

Article

Characteristics of Volatile Organic Compounds in the Pearl River Delta Region, China: Chemical Reactivity, Source, and Emission Regions

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Citation: Yang, W.; Yu, Q.; Pei, C.; Liao, C.; Liu, J.; Zhang, J.; Zhang, Y.; Qiu, X.; Zhang, T.; Zhang, Y.; et al. Characteristics of Volatile Organic Compounds in the Pearl River Delta Region, China: Chemical Reactivity, Source, and Emission Regions. *Atmosphere* **2022**, *13*, 9. <https://doi.org/10.3390/atmos13010009>

Academic Editor: Jianyin Xiong

Received: 6 November 2021

Accepted: 18 December 2021

Published: 21 December 2021

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Abstract: Volatile organic compounds (VOCs) are important precursors of photochemical ozone and secondary organic aerosol (SOA). Here, hourly variations of ambient VOCs were monitored with an online system at an urban site (Panyu, PY) in the Pearl River Delta region during August–September of 2020 in order to identify reactive VOC species and major sources of VOCs, OH loss rate (L_{OH}), SOA formation potential (SOAFP), and corresponding emission source regions. The average concentration of VOCs at PY was 31.80 ± 20.82 ppbv during the campaign. The C_2 – C_5 alkanes, aromatics, and $\geq C_6$ alkanes contributed for the majority of VOC, alkenes and aromatics showed the highest contribution to L_{OH} and SOAFP. Further, m/p-xylene, propene, and toluene were found to be the top three most reactive anthropogenic VOC species, with respective contributions of 11.6%, 6.1%, and 5.8% to total L_{OH} . Toluene, m/p-xylene, and o-xylene constituted a large fraction of calculated SOAFP. Seven major sources were identified by using positive matrix factorization model. Vehicle exhaust made the most significant contribution to VOCs, followed by liquefied petroleum gas and combustion sources. However, industrial-related sources (including industrial solvent use and industrial process emission) had the largest contribution to L_{OH} and SOAFP. By combining source contribution with wind direction and wind speed, the regions of different sources were further identified. Based on high-resolution observation data during ozone pollution, this study clearly exhibits key reactive VOC species and the major emission regions of different VOC sources, and thus benefits the accurate emission control of VOCs in the near future.

Keywords: volatile organic compounds; chemical reactivity; secondary organic aerosol formation potential; source apportionment; emission region

1. Introduction

Volatile organic compounds (VOCs) are important precursors of ozone and secondary organic aerosols (SOA) [1–6]. Ozone has long been known to cause adverse effects on human health [7–9] and has the potential to damage crops and vegetation [10–12]. It is also an important tropospheric greenhouse gas, with an estimated globally averaged

radiative forcing of $0.40 \pm 0.20 \text{ W m}^{-2}$, and directly contributes to global warming [13]. SOA is the main component of particulate matter with an aerodynamic diameter less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) [14,15], and contributes up to 20–35% of $\text{PM}_{2.5}$ during extreme haze event in megacities [16–18]. High mass concentration of $\text{PM}_{2.5}$ and its impacts on public health and visibility have become the most pressing air quality problem in China in recent years [19,20]. Thus, as the important precursors of ozone and SOA, VOCs play an important role in photochemical smog, particulate pollution, and human health impacts.

China has experienced rapid economization and industrialization in recent decades, accompanied by a serious air quality issues. Since 2013, significant efforts have been devoted to the battle against air pollution, in particular following the implementation of the Action Plan on the Prevention and Control of Air Pollution [21]. Although the emission of air pollutants, including sulfur dioxide (SO_2) and nitrogen oxides (NO_x), has decreased year by year [22,23], the emission of VOCs has increased [22,24], which leads to ozone concentration levels frequently exceeding the Chinese national ozone air quality standard [25–29]. The maximum daily 8 h average concentrations of ozone increased from approximately 69.5 ppbv in 2013 to 75.0 ppbv in 2015 in 74 Chinese cities, and the percentage of non-compliant cities increased from 22% to 38%, respectively [30]. The same is true for the Pearl River Delta (PRD) region, the largest urban agglomeration in southern China. In 2020, the number of days that ozone ranked as the primary pollutant accounted for 66.8% of the total non-attainment days in the PRD region, and ozone pollution has been considered a long-term challenge for the PRD region [31]. Ozone formation presents a complex non-linear relationship with precursors including VOCs and NO_x [1,5], and numerous studies with different approaches show that ozone formation in the PRD region is predominantly VOC-limited [32–35]. In-depth study of VOCs is essential in order to reduce the concentrations of ozone in the PRD region.

As key precursors of ozone, VOCs are composed of hundreds of species, and they are directly emitted into the atmosphere from a variety of anthropogenic sources [36,37]. The contribution of different VOCs to ozone formation potential varies significantly based on changes in their OH radical reaction rates [38]. Moreover, some VOCs (such as aromatics and alkanes) are important precursors of SOA [4,39], which is the main component of $\text{PM}_{2.5}$. Consequently, identification of the key precursors of ozone and SOA as well as the major sources of these precursors is critical for the prevention and control of ozone and $\text{PM}_{2.5}$ pollution. To date, tremendous research efforts have been devoted to investigating ambient VOCs in the PRD region, and the main sources and spatio-temporal distribution of VOCs have been obtained [40–44]. However, most of these observations were based on off-line monitoring with canister sampling [45,46], and few studies have focused on VOCs during long-term ozone pollution. Moreover, the sources of VOCs have changed greatly due to pollutant emission control in the past ten years [20,22]. Consequently, the latest observation-based online monitoring of VOCs with high resolution, in particular during heavy ozone pollution, can provide better understanding of the key VOC species and their major emission sources, which is essential for $\text{PM}_{2.5}$ and O_3 pollution control.

In this study, ambient VOCs were monitored with an online monitoring system during long-term ozone pollution at an urban site in the PRD region in order to determine the mixing ratio levels of VOCs, and the OH loss rate (L_{OH}) and SOA formation potential (SOAFP) methods were used to calculate the reactivity of VOCs. Furthermore, positive matrix factorization (PMF) was used to identify the major sources of VOCs, and the L_{OH} and SOAFP source apportionment results were further combined with wind speed and wind direction to explore the emission regions of different sources.

2. Materials and Methods

2.1. Field Sampling

The ambient VOC samples were taken at an urban site in Guangzhou located on the roof of the six-story building of Panyu (PY) middle school (Figure 1; 113.366° E , 22.913° N). The sampling site location was in the mixed residential and commercial area of PY district,

Guangzhou, situated in the central PRD, approximately 26 km and 28 km southeast of central Guangzhou and Foshan, respectively, 47 km northeast of Jiangmen city, 42 km west of Dongguan city and 80 km northwest of downtown Shenzhen. The site was selected as not only a typical urban site, but also a representative regional site in the PRD.

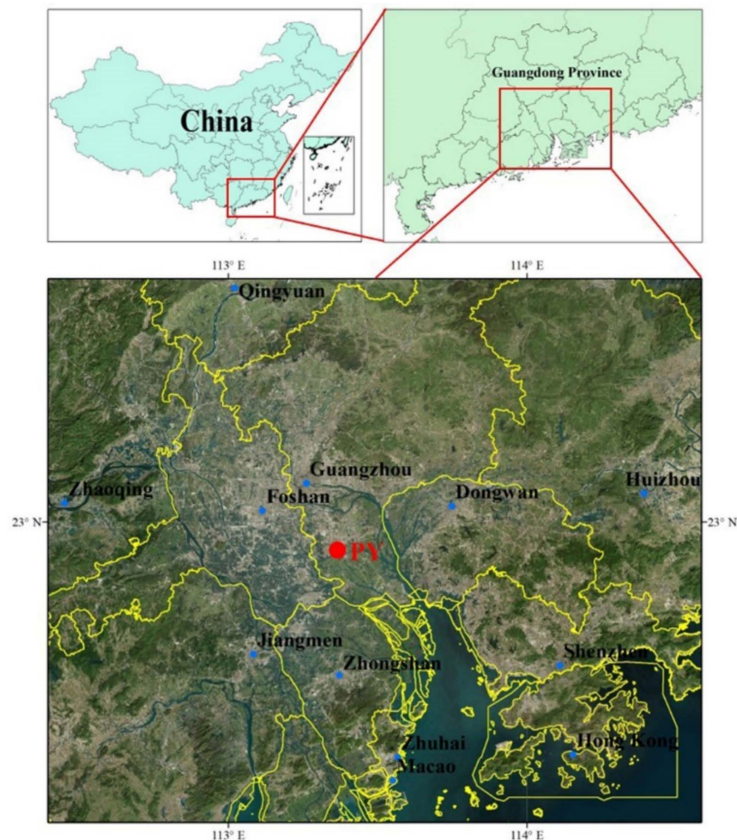


Figure 1. Location of VOC monitoring sites in the Pearl River Delta region.

2.2. Online Measurement of VOCs and Other Pollutants

Ozone pollution is more serious during autumn in the Pearl River Delta. From 17 August to 7 September 2020, thirteen episodes occurred when the maximum daily 8 h average concentration of O_3 exceeded the National Ambient Air Quality class II standard ($160 \mu\text{g m}^{-3}$) and the maximum hourly O_3 level reached $281 \mu\text{g m}^{-3}$. In order to explore the characteristics of VOCs during long-term ozone pollution, a total of 55 VOCs in ambient air, including 28 alkanes, 10 alkenes, 16 aromatics, and ethyne, were analyzed using an online system (GC-866; Chromatotec Inc., Saint-Antoine, France) from 17 August to 7 September 2020 within a 1 h interval. The VOC samples were first collected at a flow rate of 40 mL min^{-1} for 5 min, then the VOCs were analyzed with two different gas chromatographs equipped with a flame ionization detector (GC-FID), one for C_2 – C_6 compounds (AirmoVOC C_2 – C_6 ; Chromatotec Inc., France) and another for C_6 – C_{12} compounds (AirmoVOC C_6 – C_{12} ; Chromatotec Inc., France). For the C_2 – C_6 channel, the higher molecular weight compounds in samples were trapped with Carbotrap C and Carbotrap B and then the non-retained compounds were trapped at -8°C by a cell with the Peltier effect. For the C_6 – C_{12} channel, the sample was passed through a fine tube and C_6 – C_{12} compounds were extracted with porous substances according to their affinity. The second trap was then rapidly heated to 220°C and kept at that temperature for 240 s until the VOCs were transferred to the GC-FID system. The C_2 – C_6 VOCs were separated using an ultimetal column ($25 \text{ m} \times 0.55 \text{ mm I.D.}$), while C_6 – C_{12} VOCs were separated using a capillary metallic column (MXT30 CE; $30 \text{ m} \times 0.28 \text{ mm} \times 1.0 \mu\text{m}$). Detailed information about the instruments is described elsewhere [47,48].

Other air pollutants including SO₂, NO₂, CO, and O₃ were measured by 43i pulsed fluorescence, 42i chemiluminescence, 48i infrared radiation and the 49i UV photometric method using Thermo Environmental Instruments (Thermo Fisher Scientific, Boston, MA, USA) during a campaign with a 1 h interval, respectively. The hourly concentrations of PM_{2.5} were measured by the β -absorption method using a BAM 1020 instrument (Met One Instrument, Grants Pass, OR, USA).

2.3. Quality Control and Quality Assurance

Stringent quality control and quality assurance measures were taken for the online system during the campaign. The calibration standards were generated by dynamically diluting the Photochemical Assessment Monitoring Station (PAMS, Spectra Gases Inc., Kearny, NJ, USA) gas mixture. Then, the calibration curves were generated by analyzing above standards the same way as the filed samples and verified every two weeks. The responses of the GC-866 system were auto-calibrated every day with a 5 ppbv mixed standard in order to ensure that responses were lower than $\pm 10\%$ of the calibration curve. The method detection limits (MDLs) for VOC species ranged from 0.01 to 0.56 ppbv.

2.4. Data Analysis

2.4.1. The OH Loss Rate of VOCs

The L_{OH} of VOCs represents the chemical reactivity of each VOC species, and is calculated by multiplying the mixing ratio level of VOCs by its OH radical rate constant, as shown in Equation (1):

$$L_{OH_i} = [VOC]_i \times K_i^{OH} \quad (1)$$

where L_{OH_i} represents the loss rates of i VOC species that react with OH radical, VOC_i represents the concentration levels of i VOC species, and K_i^{OH} represents the rate constant for the reaction of the i VOC species with OH radical; the K_i^{OH} for 56 VOCs species were obtained from the results of Carter [49].

2.4.2. Secondary Organic Aerosol Formation Potential (SOAFP)

Some VOC species are important precursors of SOA, and the SOAFPs from VOC species were estimated in the present study as shown in Equation (2):

$$SOAFP_i = VOC_i / (1 - F_{VOCr_i}) \times FAC_i \quad (2)$$

where $SOAFP_i$ represents the SOA formed from i VOC species, VOC_i represents the concentration levels of i VOC species in ambient air, F_{VOCr_i} represents the fraction of reacted i VOC species, and FAC_i denotes the fractional aerosol coefficient for i VOC species [50–52].

2.4.3. Positive Matrix Factorization

PMF is a multivariate factor analysis tool that decomposes a matrix of sample data into two matrices, factor contributions (g) and factor profiles (f). The method is reviewed briefly here and described in greater detail elsewhere [53,54]. VOC sources were resolved according to the data matrix, X , which decomposes observed VOCs to g (factor contributions) and f (factor profiles) as represented in Equation (3). The PMF solution minimizes the objective function based on uncertainties, as shown in Equation (4).

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (3)$$

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (4)$$

The input files of PMF included the concentration of VOCs and user-provided uncertainty associated with the observed VOCs. Data values below the MDL were substituted

with MDL/2; missing data values were substituted with median concentrations. If the concentration was less than or equal to the MDL provided, the uncertainty was calculated using the equation $\text{Unc} = 5/6 \text{ MDL}$; if the concentration was greater than the MDL provided, the uncertainty was calculated as $\text{Unc} = [(\text{Error factor} \times \text{mixing ratio})^2 + (\text{MDL})^2]^{1/2}$. The number of factors in PMF was selected based on Q/Q_{exp} , as shown in Section 3.5 [55].

3. Results

3.1. Characteristics of O_3 and Ambient VOCs

Figure 2 shows the time series of observed O_3 , VOCs, NO_2 , $\text{PM}_{2.5}$, as well as the meteorological parameters (temperature, humidity, wind speed, wind direction) at the PY site during the campaign. Overall, O_3 showed a higher level from 21 August to 6 September, with maximum hourly mean concentrations above $160 \mu\text{g m}^{-3}$, and the maximum hourly O_3 level was $281 \mu\text{g m}^{-3}$ at 18:00 on 22 August. Furthermore, thirteen episode days (59%) occurred during the 22-measurement days with the maximum daily 8 h average concentration of O_3 exceeding the National Ambient Air Quality class II standard of $160 \mu\text{g m}^{-3}$. This demonstrates that O_3 pollution was serious during August–September in the PRD region. Meanwhile, the synchronous increase of O_3 and $\text{PM}_{2.5}$ during 20–22 August may be due to the reaction of VOCs.

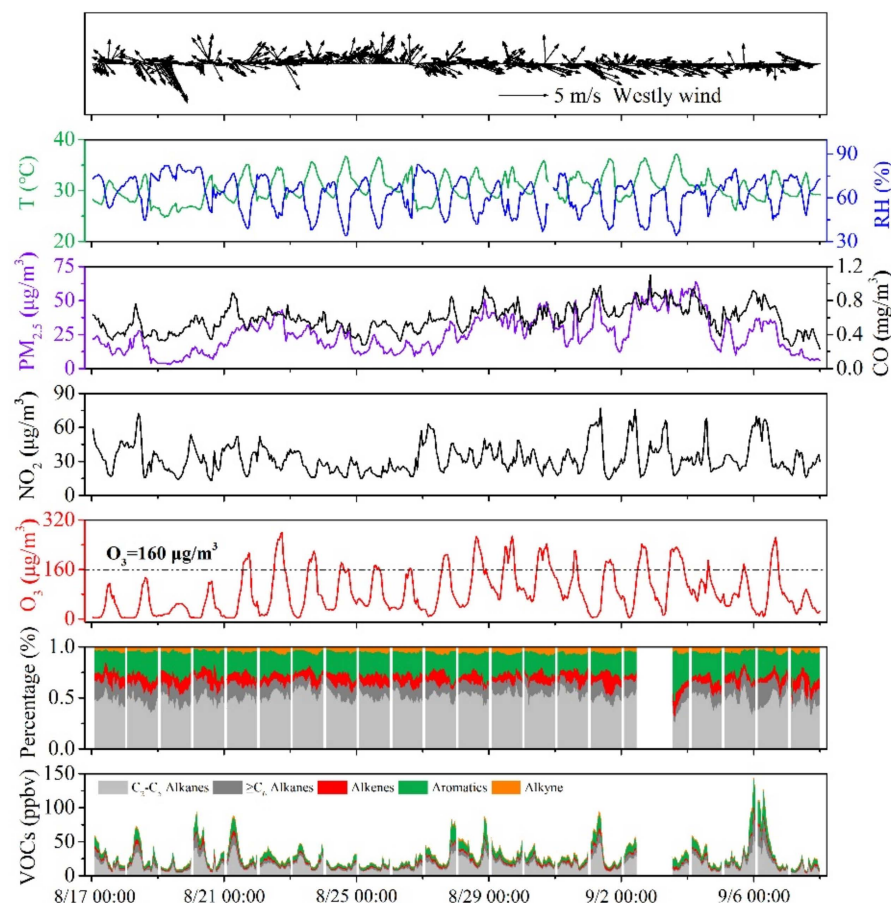


Figure 2. Time series of observed VOCs, O_3 , NO_2 , $\text{PM}_{2.5}$, and meteorological parameters (temperature, humidity, wind speed, wind direction) at PY site during the campaign.

During the campaign, the mixing ratio of VOCs ranged from 6.59 to 144.38 ppbv, averaged as 31.80 ± 20.82 ppbv. C_2 – C_5 alkanes were the most abundant VOC species, with a mean concentration of 15.33 ± 9.66 ppbv, and amounted to 48.2% of the total measured VOCs during sampling (Figure 3). The respective levels of aromatics, $\geq \text{C}_6$

alkanes, alkenes, and alkyne were 7.33 ± 5.76 , 4.60 ± 4.60 , 3.03 ± 1.31 , and 1.51 ± 0.81 ppbv, which contributed 23.0%, 14.5%, 9.5%, and 4.8% of the observed VOCs (Figure 3).

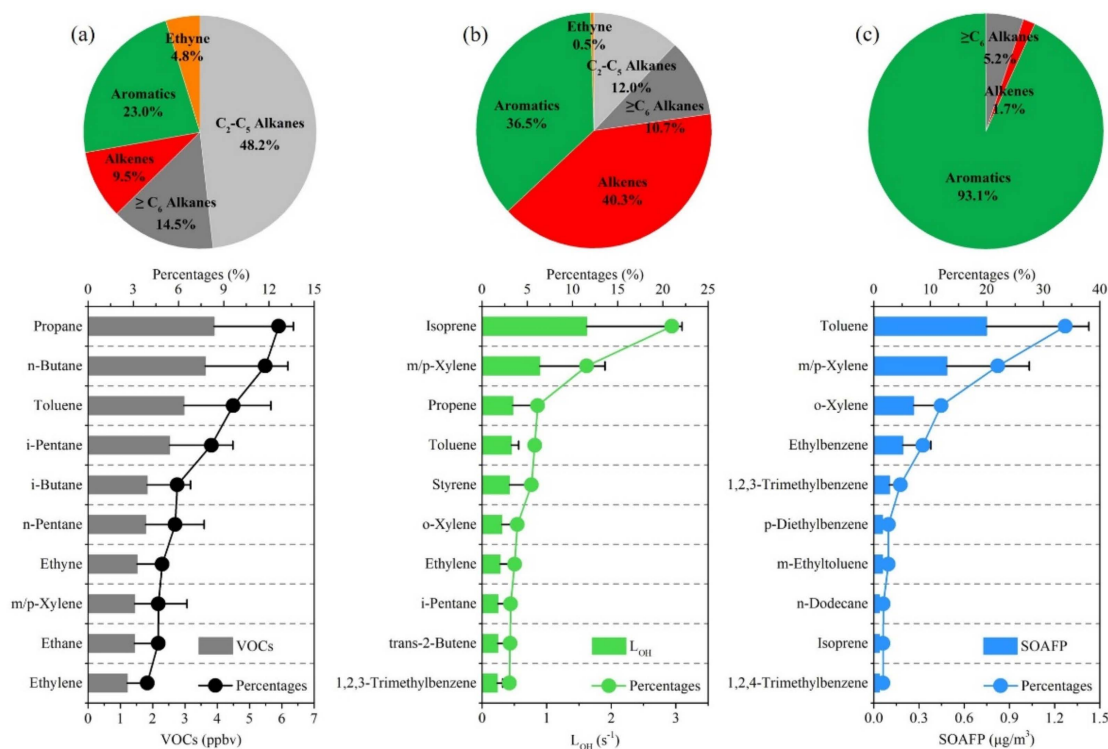


Figure 3. Composition and top ten species of (a) VOCs, (b) L_{OH} , and (c) SOAFP, respectively.

The mixing ratio of VOCs averaged 31.80 ± 20.82 ppbv in this study. Compared with the data reported in other studies from around the world (Table 1), the mixing ratio of VOCs in urban Guangzhou in this study was comparable with previously reported levels in Wuhan, China during January 2016 (32.07 ppbv) and Colorado from March–May 2015 (32.10 ppbv) [56,57], higher than those over Beijing from October–November 2014 (23.41 ppbv), Tianjin from June to August 2018 (14.10 ppbv), Shanghai from January 2007 to March 2010 (25.59 ppbv), and Guilin from May to November 2018 (21.79 ppbv) [58–61], respectively. Furthermore, the mixing ratio of VOCs in the present study were lower than those measured in Paris from January–February 2010 (67.84 ppbv) and Mexico City from November–December 2011 (88.20 ppbv) [62,63], and lower than the 44.54 ppbv recorded in Guangzhou from June 2011 to May 2012 and 41.30 ppbv during April 2013 [44,64], possibly due to the implementation of pollution control strategies in the past five years. The percentage of C₂–C₅ alkanes in the present study is similar to that in Beijing, Tianjin, Liuzhou, Paris, and Mexico City [58,59,62,63,65]. The percentage of alkenes is lower than reported in most other Chinese cities [59,66], while the proportion of aromatic hydrocarbons is higher than in Tianjin, Chengdu, and Colorado [57,59,67]. The difference in the level and composition of VOCs among cities is related to the geographical conditions and the urban energy and industrial structure. In general, the concentration of VOCs in Guangzhou is at a higher level compared to worldwide, as the Panyu site in this study is located in the southern part of urban Guangzhou with higher vehicle emission intensity, and it is also surrounded by industrial cities such as Foshan, Zhongshan, and Dongguan, with more contribution from industry-related emissions.

Table 1. Mixing ratio and composition of VOCs in Guangzhou and comparison of results with those of other studies.

Cities	Periods	VOCs (ppbv)	Percentages (%)					References
			C ₂ –C ₅ Alkanes	≥C ₆ Alkanes	Alkenes	Aromatics	Alkyne	
Beijing	October–November 2014	23.41	45.5%	8.5%	12.0%	21.0%	13.0%	[58]
Tianjin	June–August 2018	14.10	49.6%	0.0%	31.2%	10.6%	8.5%	[59]
Shanghai	January 2007–March 2010	25.59	35.1%	19.4%	7.6%	38.0%	0.0%	[60]
Wuhan	January 2016	32.07	58.7%	-	18.4%	15.2%	7.6%	[56]
Liuzhou	March 2019	22.83	49.3%	6.0%	19.4%	11.2%	14.1%	[65]
Chengdu	October 2016–September 2017	41.70	56.6%	-	19.7%	17.3%	6.5%	[67]
Guilin	May–November 2018	21.79	18.2%	2.6%	4.4%	71.4%	3.4%	[61]
Jiangmen	July–August 2016	8.47	34.6%	8.3%	17.1%	35.1%	5.0%	[66]
Guangzhou	June 2011–May 2012	44.54	38.1%	20.7%	16.5%	24.8%	0.0%	[64]
Guangzhou	April 2013	41.30	38.1%	22.4%	9.4%	24.0%	6.1%	[44]
Paris, French	January–February 2010	67.84	49.4%	2.6%	5.4%	41.6%	1.1%	[62]
Mexico City, Mexico	November–December 2011	88.20	46.7%	12.0%	10.3%	25.4%	5.6%	[63]
Colorado, USA	March–May 2015	32.10	93.8%	3.7%	0.2%	1.7%	0.6%	[57]
Colorado, USA	July–September 2015	46.49	94.0%	3.1%	1.2%	1.3%	0.4%	[57]
Guangzhou	August–September 2020	31.80	48.2%	14.5%	9.5%	23.1%	4.7%	

Propane, n-butane, and toluene were the three highest VOC species, with mixing ratios of 3.90 ± 2.46 ppbv, 3.62 ± 2.57 ppbv, and 2.97 ± 2.70 ppbv, respectively. Other top ten VOC species included i-pentane (2.52 ± 1.96 ppbv), i-butane (1.82 ± 1.35 ppbv), n-pentane (1.78 ± 1.81 ppbv), ethyne (1.51 ± 0.81 ppbv), m/p-xylene (1.44 ± 1.63 ppbv), ethane (1.43 ± 0.73 ppbv), and ethylene (1.21 ± 0.65 ppbv), and the sum of the top ten VOCs contributed 68.9% of the total VOCs. Among the above-mentioned VOCs, propane, i-butane, and n-butaness are the three most prominent species from liquefied petroleum gas (LPG) emission [68], toluene and m/p-xylene are mainly from industrial solvents and vehicle exhaust [37], i-pentane and n-pentane are typical tracers of oil evaporation [69], and ethyne, ethane, and ethylene are mainly obtained from the emissions of various combustion sources [70]. Consequently, VOCs in Guangzhou are closely related to the use of LPG and industrial solvents, vehicle exhaust, oil evaporation, and combustion sources.

3.2. Diurnal Variations in VOCs

Figure 4 shows the diurnal variations in VOCs and their main components (C₂–C₅ alkanes, ≥C₆ alkanes, alkenes, and alkyne). The mixing ratio of VOCs during the night was higher than during the day, with the highest at 8:00 and lowest at 15:00. From 21:00 to 6:00, the concentration of VOCs remained at 30–40 ppbv, then it increased and reached the daily maximum at 8:00 with 44.20 ± 26.92 ppbv. This result clearly indicates the influence of vehicle exhaust emissions during the morning rush hour. After 8:00, with the elevated temperature and planetary boundary layer height, the atmospheric diffusion conditions gradually improve, and more VOCs are consumed due to the occurrence of significant photochemical activity around noon, leading to a continuous decrease in VOCs from 8:00 to 15:00. After 15:00, the mixing ratios of VOCs gradually increased due to poor diffusion conditions and decreased photochemical activity. C₂–C₅ alkanes, ≥C₆ alkanes, aromatics, and alkyne exhibited similar diurnal variation to that of VOCs, with daily maximum and minimum values appearing at 08:00 and 15:00, respectively, and the concentration during the day much lower than at night.

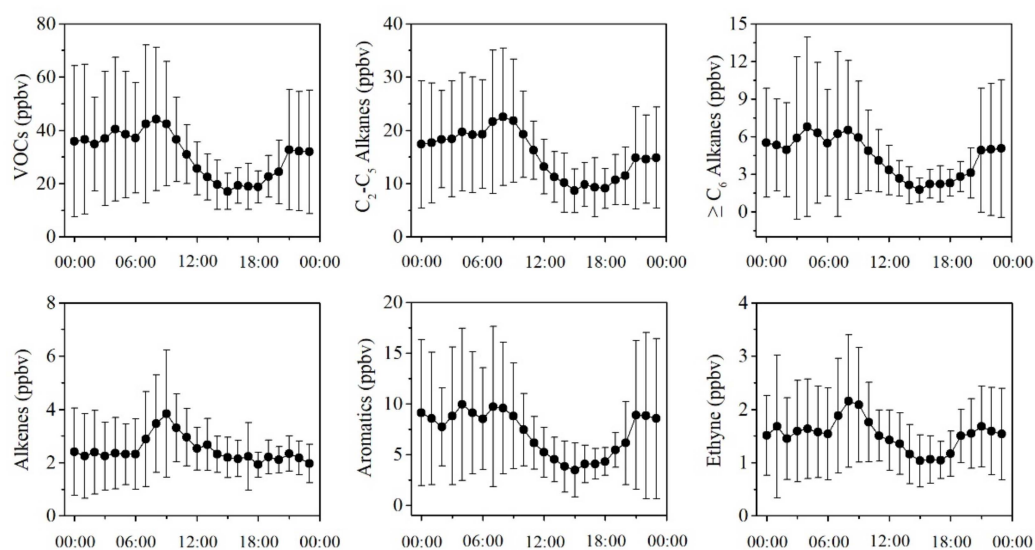


Figure 4. Diurnal variations of VOCs and the main components.

Alkenes exhibited different diurnal patterns compared with VOCs. Owing to the influence of vehicle exhaust emissions during the morning rush hour, the mixing ratio of alkenes increased rapidly from 2.31 ± 1.32 ppbv at 06:00 to 3.84 ± 2.39 ppbv at 09:00, then gradually decreased to 2.53 ± 0.80 ppbv. Except for the period from 6:00 to 12:00, the mixing ratio of alkenes was maintained at 2.00–2.40 ppbv. The photochemical reactivity of alkenes is faster than those of alkanes and aromatics [38]; however, the concentration of alkenes did not decrease around noon, which indicates that there may be more alkene emissions during the day in Guangzhou or nearby regions.

3.3. L_{OH} and SOAFP

VOCs are composed of a variety of species, and their atmospheric reactivity varies significantly. The reactivity of VOCs refers to the ability of VOCs to participate in atmospheric chemical reactions, and the reaction of VOCs with OH radical is the key factor affecting ozone formation in polluted atmosphere [38,71]. Therefore, in this study, the L_{OH} was calculated, and the reactivity of VOC species was identified. Some VOC species are also important precursors of SOA; thus, the SOAFP was calculated and the important VOC species capable of forming SOA were identified.

Figure 5 exhibits the correlation between VOCs and L_{OH} . During the campaign, VOCs were significantly correlated with L_{OH} ($r^2 = 0.87$), and L_{OH} increased with increased VOC mixing ratio. The L_{OH} /VOC ratio was 0.1673, as shown in Figure 5; furthermore, the average OH radical reaction rate constant of VOCs was calculated to be $6.25 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which was higher than that of toluene ($5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [38]. This result indicates that the reactivity of the atmosphere was relatively strong during autumn in Guangzhou; however, it was lower than that of Shanghai during summer ($8.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [72].

L_{OH} ranged from 1.96 to 28.34 s^{-1} during the campaign, with an average L_{OH} of $7.71 \pm 3.73 \text{ s}^{-1}$. Alkenes contributed 40.3% of L_{OH} , followed by aromatics (36.5%), C_2 – C_5 alkanes (12.0%), and $\geq C_6$ alkanes (10.7%) (Figure 3b). Compared with the composition of VOCs, the percentages of alkenes and aromatics increased from 9.5% and 23.0% for VOCs to 40.3% and 36.5% for L_{OH} , respectively. However, the percentages of C_2 – C_5 alkanes and $\geq C_6$ alkanes decreased, from 48.2% and 14.5% for VOCs to 12.0% and 10.7% for L_{OH} , indicating that alkenes and aromatics contributed more to ozone formation; therefore, priority control of reactive alkenes and aromatics is key to ozone pollution control. However, it is noteworthy that 22.7% of total L_{OH} was attributed to alkanes; even though the reactivity was relatively low, emission control of alkanes cannot be ignored.

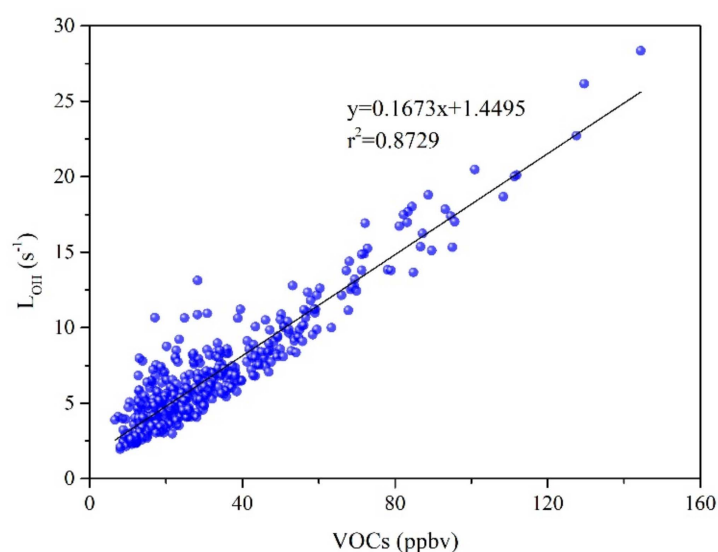


Figure 5. Correlations between mixing ratio of VOCs and L_{OH} .

Interestingly, 21.0% of L_{OH} was attributed to isoprene (Figure 3b), which is a highly reactive species and mainly emitted from plants, with large emissions during summer and autumn when the temperature is higher. m/p-Xylene, propene, and toluene were the top three anthropogenic species that contributed more to L_{OH} , with percentages of 11.6%, 6.1%, and 5.8%, respectively. Other top ten species include styrene (5.5%), o-xylene (3.9%), ethylene (3.6%), i-pentane (3.2%), trans-2-butene (3.1%), and 1,2,3-trimethylbenzene (3.0%). Propane, n-butane, and toluene were the three most abundant VOCs; however, they only contributed 1.5%, 3.0%, and 5.8% of L_{OH} . On the other hand, the percentages of isoprene, m/p-xylene, and propene increased from 1.9%, 4.7%, and 2.2% for VOCs to 21.0%, 11.6%, and 6.1% for L_{OH} , respectively.

The calculated average SOAFP was $2.21 \pm 1.70 \mu\text{g m}^{-3}$ during the campaign. Aromatics contributed up to 93.1% of SOAFP (Figure 3c). The SOAFP of $\geq C_6$ alkanes and isoprene were $0.11 \pm 0.07 \mu\text{g m}^{-3}$ (5.2%) and $0.04 \pm 0.03 \mu\text{g m}^{-3}$ (1.7%), respectively. In addition, the top ten VOCs with the largest contribution to the total SOAFP were aromatic, except for isoprene and n-dodecane. Toluene, m/p-xylene, and o-xylene were the largest contributors to SOAFP, averaged as $0.75 \pm 0.68 \mu\text{g m}^{-3}$ (33.9%), $0.48 \pm 0.55 \mu\text{g m}^{-3}$ (22.0%) and $0.26 \pm 0.20 \mu\text{g m}^{-3}$ (12.0%), respectively (Figure 3c).

3.4. Ratio Analysis

The ratios between different VOCs species have been widely used to assess the sources of VOCs. i-Pentane and n-pentane are the important alkanes. The i-Pentane/n-pentane (i-P/n-P) ratio was 2.4 in a tunnel experiment, and the ratio ranged from 1.5 to 2.6 for gasoline evaporation and 0.5 for diesel evaporation [69,73]. The ratio of i-P/n-P ranged from 0.5 to 3.4, and averaged 1.75 ± 0.6 during the campaign, as shown in Figure 6a, indicating that vehicle exhaust and oil evaporation (including gasoline and diesel evaporation) were responsible for the ambient pentanes. Ethyne is a typical tracer for combustion emissions; therefore, the ratios of VOCs species to ethyne reflected the impact of other sources relative to combustion [41,73]. The ratios of propane/ethyne and i-butane/ethyne were 2.6 ± 0.8 and 1.2 ± 0.5 in the present study, and these values were between the ratios reported in a previous study carried out in a suburban and urban site in Guangzhou in 2009; the ratio of n-butane/ethyne (2.4 ± 1.1) was higher here than in the earlier study [41].

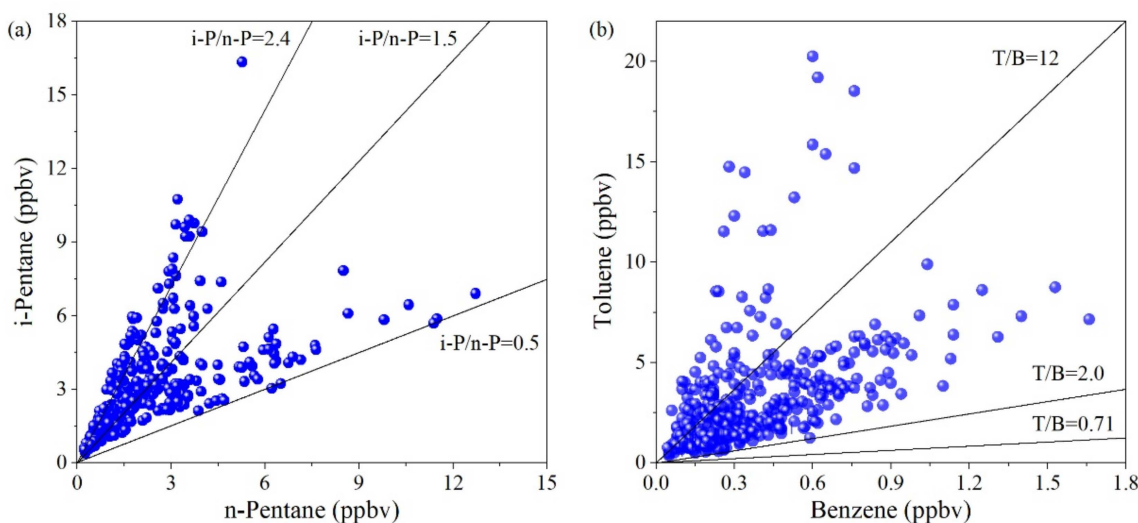


Figure 6. Ratios of (a) i-pentane/n-pentane and (b) toluene/benzene at PY site during campaign.

Benzene is a Group I human carcinogen and its use as an industrial solvent has been banned. Benzene is mainly sourced from combustion sources such as vehicle exhaust and boilers [73,74]. Toluene in ambient air is significantly influenced by both industrial solvent use and vehicle exhaust [73]. Notably, the toluene/benzene (T/B) ratio is widely used to identify the major sources of aromatics. Previous studies have shown that a $T/B < 1.0$ indicates that the main sources of aromatics are biomass and coal burning [75] while 2.0 indicates vehicle emissions and tunnel study [73,76,77], different types of industrial and solvent use emissions have shown a higher T/B ratio [73]. Figure 6b shows that the T/B ratio at the Panyu site ranged from 2.1 to 52.2 and averaged 10.0 ± 7.3 , which indicates the significant impact of industrial solvent emissions. This result is consistent with the results of research carried out in the upwind city of Dongguan, wherein it was reported that a $T/B > 5$ was influenced by industrial solvent emissions [78,79]. Furthermore, benzene is significantly correlated with ethyne, which is the typical tracer of combustion sources, indicating the influence of combustion-related sources on ambient aromatics.

3.5. Source Apportionment with PMF

3.5.1. Source Identification

In this study, PMF was further used to identify the contributing sources of VOCs during the campaign. Thirty-one VOC species with high abundance and typical source tracers were used for PMF. The PMF was operated with a factor number increasing from 4 to 8. When the factor number was 7, the Q (Robust) and Q (True) were converged to 2156.08, and the PMF results well interpreted the measured VOCs, with a slope and r^2 value of 1.01 and 0.99, respectively. Therefore, the seven-factor solution was selected as the best solution from PMF.

The source profiles resolved by PMF are shown in Figure 7. Factor 1 was rich in C_5 – C_7 alkanes; 2,3-dimethylbutane, 3-methylpentane, and 2,3-dimethylpentane were typical tracers of gasoline vehicle exhaust [58]; Higher carbon alkanes and aromatics including 3-methylhexane, 2,2,4-trimethylpentane, and toluene were mainly from diesel vehicle exhaust [76]; thus, factor 1 was considered vehicle exhaust emission. Factor 2 was identified as LPG emission, which is distinguished by a high loading of the LPG tracers propane, i-butane, and n-butane [68]. Factor 3 showed dominance of i-pentane and n-pentane, and was believed to be oil evaporation emission [69]. Factor 4 was industrial solvent use emission, with higher proportions of ethylbenzene, m/p-xylene, and o-xylene; higher toluene to benzene (T/B) ratio was also resolved in factor 4, which is consistent with the influence of solvent use [40]. Factor 5 was regarded as industrial process emission, as it was distinguished by the presence of ethylene, propene, trans-2-butene, trans-2-

pentene, and styrene; while ethylene and propene are important raw materials in chemical production [80], butenes are mainly obtained from process emissions [81], and styrene is one of the raw materials of resin and rubber. Source 6 was recognized as a combustion source, as it is associated with ethyne, ethane, propene, benzene, and some C₆–C₇ alkanes [73], which are markers of coal/biomass combustion. Factor 7 was identified as biogenic emission, as it consisted of a high proportion of isoprene, which is tracer of biogenic emission [82].

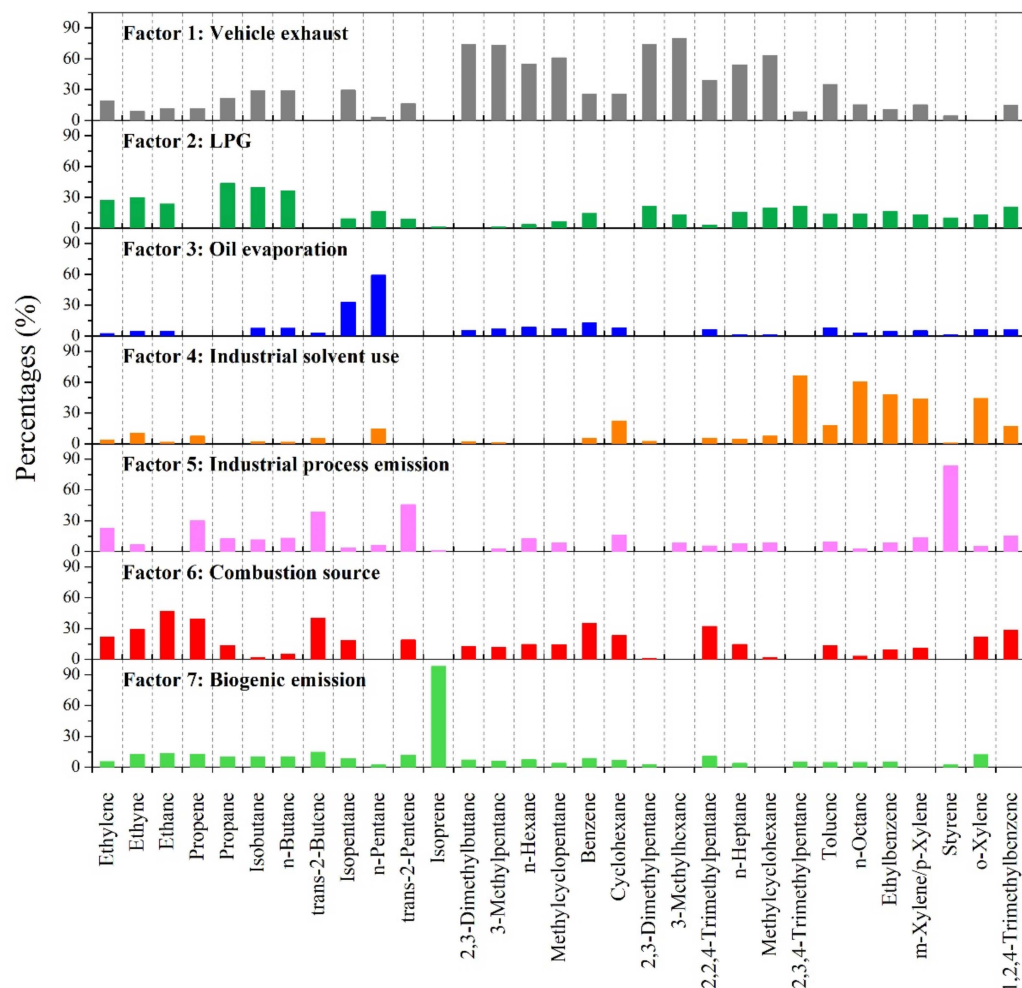


Figure 7. Source profiles of VOCs resolved from PMF.

Based on the PMF results (Figure 8a), vehicle exhaust was the largest source of VOCs, contributing 24.6%, followed by LPG (15.8%), combustion sources (15.4%), industrial solvent use (14.8%), and oil evaporation (11.3%). Industrial process emissions and biogenic emissions contributed 9.7% and 8.4% of VOCs, respectively. Industrial-related sources, including industrial solvent use and industrial process emissions, together contributed 24.5% of VOCs.

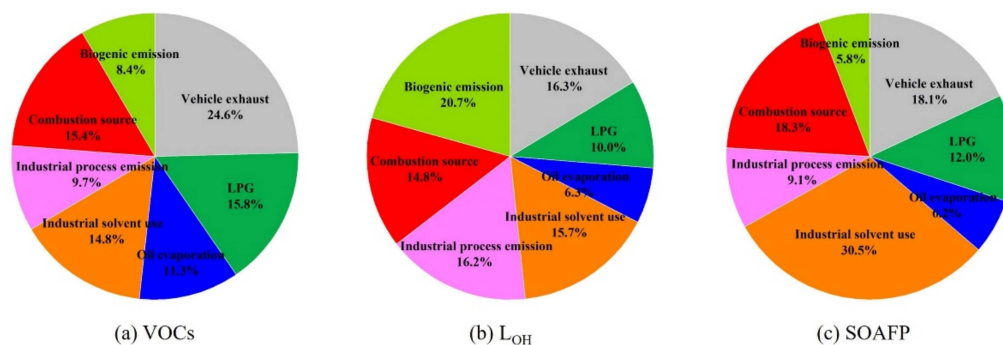


Figure 8. Source contributions of (a) VOCs, (b) L_{OH}, and (c) SOAFP.

3.5.2. Sources of L_{OH} and SOAFP

The contribution of different sources to L_{OH} and SOAFP was further calculated (Figure 8b,c). Surprisingly, biogenic emissions contributed the most to L_{OH} at 20.7%, which was comparable with the percentage of isoprene to L_{OH} (21.0%) shown in Section 3.3. Notably, in this study the ambient samples were collected during August and September, when biogenic emission intensity was the greatest and significantly higher than in other months. Vehicle exhaust was found to be the most important anthropogenic source, contributing 16.3% of L_{OH} (Figure 8b), followed by industrial process emissions (16.2%), industrial solvent use (15.7%), combustion sources (14.8%), LPG (10.0%), and oil evaporation (6.3%). In general, vehicle exhaust emissions dominate L_{OH} in urban cities. For instance, motor vehicle exhaust contributed for 50% and 19.4% of L_{OH} in Pasadena and Wuhan [83,84], respectively, higher than the percentage of vehicle exhaust to L_{OH} reported in the present study. In Houston, vehicle and petrochemical refinery emissions accounted for 42% of L_{OH} [85], similar to the sum of vehicle exhaust and industrial-related emissions in urban Guangzhou (48.2%).

Industrial solvent use, combustion sources, and vehicle exhaust ranked as the first three most important sources of SOAFP, contributing 30.5%, 18.3%, and 18.1%, respectively (Figure 8c), followed by LPG (12.0%) and industrial process emissions (9.1%). Oil evaporation and biogenic emissions contributed a mere 6.2% and 5.8% of SOAFP, respectively. The SOAFP of industrial solvent use in this study is consistent with industrialized Ningbo [86], and also similar with the result that industrial sources contributed most to SOAFP based on emission inventory study [87]. Notably, the contribution of vehicle exhaust emissions to SOAFP was lower than industrial-related sources, probably due to SOAFP being limited in this study to C₂–C₁₂ nonmethane hydrocarbons (NMHCs). Moreover, chamber simulations revealed that intermediate-volatility organic compounds (IVOCs), in particular those emitted from diesel vehicles, act as important precursors for SOA [88,89].

In summary, vehicle exhaust was found to be the largest source of VOCs. However, industry-related sources (including industrial solvent use and industrial process emissions) had the largest contribution to L_{OH} and SOAFP, followed by vehicle exhaust and combustion sources. Therefore, strengthening emission control based on reactivity instead of concentration should be considered in future policies.

3.6. Emission Regions of Different Sources

Furthermore, the emission region of different sources was analyzed by combining the wind direction and wind speed. This type of analysis can help to clarify source areas and transmission channels for future accurate control of different VOC sources (Figure 9).

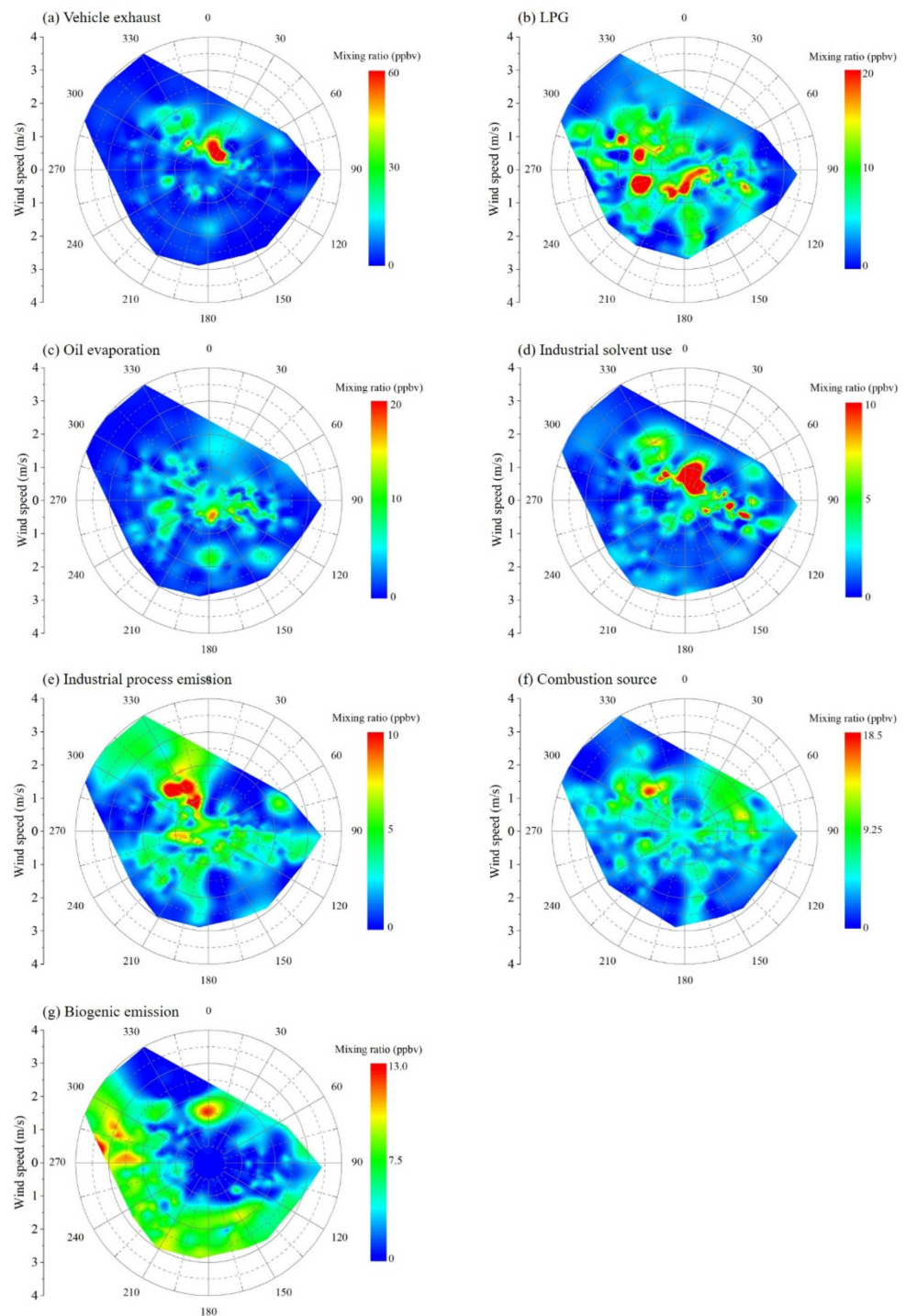


Figure 9. The distributions of mixing ratio of each source in wind direction and speed.

The hotspot of vehicle exhaust emissions was mainly concentrated in the northerly direction with wind speed $<1 \text{ m s}^{-1}$, possibly related to vehicle exhaust emission in central urban areas of Guangzhou and Panyu district under northerly winds. There were two peaks for LPG emission in the west–southwest and west–northwest with wind speed of 1.5 m s^{-1} , as well as a strip southeast of the Panyu site. For oil evaporation, the hotspot was concentrated in a southern direction with low wind speed ($<0.5 \text{ m s}^{-1}$). Similar to vehicle exhaust, industrial solvent use emissions were mainly centered on the north–northeast region with wind speed $<1 \text{ m s}^{-1}$, and several hotspots were also observed with relatively high wind speed ($2\text{--}3 \text{ m s}^{-1}$), indicating transport from other cities such

as Dongguan and Foshan, the most important manufacturing centers of furniture and commodity products in the PRD region. The industrial process emissions region was distributed in the northwest with wind speed of $0.5\text{--}2\text{ m s}^{-1}$, indicating the joint influence of local emissions and regional transport in the northwest. A hotspot was observed in the northwest for combustion sources. Different from other sources, biogenic emissions were distributed in multiple directions with high wind speed, and mainly emitted from the surrounding forest-covered areas.

4. Conclusions

To explore the reactive VOC species and identify the major sources of VOCs, LOH , SOAFP, and corresponding emission regions in the urban PRD during severe ozone pollution, the ambient VOCs were monitored with a high-resolution online system in central PRD (PY site) from August to September 2020. The results showed that the average mixing ratio of VOCs during the campaign was (31.80 ± 20.82) ppbv. Furthermore, $\text{C}_2\text{--C}_5$ alkanes, aromatics, $\geq \text{C}_6$ alkanes, alkenes, and alkyne contributed 48.2%, 23.0%, 14.5%, 9.5%, and 4.8% of the measured VOCs, respectively; propane, n-butane and toluene were the three most abundant VOC species.

The chemical reactivity of VOCs in Guangzhou was equivalent to that of toluene, with calculated average OH radical reaction rate constants of VOCs of $6.25 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Alkenes and aromatics showed the highest contribution to LOH , and the key active anthropogenic compounds were m/p-xylene, propene, and toluene. Aromatics attributed 93.1% of SOAFP, and toluene, m/p-xylene, o-xylene, ethylbenzene, and 1,2,3-trimethylbenzene were the most abundant species. Consequently, priority control of reactive alkenes and aromatics is key to ozone and $\text{PM}_{2.5}$ pollution prevention and control.

The sources of VOCs were investigated using PMF. Vehicle exhaust, LPG, and combustion emission were three most important sources at the PY site, accounting for 24.6%, 15.8%, and 15.4% of observed VOCs, followed by industrial solvent use (14.8%), oil evaporation (11.3%), industrial process emissions (9.7%), and biogenic emissions (8.4%), respectively. Moreover, the LOH and SOAFP were mostly contributed by industry-related sources (including industrial solvent use and industrial process emissions), vehicle exhaust, and combustion sources, indicating that control of industry-related sources and vehicle exhaust emissions are key to reducing the chemical reactivity of VOCs in Guangzhou. The transport channels and emission regions of different sources were further identified by combining source contribution with wind direction and wind speed, and different hotspot areas for different sources were explored. Based on high resolution observed VOC data, this study demonstrated the key reactive VOC species and identified the major sources and corresponding emission regions. It is thus of benefit for the accurate emission control of VOCs in the PRD region, and aids in the formulation of an emission control strategy for VOCs in similar cities around the world.

Author Contributions: Investigation, C.L., J.L. and Y.Z. (Yongbo Zhang); Methodology, W.Y.; data analysis and curation, Q.Y., J.Z., X.Q. and T.Z.; writing—original draft preparation, W.Y.; writing—review and editing, C.P., Y.Z. (Yanli Zhang) and X.W.; discussion of the results, C.L., J.L., Y.Z. (Yanli Zhang) and Y.Z. (Yongbo Zhang). All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (Grant No. 41907196), Key-Area Research and Development Program of Guangdong Province (Grant No. 2020B1111360003), State Key Laboratory of Organic Geochemistry, GIGCAS (Grant No. SKLOG202003), and the Director's Fund of Guangzhou Institute of Geochemistry, CAS (2019SZJJ-04).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available upon request on the official website of Department of Guangzhou Sub-branch of Guangdong Ecological and Environmental Monitoring Center.

Acknowledgments: We would like to express our immense gratitude to the reviewers and editors who have contributed valuable comments that helped us to improve the quality of the paper.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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