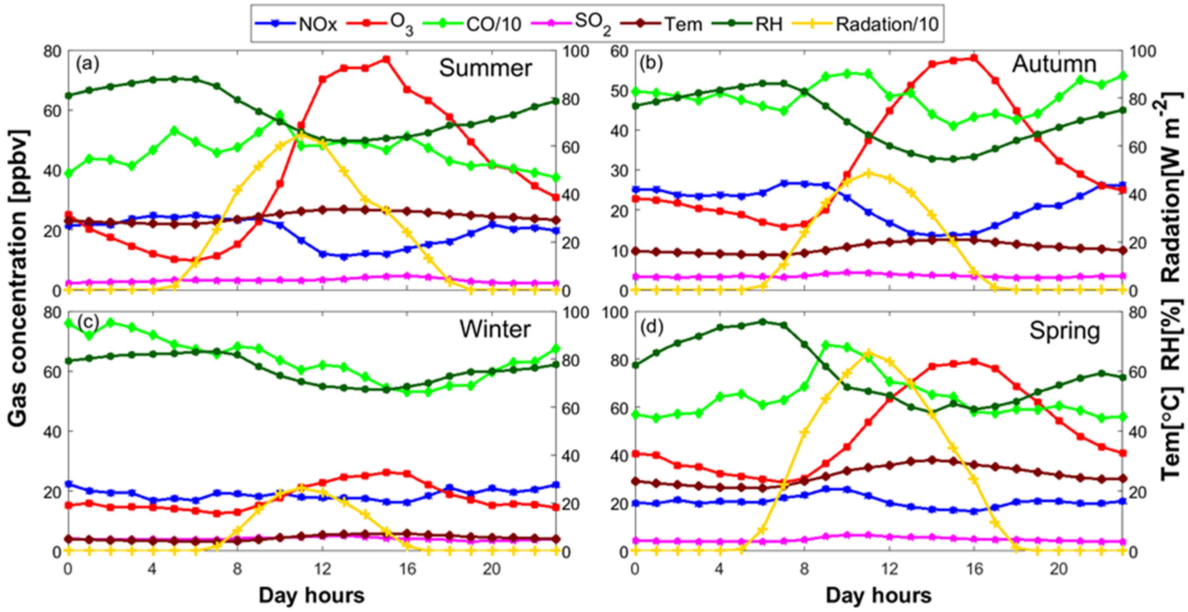


Figure 2: Diurnal variations in ~~TVOCs and~~ different VOC-groups, TVOCs, TVOCs without halocarbons concentrations in different seasons (a, b, d, & e) and seasonal variations in average concentrations and proportion of different VOC-groups, TVOCs, TVOCs without halocarbons~~TVOCs and different VOC-groups~~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



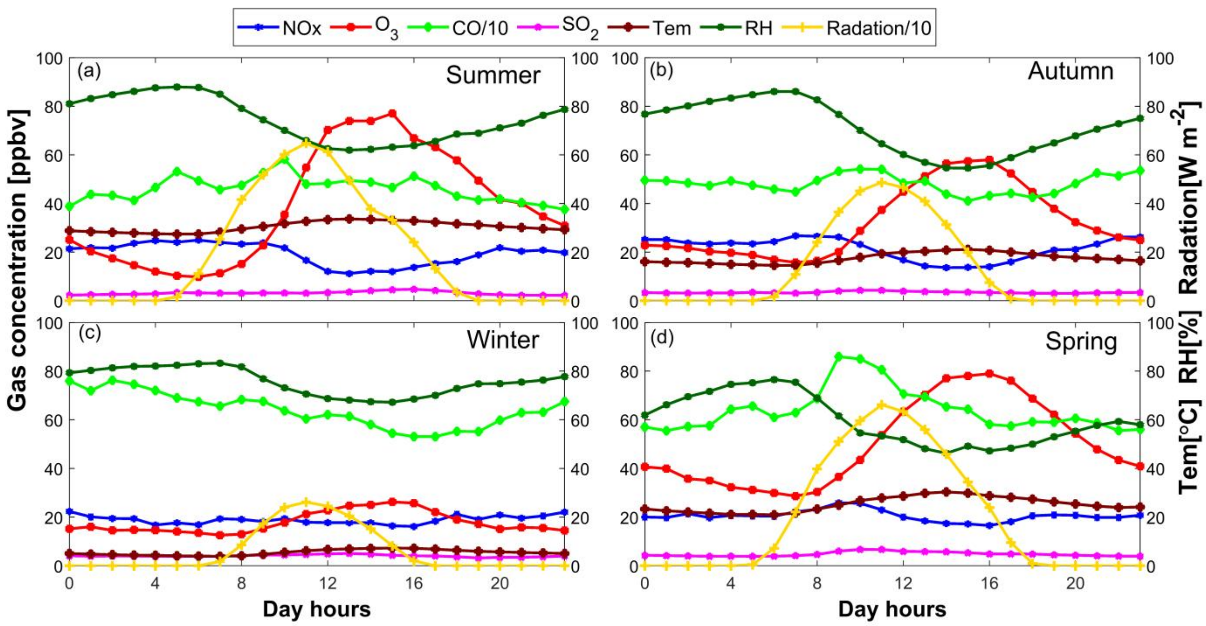
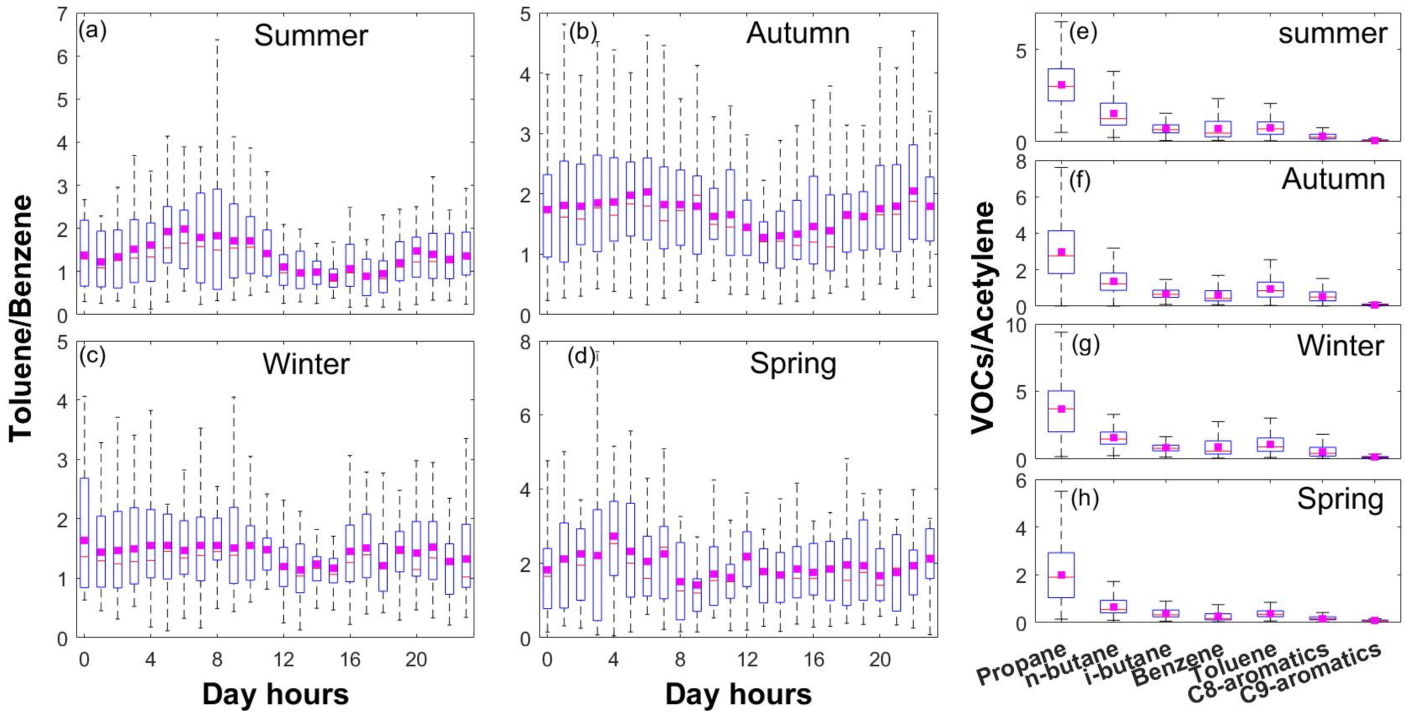
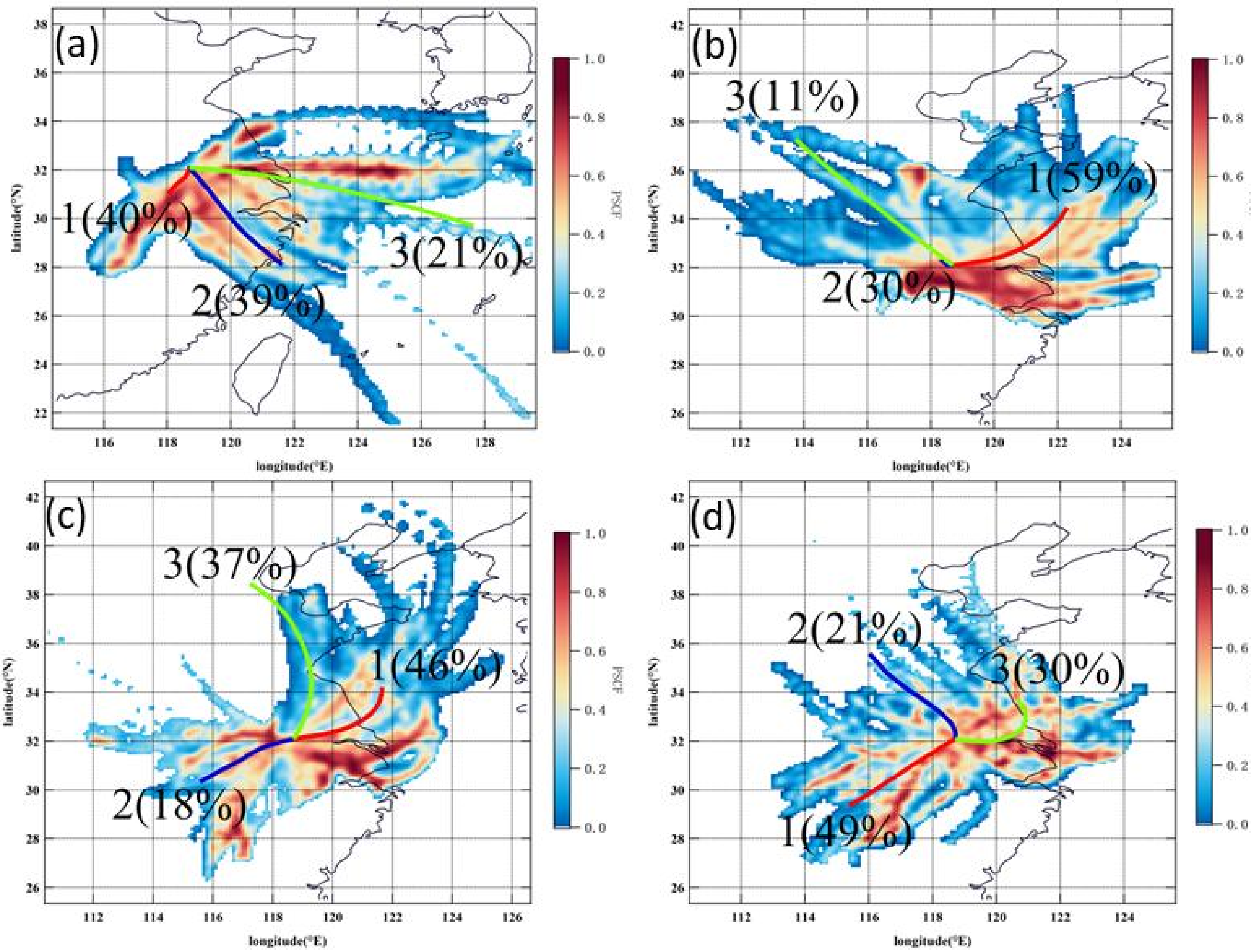


Figure 3: Diurnal variations in weather conditions and NOx, O3, CO, and SO2 concentrations in different seasons. Note that the plotted CO concentrations and solar radiation values are reduced by 10-folds for a better visualization.



~~**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.**~~



(a)
1(40%)
2(39%)
3(21%)
latitude(°N)
longitude(°E)
PSCF
(b)
3(11%)
1(59%)
2(30%)
latitude(°N)
longitude(°E)
PSCF
(c)
3(37%)
1(46%)
2(18%)
latitude(°N)
longitude(°E)
PSCF
(d)
2(21%)
3(30%)
1(49%)
latitude(°N)
longitude(°E)
PSCF

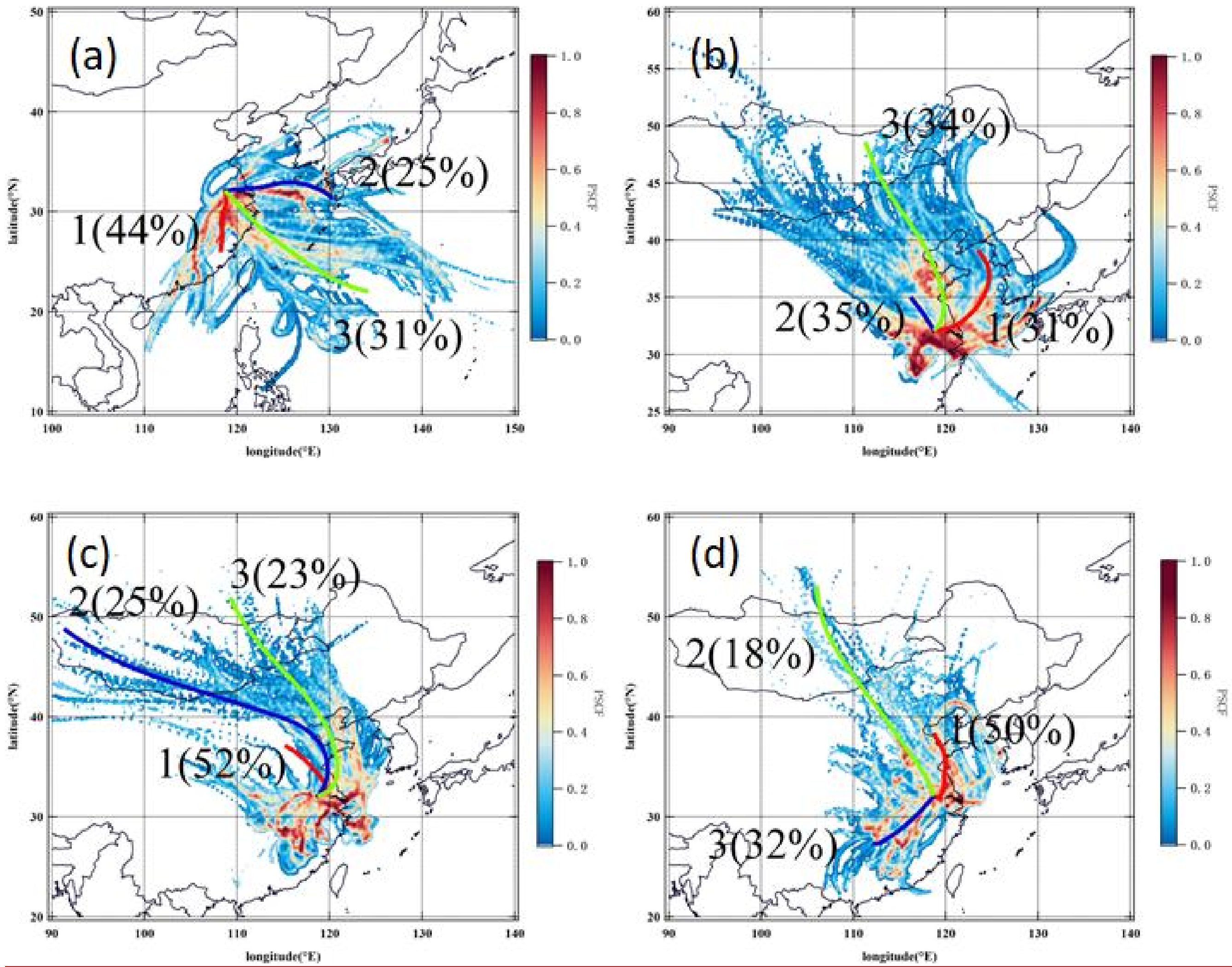
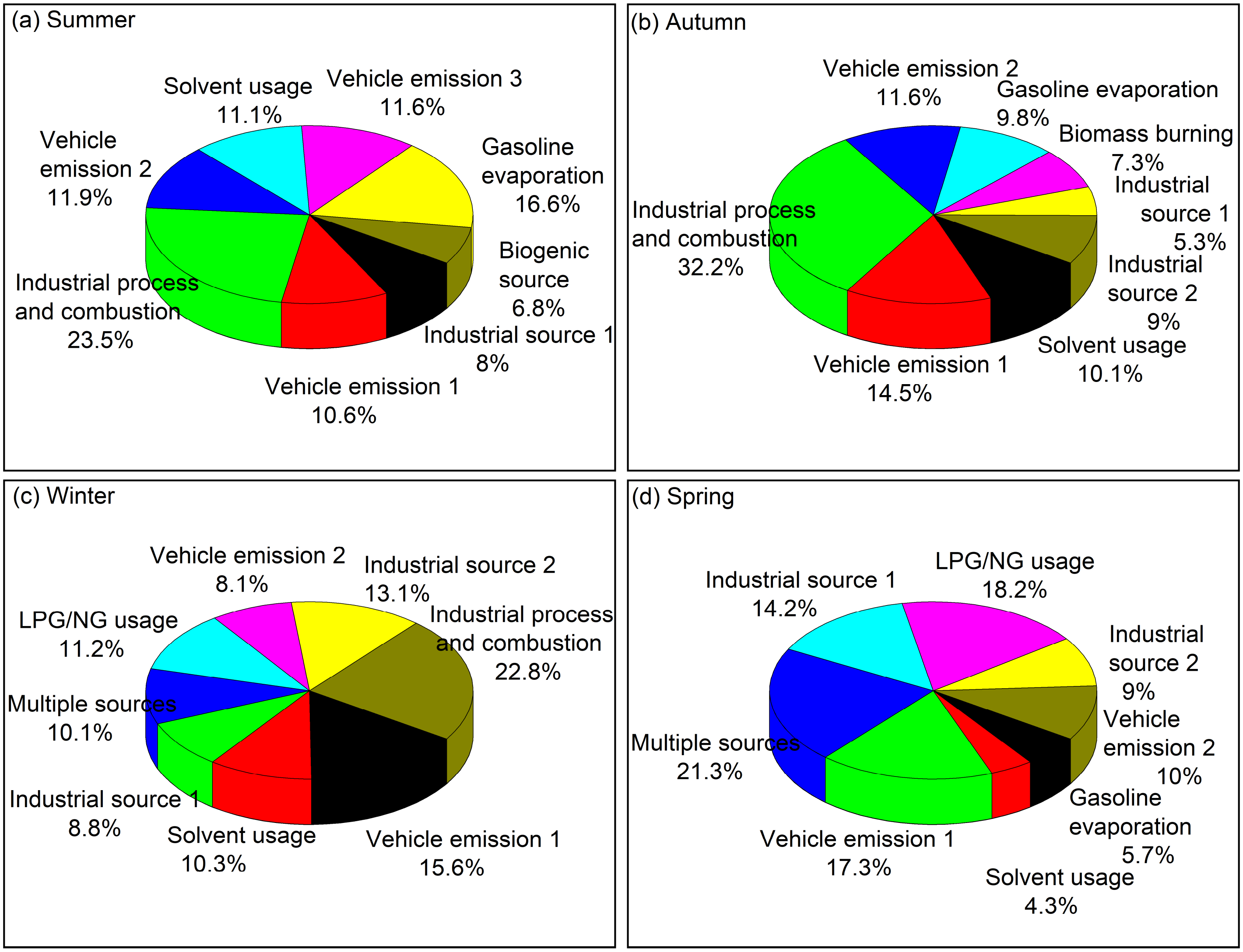


Figure 5: Wind cluster and PSCF analysis during (a) summer (b) autumn, (c) winter, and (d) spring based on the ~~24~~ 72 hours backward air mass trajectories from the study area.


(a) Summer
Solvent usage 11.1%
Vehicle emission 3 11.6%
Vehicle emission 2 11.9%
Gasoline evaporation 16.6%
Biogenic source 6.8%
Industrial process and combustion 23.5%
Industrial source 1 8%
Vehicle emission 1 10.6%
(b) Autumn
Vehicle emission 2 11.6%
Gasoline evaporation 9.8%
Biomass burning 7.3%
Industrial source 1 5.3%
Industrial process and combustion 32.2%
Industrial source 2 9%
Solvent usage 10.1%
Vehicle emission 1 14.5%
(c) Winter
Vehicle emission 2 8.1%
Industrial source 2 13.1%
Industrial process and combustion 22.8%
LPG/NG usage 11.2%
Multiple sources 10.1%
Industrial source 1 8.8%
Solvent usage 10.3%
Vehicle emission 1 15.6%
(d) Spring
Industrial source 1 14.2%
LPG/NG usage 18.2%
Industrial source 2 9%
Vehicle emission 2 10%
Multiple sources 21.3%
Gasoline evaporation 5.7%
Vehicle emission 1 17.3%
Solvent usage 4.3%

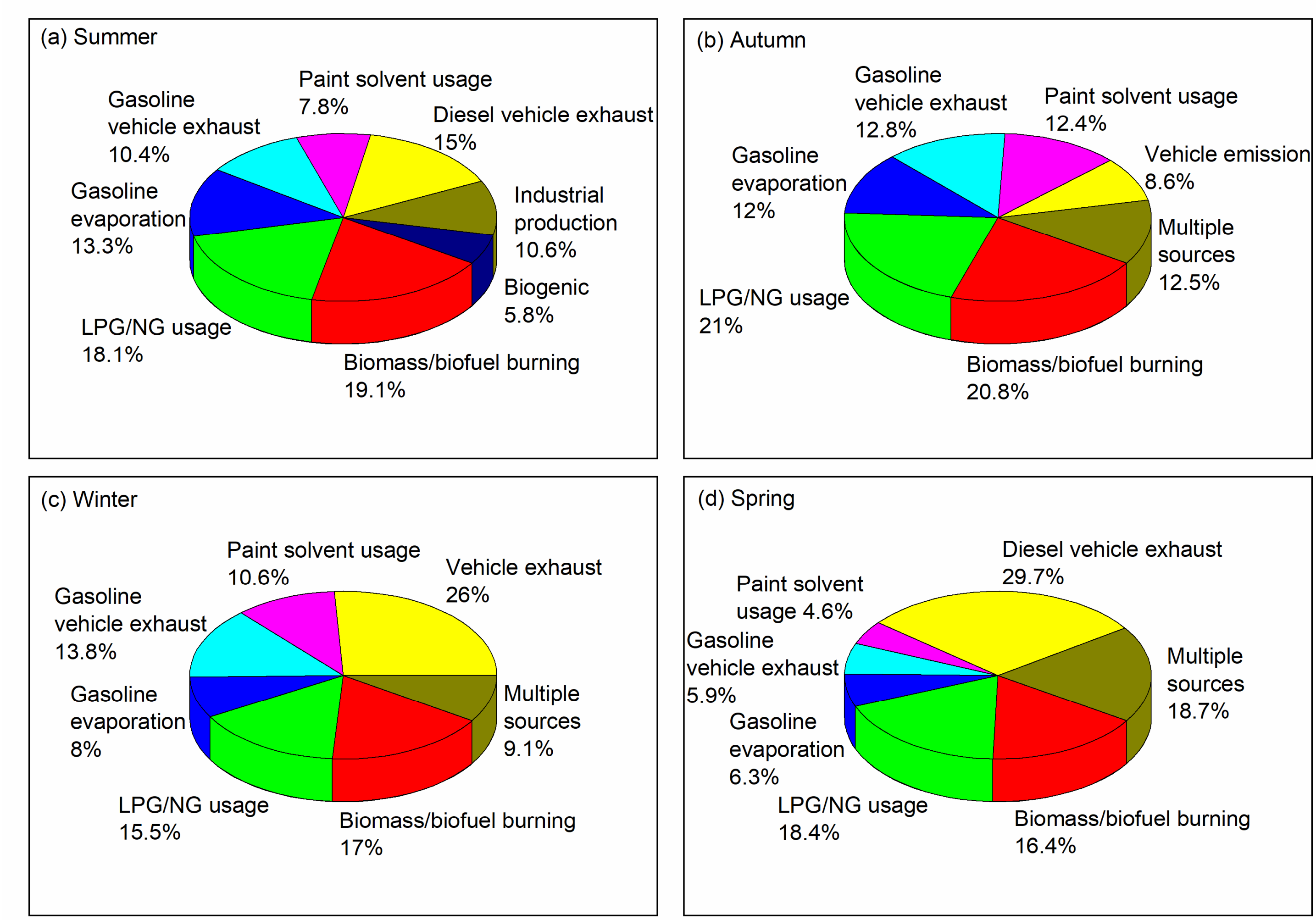


Figure 6: relative contributions of different sources to ambient VOCs in Nanjing industrial area during different seasons

915

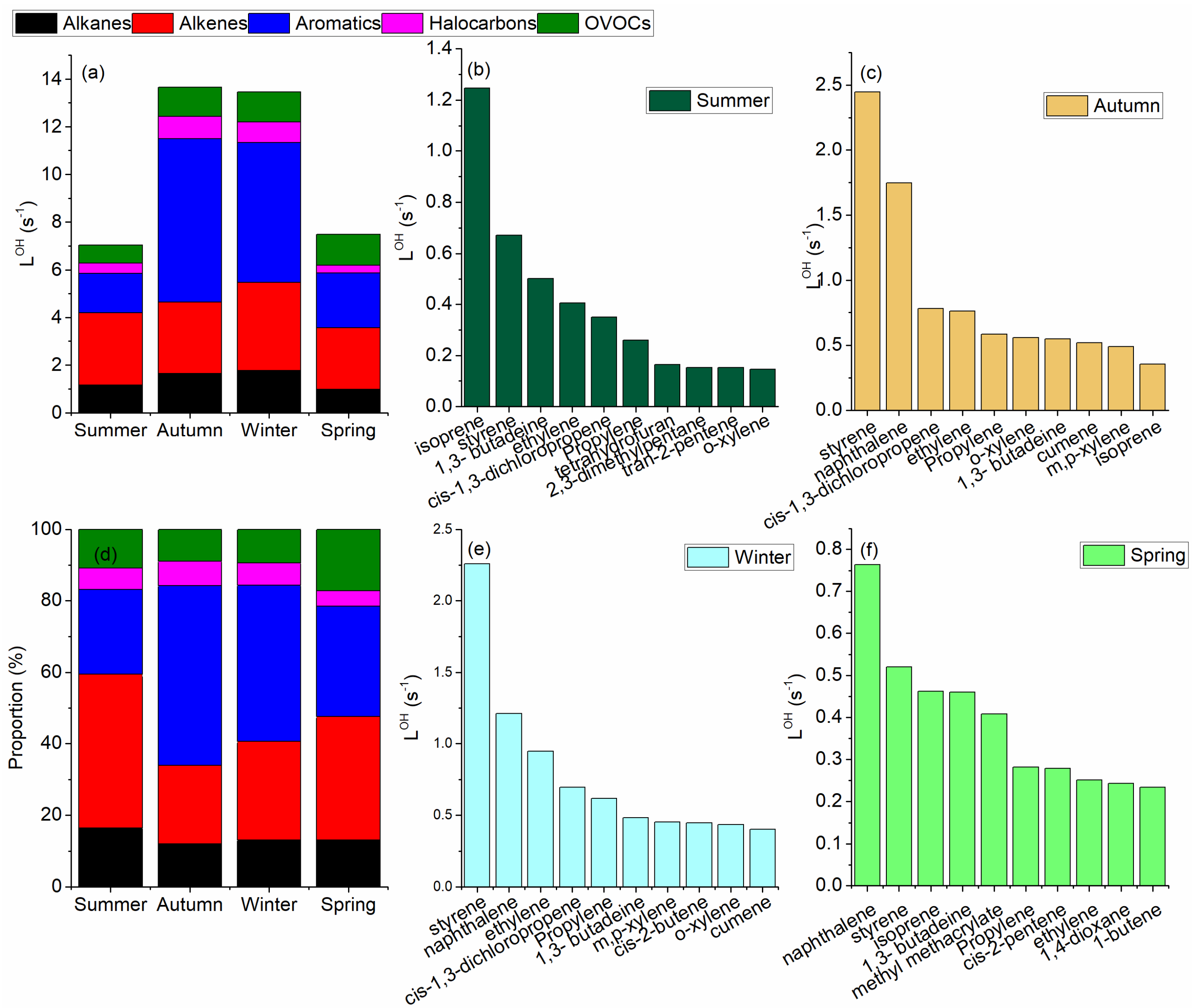


Figure 7: Contribution to OH loss rates of different VOC-groups and the top 10 VOC species in different seasons

920

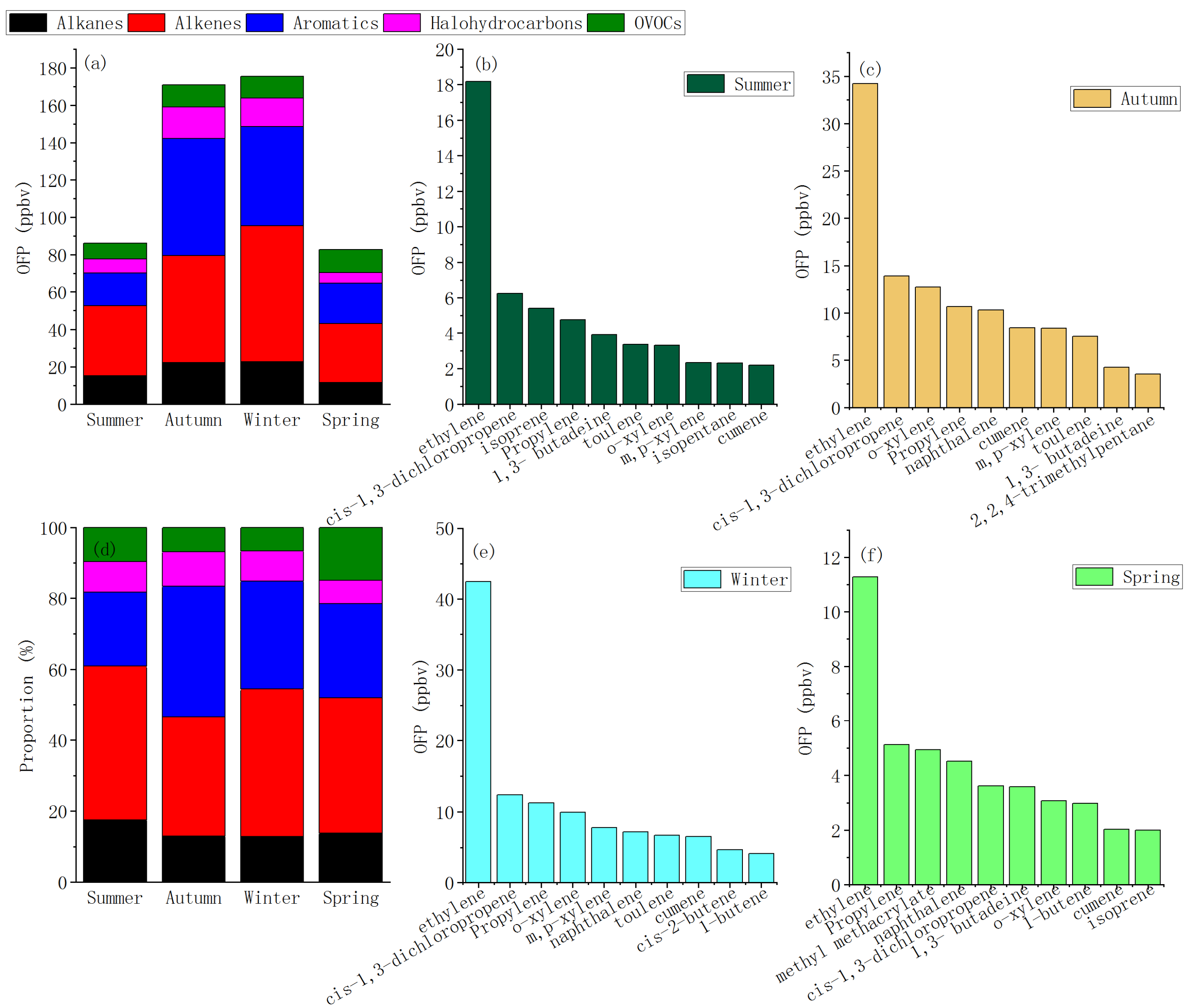
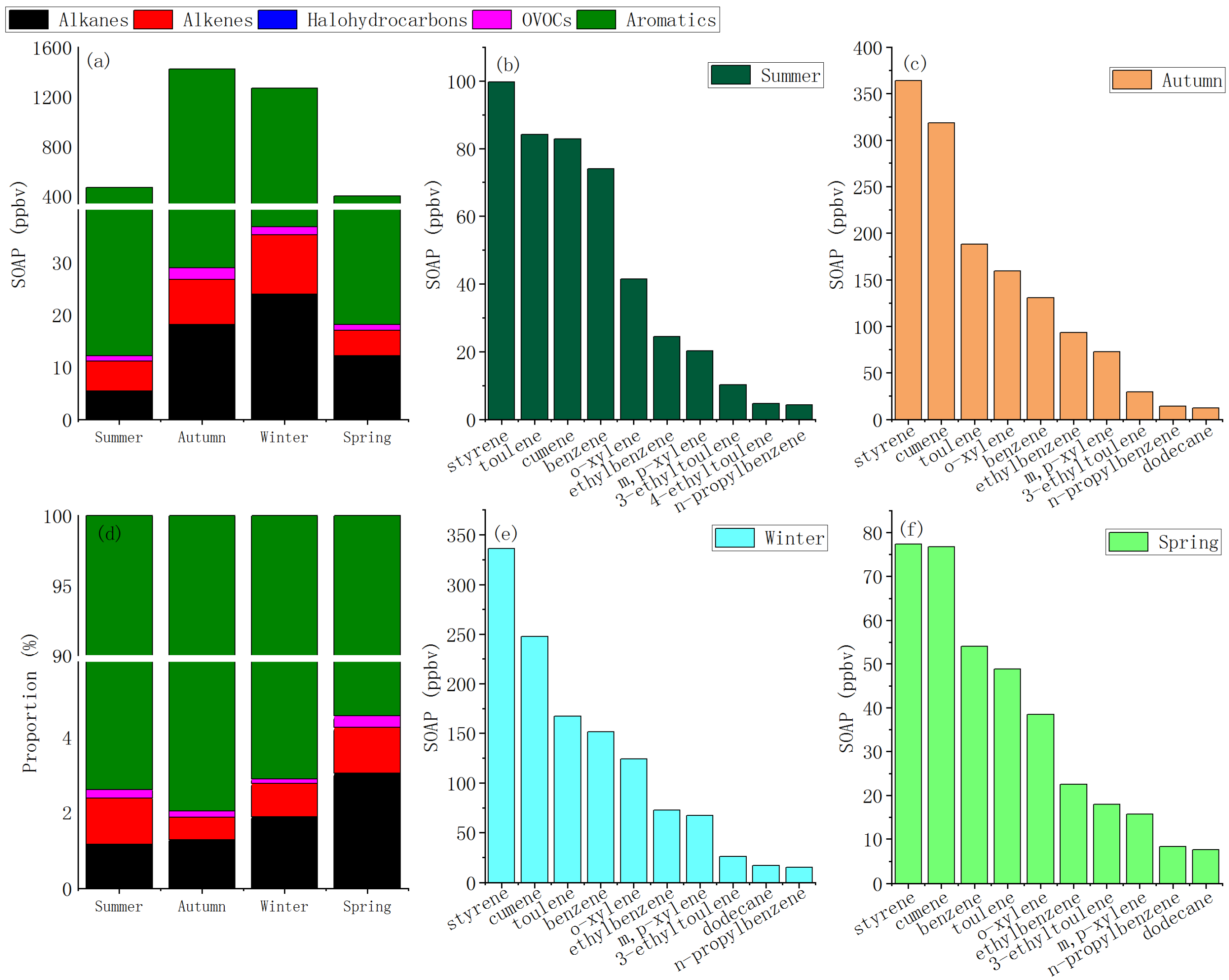


Figure 8: Contribution to ozone formation potential of different VOC groups and the top 10 VOC species in different seasons



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

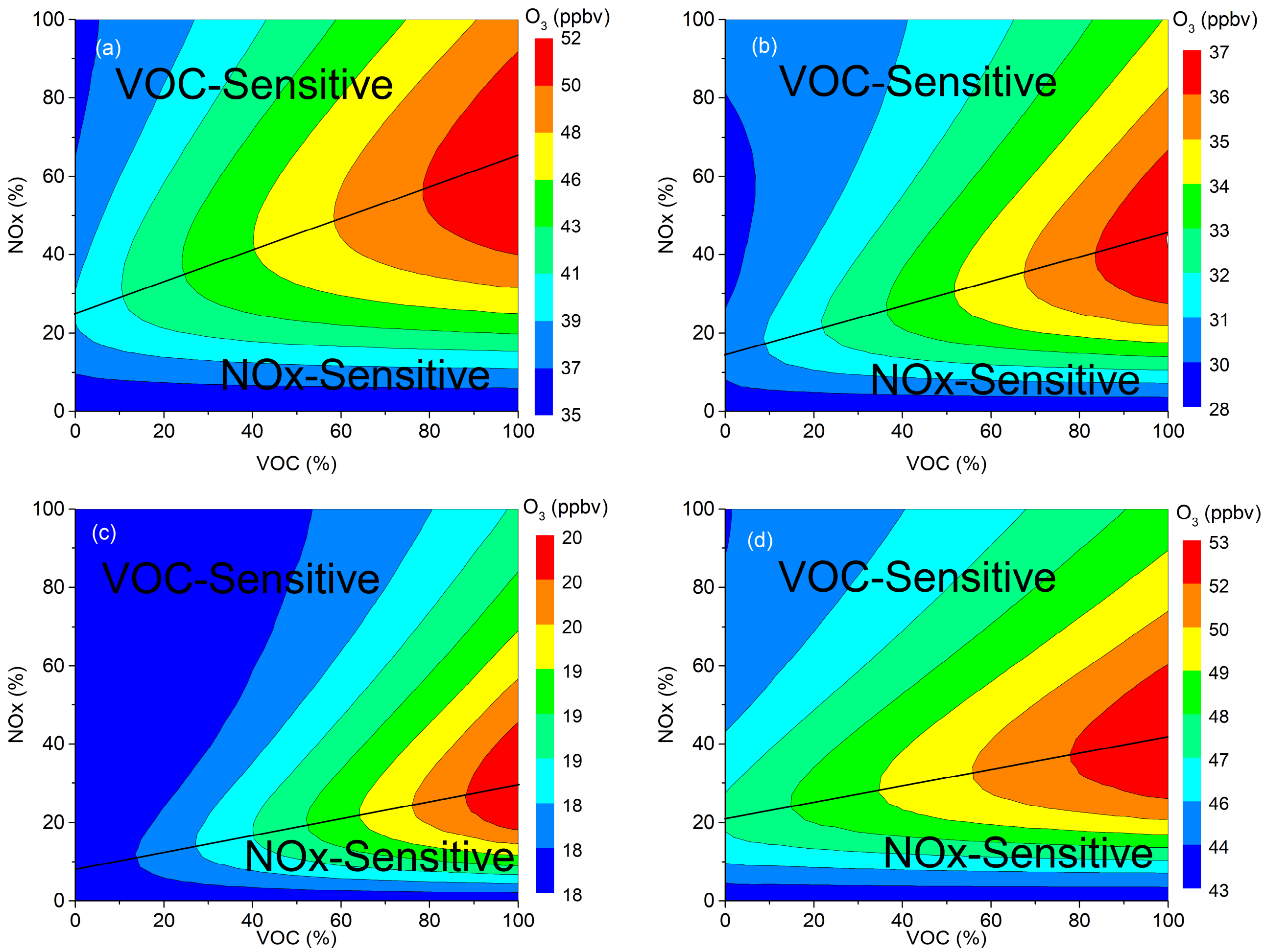


Figure 10: O_3 isopleth diagram for (a) summer (b) autumn, (c) winter, and (d) spring based on percentage changes in VOCs and NOx concentrations in Nanjing and corresponding modelled O_3 production.

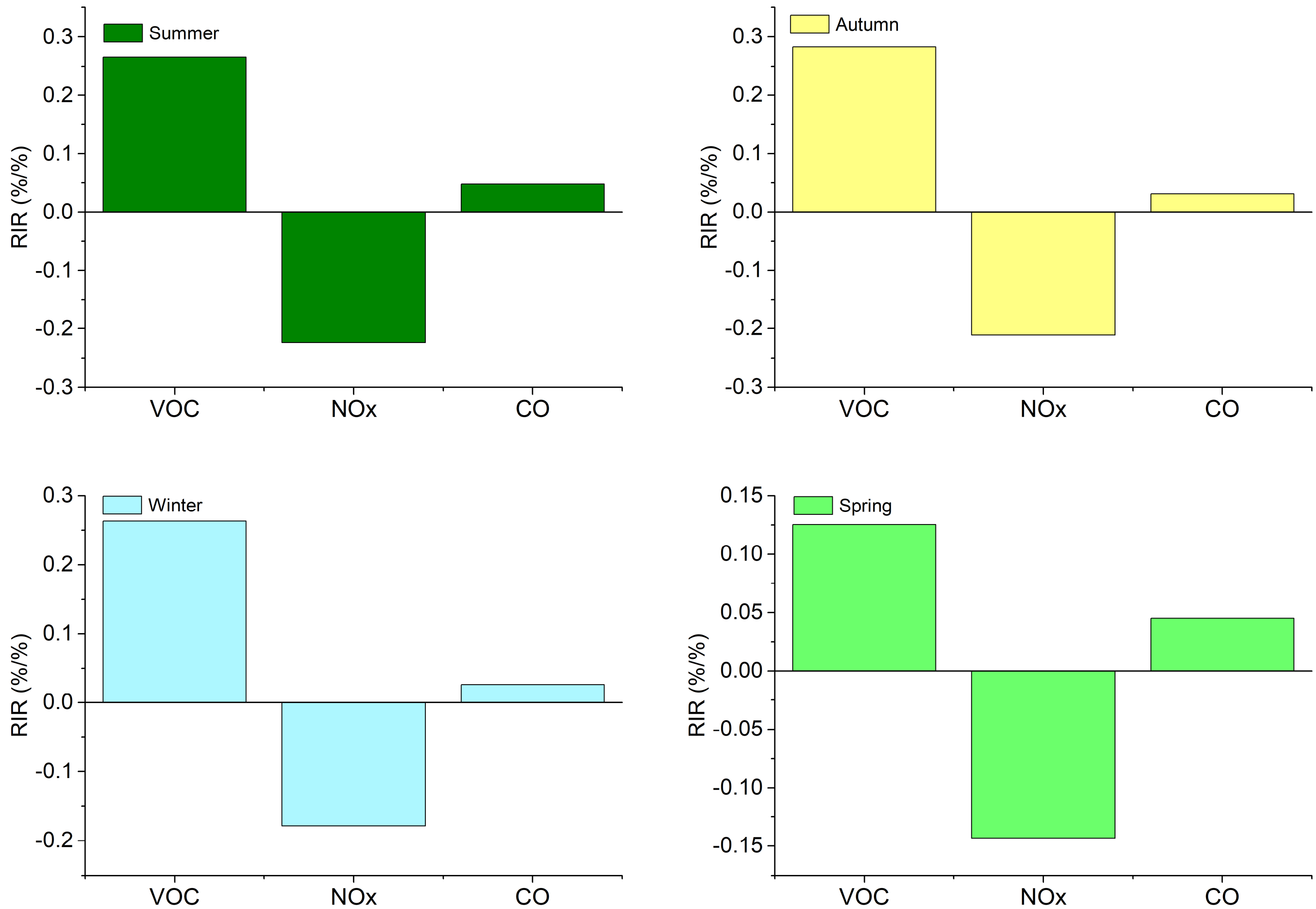


Figure 11: The RIR values of the VOC, NOx, and CO for the different seasons in Nanjing

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

Ahsan Mozaffar [1,2,3], Yan-Lin Zhang [1,2,3*], Yu-Chi Lin[1,2,3], Feng Xie [1,2,3], Mei-Yi Fan [1,2,3], and Fang Cao [1,2,3]

[1]Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[2]Key Laboratory Meteorological Disaster; Ministry of Education & Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disaster, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[3]Jiangsu Provincial Key Laboratory of Agricultural Meteorology, College of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China.

Correspondence to: Yan-Lin Zhang (dryanlinzhang@outlook.com)

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

Compounds	k_{OH} (cm^3 $molecule^{-1}$ 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- butadeine	6.59E-11	
1-pentene	3.14E-11	Yes
tran-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-ethyltoulene	1.86E-11	Yes
4-ethyltoulene	1.18E-11	Yes
Mesitylene	5.67E-11	Yes
2-ethyltoulene	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

Table S2: VOC concentrations (ppbv) measured in the industrial area in Nanjing. VOC concentrations (ppbv) observed in 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-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- butadeine	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	0.08	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 briomide	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			
trichloroflorome thane	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-Trichlor-1,2,2-trifluorethan	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
bromodichloromethane	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
tetrachloroethylene	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	0.94	0.30	3.43	0.97	3.16	0.70	0.73	0.30	2.06	1.43

e										
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 dichlorobebezne	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
TVOC	**38.81**	**10.21**	**83.05**	**20.07**	**77.51**	**16.77**	**39.62**	**13.12**	**59.75**	**28.57**

S1. Source apportionment of VOCs

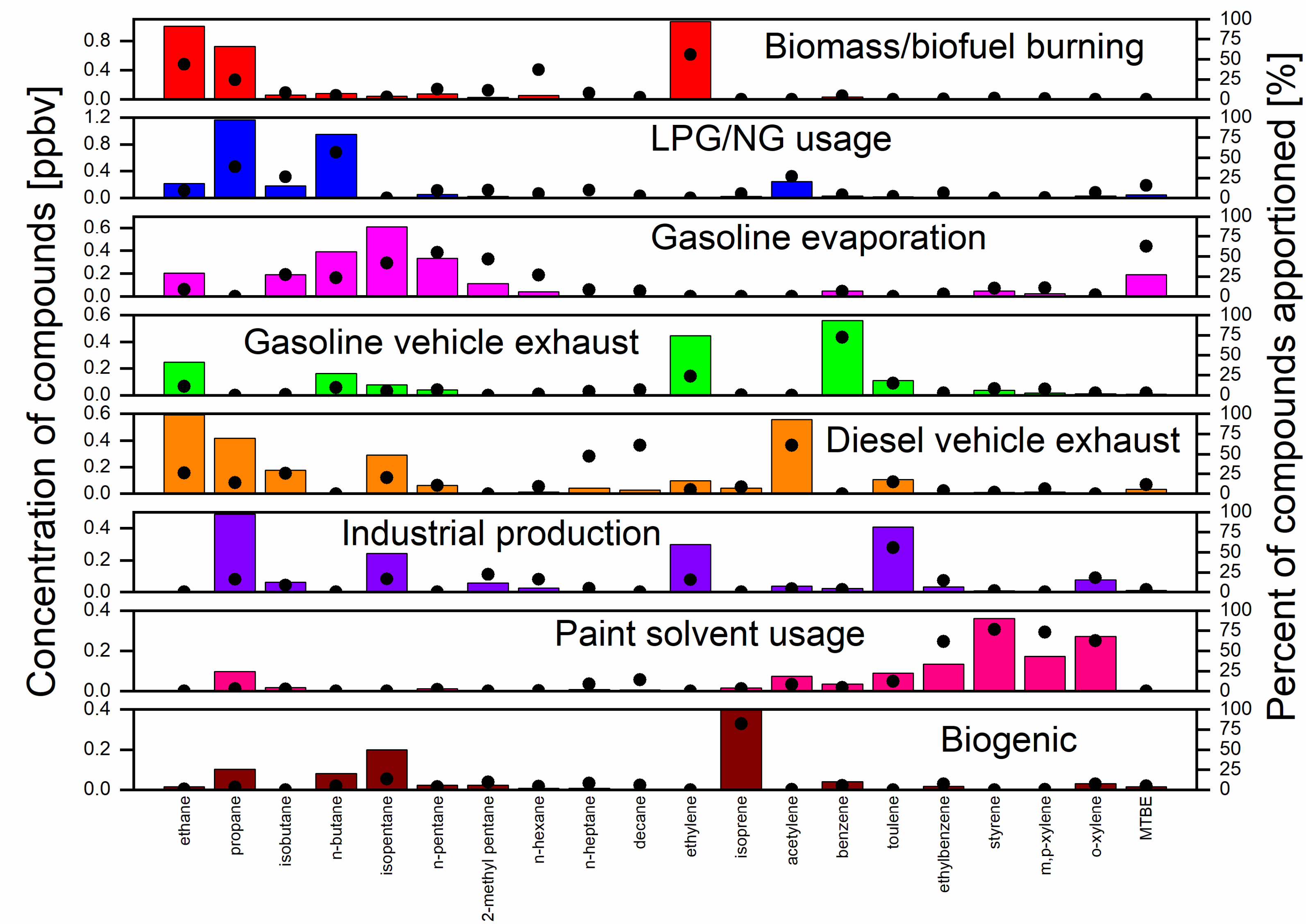
Figure S1 shows the source profile of summertime VOCs. The resolved factors were identified as biomass/biofuel burning, LPG/NG usage, gasoline evaporation, gasoline vehicle exhaust, diesel vehicle exhaust, industrial production, paint solvent usage, and biogenic source. Factor 1 was characterized by high concentrations of ethane and ethylene. These compounds are tracers of incomplete combustion emitted from vehicle exhaust and biomass/biofuel burning (An et al., 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). 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. 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., 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 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, benzene was several folds higher than toluene. The 4th 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, 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).

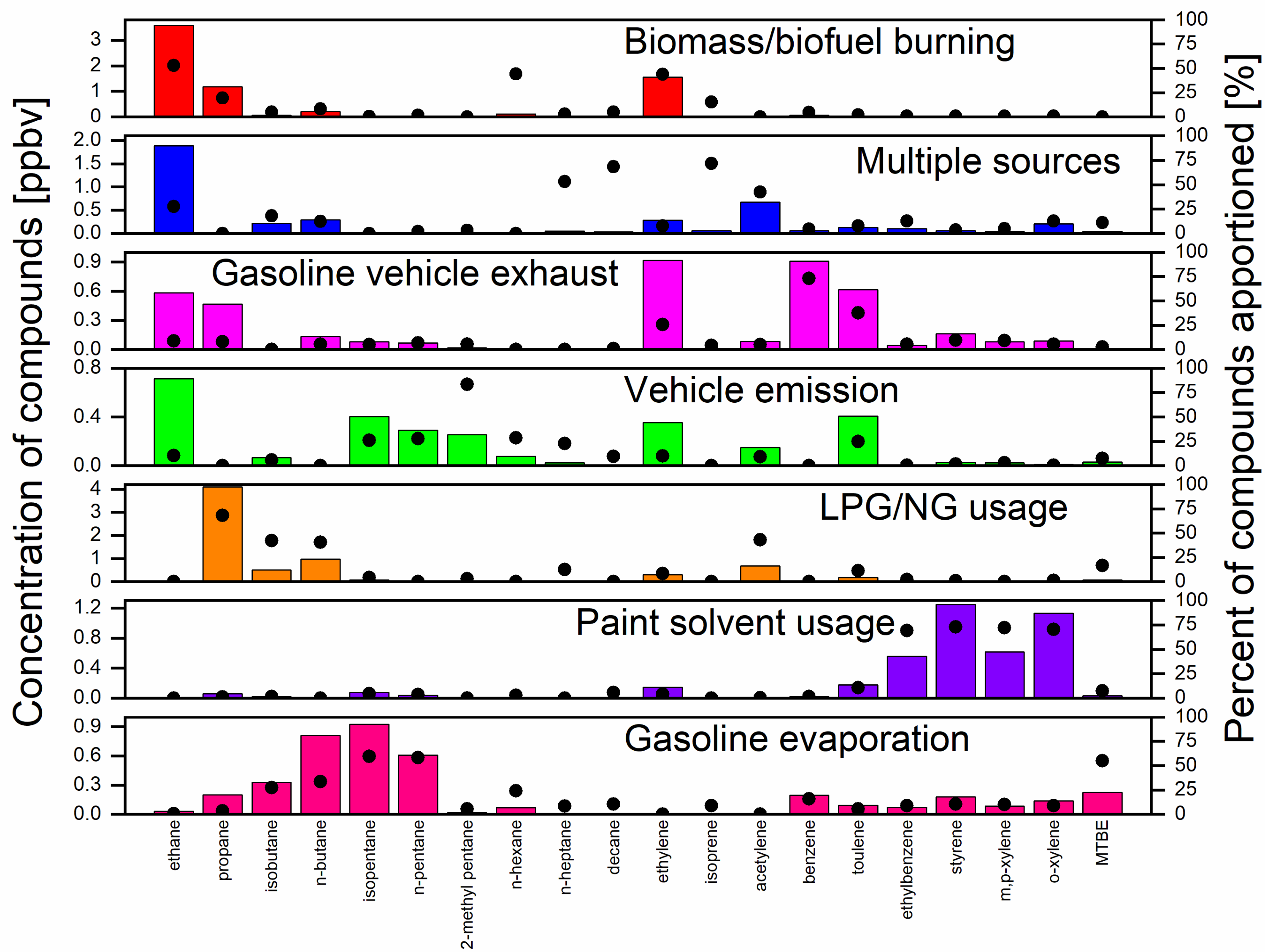
During winter, the source factors were gasoline vehicle exhaust, vehicle exhaust, gasoline evaporation, biomass/biofuel burning, multiple sources, LPG/NG usage, and paint solvent usage (Fig. S3). Factor 1 was assigned to gasoline vehicle exhaust. It was dominated by benzene and toluene; the contribution 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 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 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 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.

1040

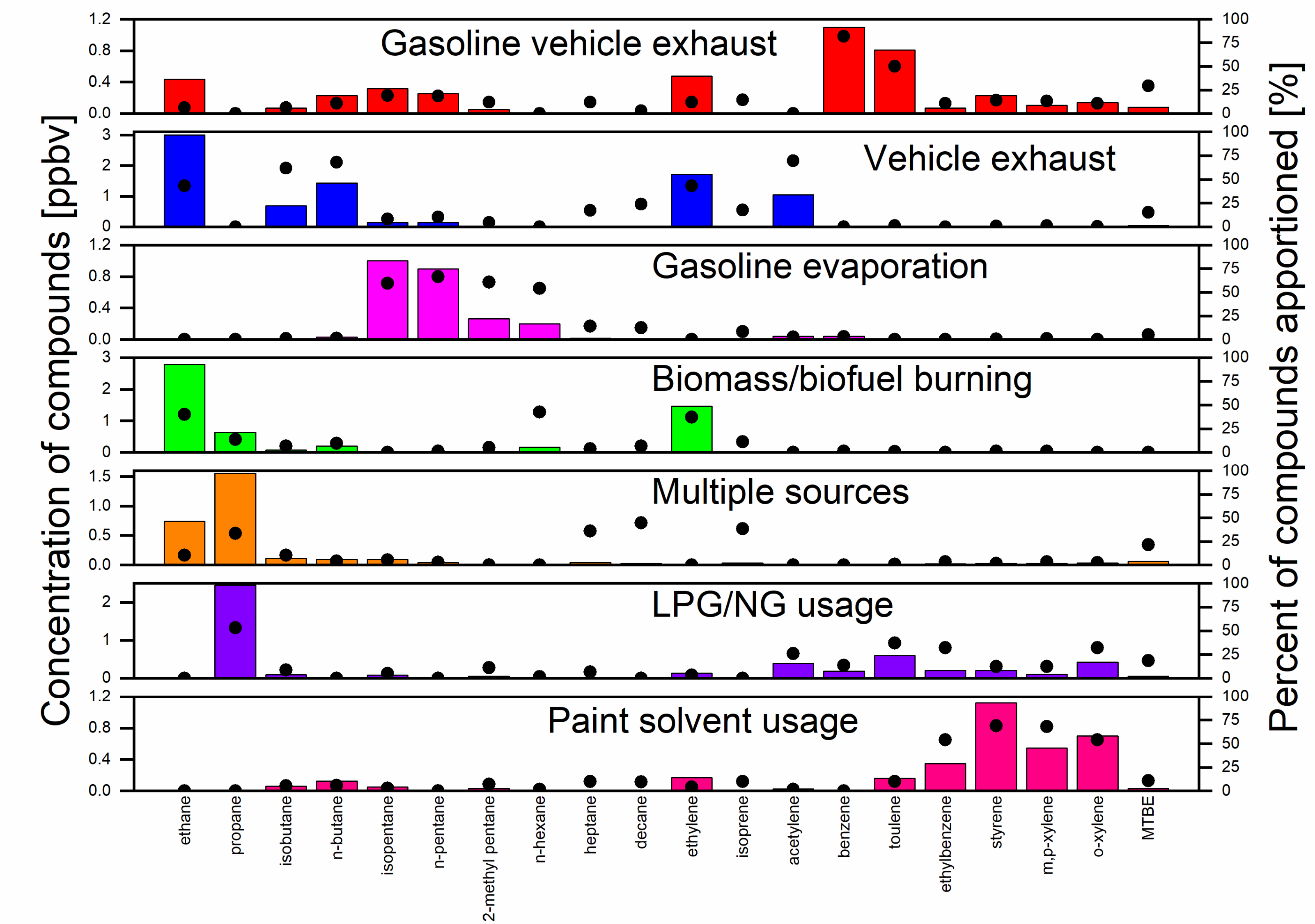


1041 **Figure S1: Source profile of VOCs during summer in Nanjing industrial area. Bars and dots represent the concentrations and**
1042 **percentages of the compounds, respectively.**



1043

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.**



1046

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.**

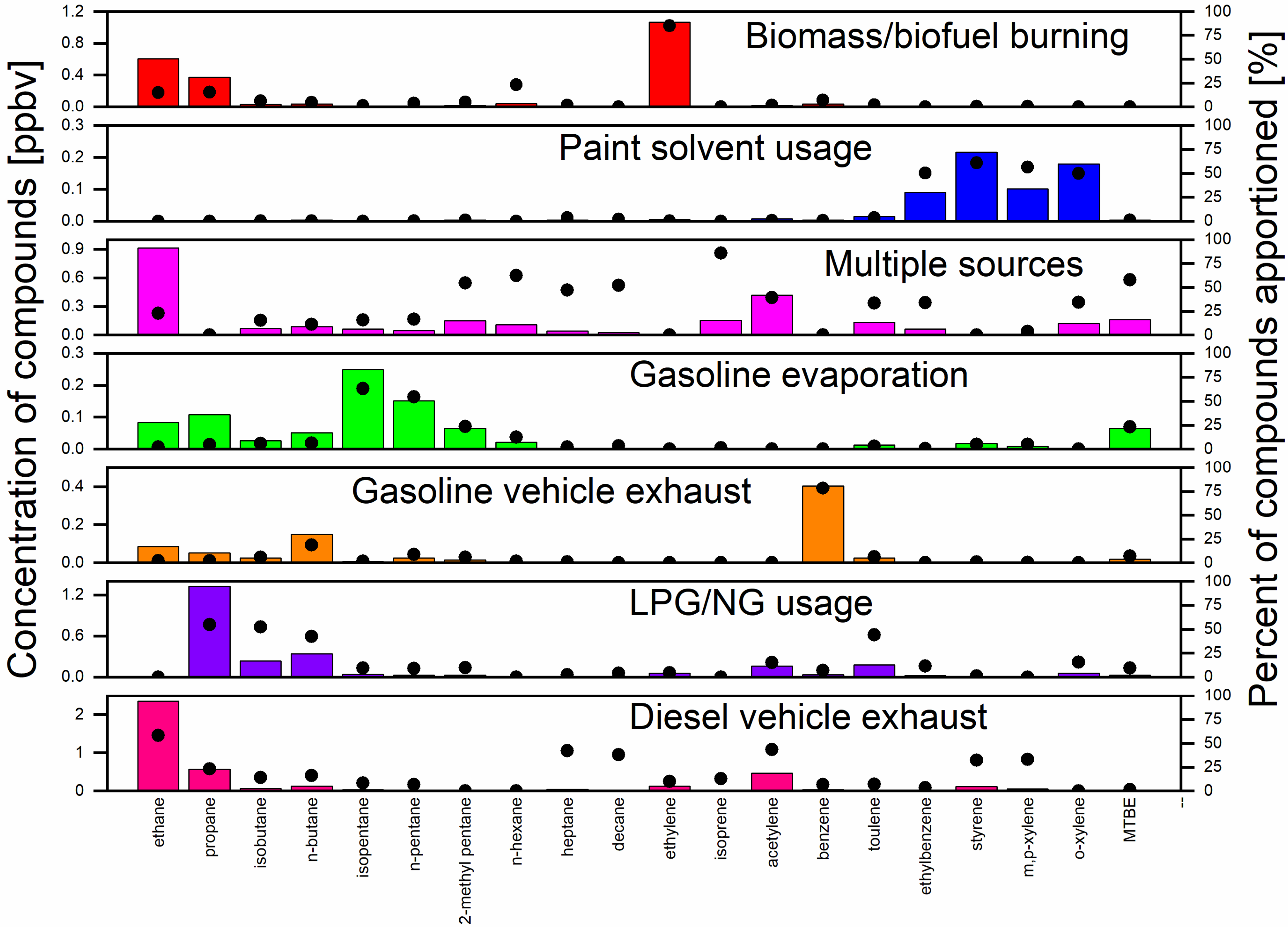


Figure S4: Source profile of VOCs during spring in Nanjing industrial area. Bars and dots represent the concentrations and percentages of the compounds, respectively.

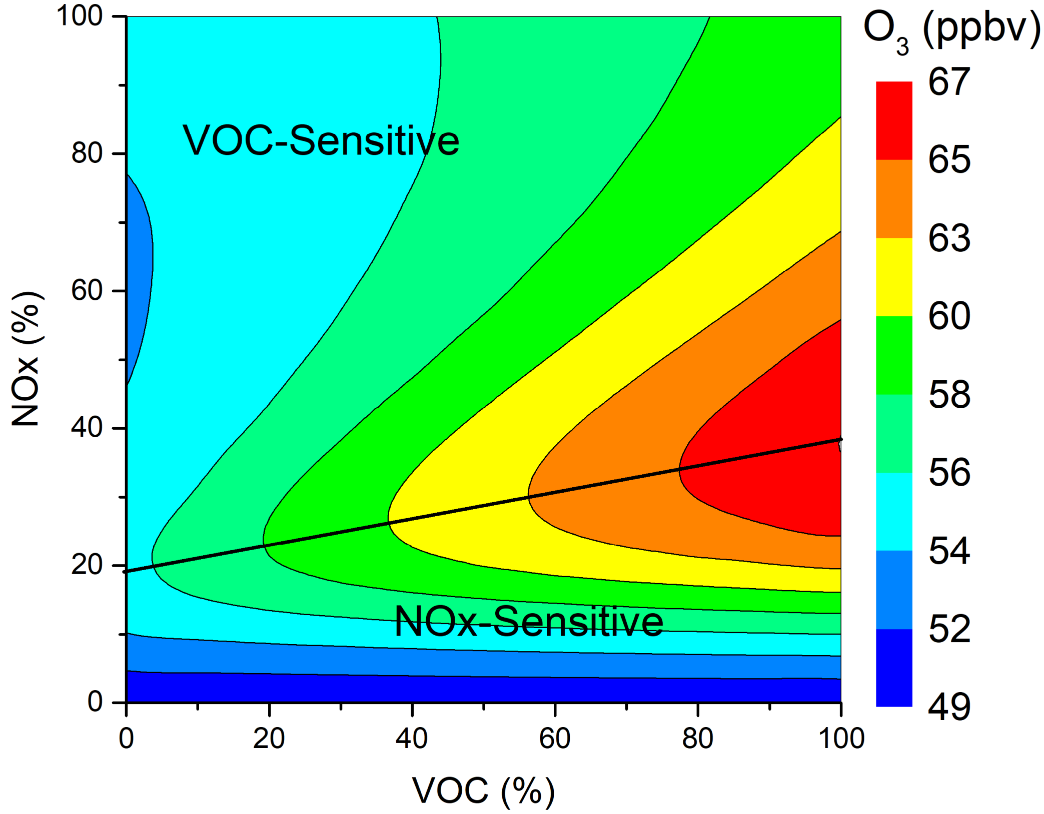


Figure S5: O_3 isopleth diagram on a high O_3 episode day (July 29 2018) in Nanjing industrial area.

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