



Non-methane Hydrocarbons and Their Ozone Formation Potentials in Foshan, China

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ABSTRACT

Concentrations of non-methane hydrocarbons (NMHCs) were measured to investigate their temporal variations and major sources, and to explore the ozone formation potentials (OFP) of each NMHCs for the first time in December 2008 in Foshan. Ethane, propane, *n*-butane, *i*-pentane, 2,3-dimethylbutane, ethene, propene, ethyne, benzene and toluene were the 10 most abundant hydrocarbons, accounting for 82% of the concentration of total NMHCs. Concentrations of these hydrocarbons as well as their fractional contributions to the total NMHCs were higher in the morning and evening than in the afternoon, consistent with the variations in vehicle volumes during these periods. This suggests that the vehicular emission was likely the major source of NMHCs at this site. The mean B/T ratio (0.45 ± 0.24) further supported vehicular emission as the main source of the ambient NMHCs except for aromatic hydrocarbons. These aromatic hydrocarbons were mainly from solvent evaporation, as indicated by the diurnal variations in the ratios of toluene and *m/p*-xylene to benzene. The results from factor analysis also showed that combustion process and solvent usage were the major sources of NMHCs. On average, total Prop-Equiv and OFP were 153.0 ppbc and 863.4 $\mu\text{g}/\text{m}^3$, respectively. Based on MIR (maximum incremental reactivity) scale, the leading contributors to OFP in decreasing concentrations were ethene, toluene, propene, *i*-pentane, *m/p*-xylene, 1-butene, ethylbenzene, *o*-xylene, 2,3-dimethylbutane and *trans*-2-butene, which in total explained 77% of the total OFP. Ranking by Prop-Equiv, the top 10 species were propene, toluene, ethene, 1-butene, *i*-pentane, *m/p*-xylene, isoprene, 2,3-dimethylbutane, *trans*-2-butene and ethylbenzene, accounting for 66% of the total Prop-Equiv. Thus, alkenes played the most important role in O₃ formation, followed by aromatics and alkanes during the study periods in Foshan.

Keywords: Non-methane hydrocarbons; Vehicular emission; Solvent evaporation; Ozone formation potential; Foshan.

INTRODUCTION

Foshan is one of the most populated areas in Pearl River Delta (PRD) in south China. It is also one of the largest manufacturing bases in the world. Accompanying with the substantial economic development, large amounts of air pollutants were emitted into the atmosphere, which leads to a rapid deterioration of air quality in and around the area.

Air pollutants including ozone (O₃), sulfur dioxide (SO₂) and nitric oxides (NO_x) in Foshan frequently exceeded the National Ambient Air Quality Standard (NAAQS). Among these pollutants, O₃ is often the most concerned species due to its adverse effect on human health (Lai *et al.*, 2009; Shao *et al.*, 2009; Hwang *et al.*, 2011).

Currently, the major environmental problems in Foshan include photochemical smog, haze pollution and acid deposition (GDEM, 2008), among which photochemical smog is characterized by high concentrations of O₃ and fine particles in urban areas. O₃ is not emitted directly; instead, it is formed from photochemical reactions involving volatile organic compounds (VOCs) and NO_x (Duan *et al.*, 2008;

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Han *et al.*, 2011). Non-methane hydrocarbons (NMHCs), a major group of atmospheric VOCs and the key O₃-producing precursors through OH radical initiated oxidation and subsequent reactions with NO_x (Atkinson, 1997, 2000; Tang *et al.*, 2007), are known to be released into the atmosphere by a variety of natural and anthropogenic sources (Sharma *et al.*, 2000). Their sources in urban air are often dominated by anthropogenic emissions such as vehicular emission, industrial emission, evaporative emission, liquefied petroleum gas (LPG) and natural gas (NG) leakages (Barletta *et al.*, 2005; Tang *et al.*, 2007; Duan *et al.*, 2008). In urban area where NMHCs concentrations are high, OH radicals attack on the various NMHCs plays a critical role in atmospheric photochemical reaction cycle (Blake *et al.*, 1992; Sharma *et al.*, 2000; Offenberger *et al.*, 2011).

Several field studies on atmospheric NMHCs in PRD region have been conducted and provided valuable information in understanding the NMHCs (Wang *et al.*, 2002; Wang *et al.*, 2005; Tang *et al.*, 2007; Shao *et al.*, 2009). It was found that under favorable meteorological conditions, high concentrations of NMHCs can be prone to form elevated O₃ level, and the O₃ level in PRD can easily surpass 150 ppbv in normal days and even 200–300 ppbv in heavy pollution episodes (Lai *et al.*, 2009). Recently, photochemical smog pollution in PRD region is becoming worse than before (Shao *et al.*, 2009), and air pollution episodes have often occurred in the region, especially in the winter time (Tan *et al.*, 2009). Therefore, the diagnosis of the O₃ problem and the further containment of the O₃ level in PRD require the knowledge of the sources, speciation and abundance of main O₃ precursors (Lai *et al.*, 2009).

Foshan is the most polluted city in the PRD (GDEMC, 2008); however, until now, little is known on concentration and speciation of VOCs including NMHCs in the city. Such data are thus essential for a better understanding of O₃ formation in PRD region. The aim of this study is to investigate the NMHCs levels, their sources and O₃ formation potentials in Foshan.

METHODS

Sample Collection

The sampling site was located in Foshan Environmental Monitoring Station (a 10-storey building) (Fig. 1). This station is situated in the urban center of Foshan, which is surrounded by four main roads, residential buildings and business offices. There are two main roads (Fenjiang Road and Lujin Road) near the station. The third (Kuiqi Road) and fourth (Linnan road) roads are 900 m and 1400 m away from the sampling site.

Air samples were collected in the morning (08:00–08:05), afternoon (14:00–14:05) and evening (20:00–20:05) on 6–8th, 10–13th and 27–31st December 2008 (typical wintertime in Foshan) and temperature and wind speed during the winter sampling days in Foshan was illustrated in Table 1. The NMHCs were collected with stainless steel canisters (Polar Ware Company, USA) (Wang *et al.*, 2002; Duan *et al.*, 2008). All canisters were pre-cleaned 5 times using ultra-pure N₂ (> 99.999%) and then pre-evacuated by a canister cleaner (Entech Instruments Inc, Model 3100) before sampling. Sampling and analysis followed the US EPA Compendium Method TO-14A (US EPA, 1997). A flow-controlling valve was used to collect 5 min integrated sample by slightly opening the valve. Sampling inlet was placed at about 1.5 m above the rooftop of the building, through which air was drawn by opening the valve.

Sample Analysis

Forty NMHCs (including alkanes, alkenes and aromatic hydrocarbons) were measured in each sample. The analytical details were reported in previous studies (Wang *et al.*, 2002; Lü *et al.*, 2006; Duan *et al.*, 2008). Briefly, samples were concentrated in the Model 7100 preconcentrator (Entech Instruments Inc., California, USA) and then injected into an HP6890 gas chromatography coupled with an HP5973 mass-selective detector (GC/MSD). A RESTEK RTX-1 capillary column (60 m × 0.32 mm × 1.0 μm) was used in

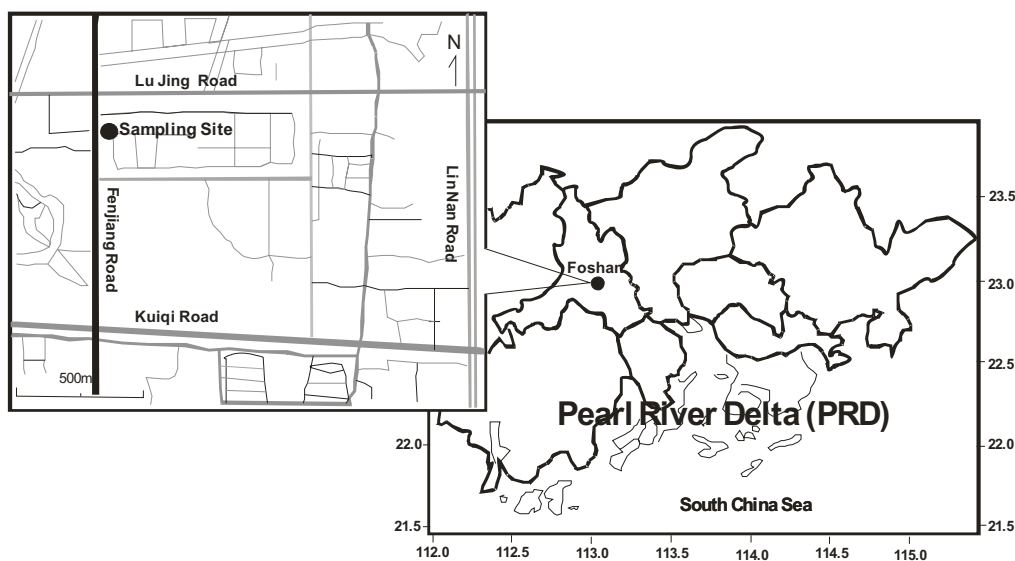


Fig. 1. Location of the sampling site in Foshan, China.

Table 1. Temperature and wind speed during the winter sampling periods in Foshan.

date	Temperature(°C)			Wind speed(m/s)		
	Morning	Afternoon	Evening	Morning	Afternoon	Evening
12-6	11.7	18.0	13.0	3.5	4.0	1.5
12-7	10.5	20.5	12.5	1.0	1.0	1.0
12-8	14.0	22.0	16.0	3.0	5.0	2.0
12-9	12.5	24.0	17.0	1.0	1.0	1.0
12-10	14.5	25.5	16.0	1.0	1.0	0.2
12-11	16.0	22.5	20.0	0.2	1.5	1.5
12-12	16.3	26.0	21.0	0.5	4.0	1.8
12-13	15.0	16.0	15.3	0.3	1.5	0.5
12-14	15.3	18.0	17.0	2.0	0.5	0.1
12-15	15.1	16.0	15.0	5.5	6.0	3.5
12-16	13.0	17.0	14.7	6.0	6.3	6.0
12-17	10.0	15.6	14.0	6.5	7.0	5.0

the system. The column temperature was initially held at 40°C for 2 min, then programmed at a rate of 6 °C/min to 230°C, and isothermally held for 5 min. Compounds were identified by their retention times and mass spectra. Standard gas mixtures (1.0 ppm, Supelco To-14 Calibration Mix) were first dynamically diluted with zero air, then sampled and analyzed using identical conditions to those for the field samples, and seven-point calibration (0.0, 1.0, 5.0, 10.0, 20.0, 40.0, 50.0 ppbv) was performed. The detection limits of our method for all compounds were < 0.2 ppb.

RESULTS AND DISCUSSION

Concentration Levels

The statistics of concentrations of forty NMHCs (including alkanes, alkenes and aromatic hydrocarbons) were listed in Table 2. The concentrations of total NMHCs ranged from 64.0 to 320.7 ppbv, with an average of 145.0 ± 67.8 ppbv. Alkanes were the most abundant NMHCs species, contributing 48% to total NMHCs mass, followed by alkenes (38%) and aromatic hydrocarbons (14%). Of all these NMHCs, ethane, propane, *n*-butane, *i*-pentane, 2,3-dimethylbutane, ethene, propene, ethyne, benzene and toluene were the 10 most abundant species, accounting for 82% of total NMHCs mass. Their mean concentrations descended in the order: ethyne > ethene > ethane > *i*-pentane ≈ propane > toluene > propene > 2,3-dimethylbutane > benzene > *n*-butane.

Fig. 2 showed the concentration levels of the measured hydrocarbons from different regions including Foshan. The concentrations of the most abundant hydrocarbons were much higher in Foshan than those in other regions. For example, the mean level of ethane (18.5 ppbv) in Foshan exceeded the upper end of hydrocarbons range (3.7–17.0 ppbv) measured in the 43 Chinese cities and toluene (11.0 ppbv) was at the upper of the range (0.4–11.2 ppbv) (Barletta *et al.*, 2005).

Diurnal Variations

As shown in Table 2, the concentrations of most hydrocarbons were high in the morning, decreased in the afternoon, and then increased to the high values in the

evening. For instance, ethyne decreased by 40% from morning to afternoon, and then increased by 60% from afternoon to evening. This diurnal variation trends have also been observed for hydrocarbons in Guangzhou (Tang *et al.*, 2007).

The diurnal variations corresponded with the traffic volumes, which are higher in the morning and evening, suggesting that the main sources of these hydrocarbons were vehicular emission. One of the potential reasons for the lowest levels of these hydrocarbons in the afternoon was the reaction with OH, which reaches its peak due to the highest solar radiation (Tang *et al.*, 2007). Another reason is the enhanced dispersion of air pollutants due to elevated planetary boundary layer (PBL) and increased average wind speed (e.g., 3.2 m/s in the afternoon compared to 2.5 m/s in the morning and 2.0 m/s in the evening) (Table 1).

In contrary, *i*-pentane exhibited a completely different diurnal variation trend from that of the other more abundant hydrocarbons, with the highest levels occurring in the afternoon (Table 2). This implies that its major source is not vehicular exhaust. Barletta *et al.* (2005) indicated that a major source of *i*-pentane is gasoline evaporation. Its higher level in the afternoon implied the contributions of solvent evaporation to ambient hydrocarbons. Given the higher average temperature in the afternoon than in the morning and evening by ~5°C during the sampling periods (Table 1), favoring the solvent evaporation.

In general, diurnal variations of the fractions of the most abundant hydrocarbons to total NMHCs (Fig. 3) were similar to the diurnal variations of their atmospheric concentrations (Table 2). An exception is the propane, whose contribution to the total NMHCs was higher in the afternoon than in the morning and evening, clearly differing from its diurnal concentration variation. This pointed to a major additional source, the LPG leakage (Tang *et al.*, 2007). In the early 2008, there were over 650000 taxis and cars in Foshan (<http://fs.pcauto.com.cn/focus>) and LPG-fueled vehicles have been promoted since 2005, which accounted for ≥ 65% of the total of number taxis and cars. It was reported propane was generally associated with LPG leakage in PRD (Tang *et al.*, 2007). Therefore, the observed different diurnal variations between the absolute and relative concentrations for propane were likely due to LPG leakage in Foshan.

Vehicular and Evaporative Emissions

Generally, alkenes and alkynes are characteristic products of internal combustion engines. Alkanes are emitted from evaporative emission and LPG leakage, and aromatic hydrocarbons are emitted by fuel combustion and evaporation

of fuels and solvents (Cheng *et al.*, 2001; Na *et al.*, 2001, 2003; Tang *et al.*, 2007). In urban environments, vehicular emission is by far the most important combustion source (Watson *et al.*, 2001), and ethyne was used extensively as a tracer for vehicular exhaust in urban air (Tang *et al.*, 2007).

Table 2. Statistics of concentrations (ppbv) of NMCHs in Foshan.

	A.M. \pm S.D. ^a			Min. ^b	Max. ^b	A.M. \pm S.D. ^c Average
	Morning	Afternoon	Evening			
<i>Alkanes</i>						
Ethane	18.54 \pm 12.40	16.36 \pm 8.94	20.65 \pm 9.92	7.36	47.22	18.52 \pm 10.37
Propane	13.67 \pm 4.91	11.25 \pm 3.15	14.03 \pm 4.71	8.22	24.71	12.98 \pm 4.39
<i>i</i> -Butane	3.23 \pm 2.07	2.36 \pm 1.02	3.47 \pm 1.74	0.99	8.48	3.02 \pm 1.69
<i>n</i> -Butane	4.47 \pm 3.41	2.91 \pm 1.81	3.91 \pm 1.61	1.33	14.00	3.76 \pm 2.44
<i>i</i> -Pentane	10.51 \pm 8.56	16.16 \pm 11.68	12.54 \pm 11.61	0.86	43.37	13.07 \pm 10.67
<i>n</i> -Pentane	1.20 \pm 0.98	0.73 \pm 0.47	1.39 \pm 0.89	0.14	4.05	1.11 \pm 0.83
Cyclopentane	0.25 \pm 0.17	0.20 \pm 0.11	0.27 \pm 0.16	0.03	0.56	0.24 \pm 0.15
2,3-Dimethylbutane	4.47 \pm 3.76	3.47 \pm 1.56	4.69 \pm 2.87	0.80	14.64	4.21 \pm 2.84
3-Methylpentane	0.99 \pm 0.69	0.68 \pm 0.34	1.29 \pm 0.80	0.18	2.94	0.99 \pm 0.67
<i>n</i> -Hexane	2.43 \pm 1.77	2.64 \pm 4.46	2.54 \pm 3.19	0.23	16.26	2.54 \pm 3.23
2,3-Dimethylpentane	3.16 \pm 4.53	0.85 \pm 0.73	2.71 \pm 2.44	0.15	13.15	2.24 \pm 3.08
Methylcyclopentane	0.30 \pm 0.23	0.18 \pm 0.14	0.49 \pm 0.34	0.05	1.30	0.32 \pm 0.27
2,4-Dimethylpentane	0.30 \pm 0.30	0.15 \pm 0.10	0.38 \pm 0.23	0.06	1.07	0.28 \pm 0.24
Cyclohexane	0.33 \pm 0.31	0.21 \pm 0.16	1.50 \pm 3.73	0.06	13.28	0.68 \pm 2.18
2-Methylhexane	0.67 \pm 0.98	0.21 \pm 0.13	0.57 \pm 0.48	0.06	3.16	0.48 \pm 0.65
3-Methylhexane	0.15 \pm 0.09	0.13 \pm 0.06	0.19 \pm 0.10	0.02	0.37	0.15 \pm 0.09
2,2,4-Trimethylpentane	1.16 \pm 1.80	0.27 \pm 0.35	1.40 \pm 1.85	0.02	6.24	0.94 \pm 1.54
<i>n</i> -Heptane	1.23 \pm 1.71	0.43 \pm 0.39	1.55 \pm 1.91	0.09	6.02	1.07 \pm 1.53
Methylcyclohexane	0.48 \pm 0.52	0.22 \pm 0.18	0.81 \pm 1.22	0.05	4.53	0.50 \pm 0.79
2-Methylheptane	0.35 \pm 0.36	0.16 \pm 0.10	0.40 \pm 0.39	0.04	1.36	0.30 \pm 0.32
3-Methylheptane	0.25 \pm 0.26	0.12 \pm 0.05	0.31 \pm 0.24	0.04	0.93	0.23 \pm 0.22
<i>n</i> -Octane	1.28 \pm 1.65	0.71 \pm 0.84	1.95 \pm 2.16	0.04	7.01	1.31 \pm 1.68
<i>Alkenes</i>						
Ethene	20.41 \pm 11.85	18.56 \pm 6.02	22.76 \pm 9.17	7.26	52.64	20.58 \pm 9.22
Propene	8.08 \pm 5.05	4.36 \pm 2.29	8.07 \pm 3.47	1.98	20.20	6.84 \pm 4.07
<i>l</i> -Butene	2.04 \pm 1.35	1.33 \pm 0.76	2.44 \pm 1.64	0.46	6.10	1.93 \pm 1.35
<i>trans</i> -2-Butene	0.66 \pm 0.61	0.32 \pm 0.16	0.87 \pm 0.55	0.12	2.08	0.62 \pm 0.52
<i>cis</i> -2-Butene	0.49 \pm 0.41	0.26 \pm 0.10	0.65 \pm 0.41	0.12	1.50	0.47 \pm 0.37
<i>l</i> -Pentene	0.67 \pm 0.21	0.66 \pm 1.41	0.74 \pm 0.82	0.09	5.05	0.69 \pm 0.92
Isoprene	0.30 \pm 0.20	0.32 \pm 0.14	0.45 \pm 0.21	0.06	0.81	0.36 \pm 0.19
<i>trans</i> -2-Pentene	0.35 \pm 0.30	0.15 \pm 0.08	0.36 \pm 0.26	0.03	0.90	0.29 \pm 0.25
<i>cis</i> -2-Pentene	0.26 \pm 0.11	0.21 \pm 0.11	0.32 \pm 0.15	0.08	0.56	0.26 \pm 0.13
<i>l</i> -Hexene	0.44 \pm 0.20	0.46 \pm 0.29	0.48 \pm 0.24	0.11	0.99	0.46 \pm 0.24
Ethyne	26.48 \pm 15.04	16.69 \pm 10.25	26.96 \pm 14.16	7.03	64.10	23.38 \pm 13.79
<i>Aromatic hydrocarbons</i>						
Benzene	3.50 \pm 2.38	3.17 \pm 2.42	5.48 \pm 3.51	1.01	13.84	4.05 \pm 2.93
Toluene	11.54 \pm 11.61	6.58 \pm 5.53	14.82 \pm 13.29	1.40	49.03	10.98 \pm 10.92
Ethylbenzene	2.92 \pm 4.53	1.17 \pm 1.40	3.23 \pm 3.66	0.21	12.73	2.44 \pm 3.48
<i>m/p</i> -Xylene (average)	1.52 \pm 2.08	0.69 \pm 1.05	1.94 \pm 1.90	0.13	5.97	1.38 \pm 1.77
Styrene	0.25 \pm 0.31	0.12 \pm 0.16	0.45 \pm 0.45	0.02	1.53	0.27 \pm 0.35
<i>o</i> -Xylene	0.94 \pm 1.40	0.37 \pm 0.47	1.01 \pm 1.07	0.06	4.31	0.77 \pm 1.06
1,2,4-Trimethylbenzene	0.33 \pm 0.40	0.12 \pm 0.15	0.30 \pm 0.24	0.03	1.28	0.25 \pm 0.29
Total NMHCs ^d	150.59 \pm 71.77	115.96 \pm 47.95	168.38 \pm 75.05	64.02	320.74	144.98 \pm 67.82

^a The arithmetic mean (A.M.) and standard deviation (S.D.) of measured hydrocarbons during same sampling duration (referring to morning, afternoon and evening).

^b Minimum (Min.) or maximum (Max.) values of measured hydrocarbons during sampling periods.

^c The arithmetic mean and standard deviation for all samples during sampling periods.

^d Total NMHCs was equal to sum of concentrations of the listed compounds in this Table.

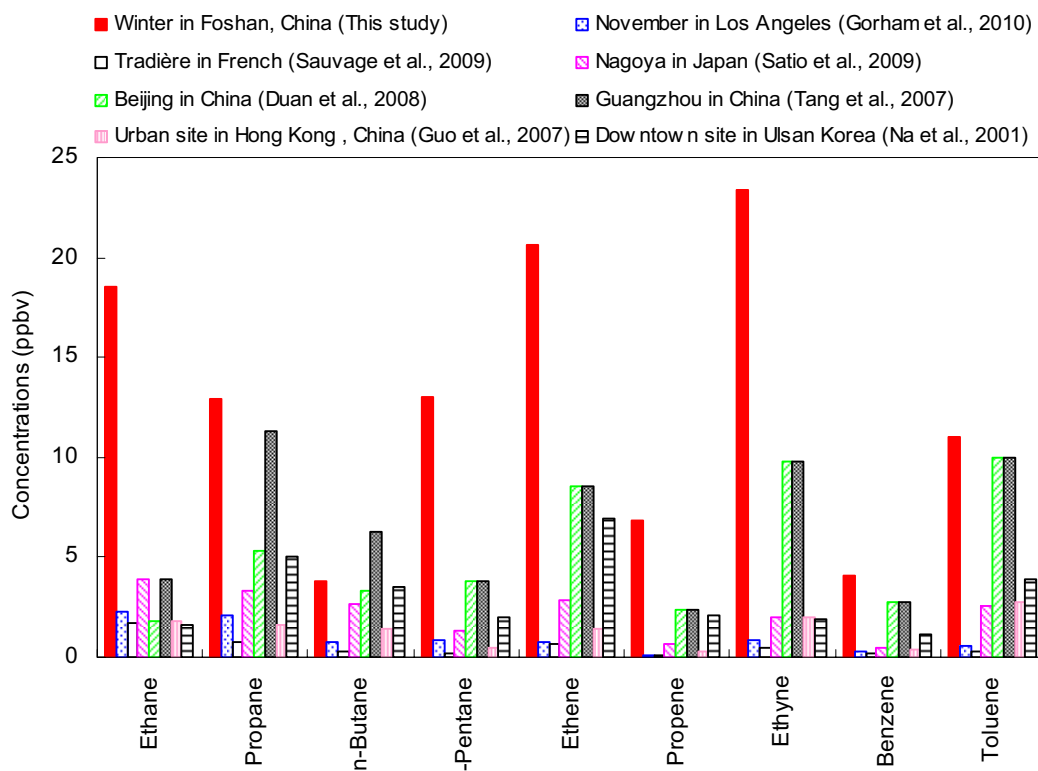


Fig. 2. Comparison of selected abundant NMHCs during winter in Foshan with those in other regions.

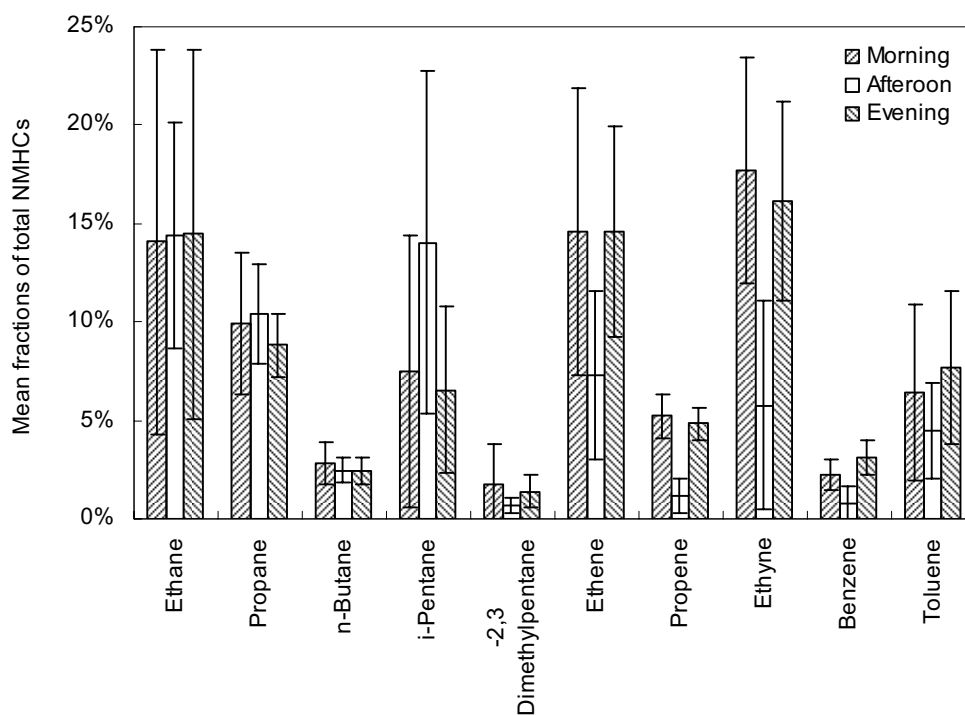


Fig. 3. Mean fractions of total NMHCs for abundant hydrocarbons during sampling periods in Foshan.

The high level of ethyne (23.5 ± 13.8 ppbv) was observed in Foshan, supporting a high contribution of vehicular emission to ambient hydrocarbons. To assess the impact of vehicular emission on NMHCs levels, the benzene to toluene ratio (B/T) is calculated. The B/T ratio of ~ 0.5 (wt/wt) has been

reported to be characteristic of vehicular emission (Perry and Gee, 1995; Brocco *et al.*, 1997), and the higher B/T ratio had been reported for burning of biofuel, charcoal and coal (Andreae and Merlet, 2001; Moreira dos Santos *et al.*, 2004). In this study, the measured mean B/T ratios were $0.43 \pm$

0.24 in the morning, 0.48 ± 0.28 in the afternoon, 0.45 ± 0.31 in the evening, and 0.45 ± 0.24 during the whole sampling periods. These B/T data were very close to the value (0.5) measured in traffic related cities in China by Barletta *et al.* (2005), which provides further evidence that vehicular emission was the main source of ambient total NMHCs in Foshan.

Solvent usage is another potential source for hydrocarbon emissions, which include paint application, printing processes, dry cleaning, solvent evaporation from household products and other industrial processes (Yuan *et al.*, 2010). Toluene and *m/p*-xylene can be released from solvent usage as well as vehicular emission (Na *et al.*, 2003). However, benzene is usually present in vehicular emission but not in solvent evaporation. Thus the ambient toluene/benzene and *m/p*-xylene/benzene concentration ratios can be considered as a reliable marker for solvent usage (Na *et al.*, 2001, 2003).

To examine the effect of solvent use on the ambient hydrocarbons, diurnal variations of the concentration ratios of toluene and *m/p*-xylene to benzene were plotted in Fig. 4. A decreasing ratios from morning to afternoon suggested that the contribution of the solvent evaporative emission to the ambient hydrocarbon decreases from the morning to afternoon. The toluene/benzene and *m/p*-xylene/benzene ratios (Fig. 4) in the afternoon were observed at the lower ranges of the values between the morning and the evening, and their total mean ratios were lower than that in the morning and the evening, respectively. This suggests that the contribution of solvent evaporative emission in the afternoon was lower than that in the morning and evening.

Factor analysis for NMHCs in Foshan city in winter of 2008 was investigated in morning, afternoon and evening, separately (Table 3). The details of PCA receptor model have been reported elsewhere (Duan *et al.*, 2008). In the

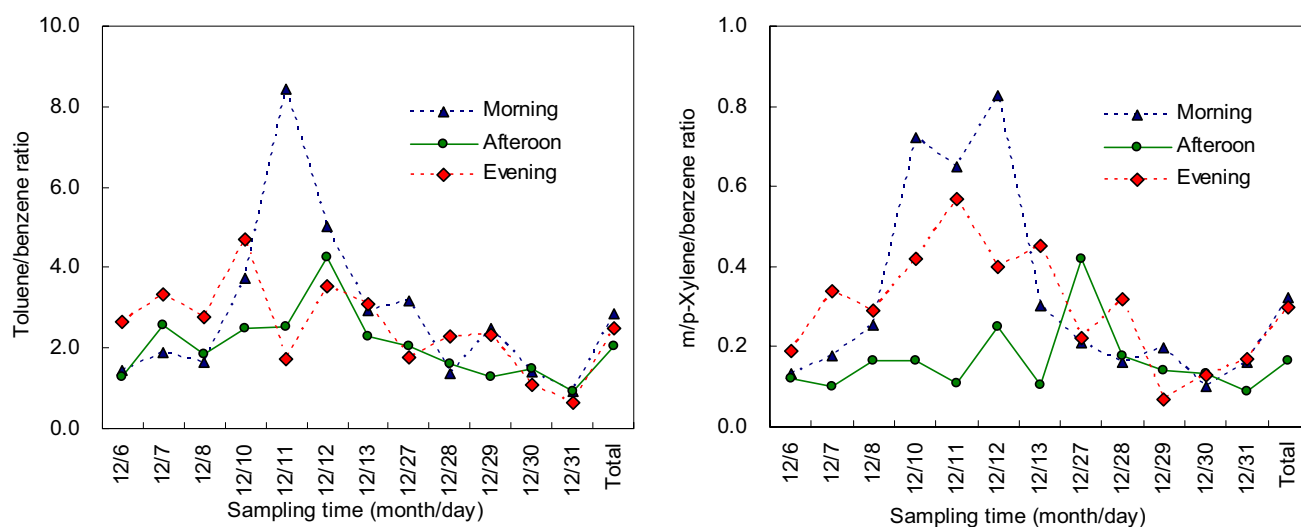


Fig. 4. Diurnal variations of toluene (*m/p*-xylene)/benzene concentration ratio during sampling periods in Foshan.

Table 3. Factor analysis for NMHCs in Foshan city in winter of 2008.

	Morning			Afternoon			Evening		
	F1	F2	F3	F1	F2	F3	F1	F2	F3
Isobutane	0.898				0.855			0.626	
i-butene	0.843				0.610				
n-butane	0.869			0.850			0.616		
l-pentane		0.872			0.978			0.950	
n-hexane		0.817			0.681				
benzene	0.778			0.893			0.881		
toluene	0.740	0.541		0.643	0.518		0.704	0.535	
p-xylene	0.899			0.850			0.764		
ethene			0.859			0.970			0.968
ethyne	0.688			0.986			0.992		
ethane			0.891			0.920			0.598
propene	0.913			0.811			0.730		
propane	0.759			0.602	0.671		0.876		
ethylbenzene	0.880			0.749			0.913		

Extraction method: principal component analysis.

Rotation method: Varimax with Kaiser normalization.

Only factor loadings > 0.5 listed.

morning, PC1 is heavily loaded with ethyne, propene, propane, butanes, p-xylene, benzene and Toluene. Among these species, ethyne and benzene are usually associated with combustion processes; propane and butanes are associated with both unburned product of vehicular emission and LPG leakage; i-pentane is a marker for gasoline evaporation and combustion processes (Barletta *et al.*, 2005). This indicates PC1 is combustion emission related and the most important NMHCs source. PC2 is heavily loaded with n-hexane, i-pentane and toluene, indicating PC2 might be solvent related. With heavy loading of ethene, and ethane, PC3 should be LPG leakage related, and little difference was found during morning, afternoon and evening. In the afternoon, solvent has a more contribution to different NMHCs than morning and evening.

Ozone Formation Potentials

The contribution of hydrocarbons to the production of photochemical O₃ is related to their reaction with OH and NO_x. Under high NO_x conditions, the amount of O₃ formed is determined by the levels of radicals formed from the reactions of NMHCs; however, under lower NO_x conditions it is the availability of NO_x that limits O₃ formation (Carter, 1994). Photochemical reactions of NMHCs are mainly initiated by the OH radical, and the mechanism of O₃ formation for each hydrocarbon varies greatly. To estimate the reactivity and the contribution of individual hydrocarbons to photochemical O₃ formation, the propylene-equivalent concentration (Prop-Equiv) (Chameides *et al.*, 1992; So and Wang, 2004) and the maximum incremental reactivity (MIR) (Carter, 1994) were calculated. The Prop-Equiv (*j*) of hydrocarbon *j* is defined as:

$$\text{Prop-Equiv}(j) = \text{Conc.}(j) \times k_{\text{OH}}(j)/k_{\text{OH}}(\text{propene}) \quad (1)$$

where Conc.*(j)* is the concentration of hydrocarbon *j* expressed in ppbc; *k*_{OH}(*j*) and *k*_{OH}(propene) are rate constants for the reaction of hydrocarbon *j* and propene with OH, respectively. Prop-Equiv(*j*) is a measure of the concentration of hydrocarbon *j* on an OH-reactivity based scale normalized to the reactivity of propene. The O₃ formation potential (OFP) can be evaluated as the product of the concentration of NMHCs and the MIR coefficient (dimensionless, gram of O₃ produced per gram of hydrocarbon *j*). The photochemical formation of O₃ is influenced by many factors besides the reactivity of hydrocarbon, such as the NO_x concentration, solar radiation intensity and meteorological conditions. MIR is a good indicator for comparing OFP of individual hydrocarbons. The following equation was used to calculate the contribution of O₃ formation by each hydrocarbon under optimal conditions:

$$\text{OFP}(i) = \text{Concentration}(i) \times \text{MIR coefficient}(i) \quad (2)$$

MIR coefficients were taken from Carter (1994).

As shown in Table 4, ranking by Prop-Equiv, the top 10 NMHCs were propene (20.5 ppbc), toluene (17.4 ppbc), ethene (13.3 ppbc), *i*-butene (9.2 ppbc), *i*-pentane (8.9 ppbc), *m/p*-xylene (8.0 ppbc), isoprene (6.8 ppbc), 2,3-

dimethylbutane (6.1 ppbc), *trans*-2-butene (6.0 ppbc), ethylbenzene (5.3 ppbc), which accounted for 66% of total Prop-Equiv concentration. Ranking by OFP, ethene (190.3 μg/m³), toluene (121.8 μg/m³), propene (120.5 μg/m³), *i*-pentane (58.0 μg/m³), *m/p*-xylene (48.5 μg/m³), *i*-butene (43.0 μg/m³), ethylbenzene (31.2 μg/m³), *o*-xylene (23.8 μg/m³), 2,3-dimethylbutane (17.3 μg/m³) and *trans*-2-butene (15.4 μg/m³) were the top 10 species, which accounted for 77% of total OFP. The total concentrations for all measured species of Prop-Equiv and OFP were 153.0 ppbc and 863.4 μg/m³, respectively. These results indicated that alkenes played the most important role in O₃ formation and accounted for ~49.5% of total OFP, followed by aromatic hydrocarbons (~28%), alkanes (~20.5%) and acetylenes (< 0.5%).

Table 5 shows the concentration of ozone production of selected abundant hydrocarbons during wintertime in Foshan and other regions. The total concentration of ozone production in our study has the highest concentration among other regions. The OFP concentrations of most abundant hydrocarbons were much higher in Foshan than other regions. Ethene was the most important NMHCs in terms of ozone production in Foshan city, and similar with the result in Los Angeles (Gorham *et al.*, 2010), Tradière in French (Sauvage *et al.*, 2009) and Downtown site in Ulsan Korea (Na *et al.*, 2001). High concentrations of ozone production of ethene were also found in 43 cities in China (Barletta *et al.*, 2005). In previous studies, So and Wang (2004) and Zhang *et al.* (2007) also found that toluene and xylenes were the most important NMHCs towards ozone formation in urban Hong Kong where the reactivity of VOCs was dominated by anthropogenic sources. In our study, ozone production of propane, *i*-pentane and ethyne were significantly higher than other studies (Table 5).

The samples were strongly influenced by meteorological conditions. In order to investigate the influence of meteorological conditions on the distribution of NMHCs, we split our data into two groups: Haze days (Visibility < 10 km) and normal days (Visibility > 10 km). Twenty most important NMHCs in terms of ozone production and Prop-Equiv for the ambient samples were investigated in haze and normal days (Fig. 5). The concentrations of ozone production and Prop-Equiv in haze days were significantly higher than normal days. The variation trends of ozone production and Prop-Equiv have also been observed for other air pollutants like carbonyls and particles between haze days and normal days in Guangzhou (Lü *et al.*, 2006; Tan *et al.*, 2009). These studies indicated that haze days represent more serious pollution of hydrocarbons than normal days. High concentrations of ozone production of ethane and toluene were also found in haze and normal days. However, high concentrations of Prop-Equiv of toluene and propene were found in haze days, and propene and ethane were found in normal days. Toluene is emitted from both vehicular emission and solvent usage (painting, printing and dry cleaning, etc.) (Klimont *et al.*, 2002; Na *et al.*, 2003; Yan *et al.*, 2010), and most of the solvents did not contain benzene (Na *et al.*, 2003). The lower wind speed, weaker air convection and weaker atmospheric diffusion in haze days might have favored the accumulation of toluene. The

B/T in haze days (3.73) was higher than that in normal days (1.73) although traffic volume showed no significant differences in haze and normal days (Fig. 6), indicating vehicular emission is more dominant in haze days.

CONCLUSION

Forty hydrocarbons were measured and their OFP

calculated in Foshan. Ethane, propane, *n*-butane, *i*-pentane, 2,3-dimethylbutane, ethene, propene, ethyne, benzene and toluene were the 10 most abundant species, accounting for 82% of the total NMHCs. The concentrations of most hydrocarbons were higher in the morning and evening than in the afternoon. Their contributions to the total NMHCs showed a similar temporal pattern. These results suggest that vehicular emission was a major source of ambient NMHCs.

Table 4. Averaged concentrations and photochemical properties of measured species in Foshan.

	ppbc	($\mu\text{g}/\text{m}^3$)	$10^{12} \times k_{\text{OH}}^{\text{a}}$	MIR ^b	Prop-Equiv (ppbc)	O ₃ formation ($\mu\text{g}/\text{m}^3$) ^c
<i>Alkanes</i>						
Ethane	37.04	24.80	0.26	0.25	0.37	6.20
Propane	38.95	25.50	1.15	0.48	1.70	12.24
<i>i</i> -Butane	12.08	7.82	1.12	1.21	0.51	9.46
<i>n</i> -Butane	15.05	9.74	2.54	1.02	1.45	9.94
<i>i</i> -Pentane	65.37	42.02	3.60	1.38	8.95	57.99
<i>n</i> -Pentane	5.54	3.56	3.94	1.04	0.83	3.71
Cyclopentane	1.20	0.75	5.16	2.40	0.24	1.80
2,3-Dimethylbutane	25.24	16.15	6.30	1.07	6.05	17.28
3-Methylpentane	5.94	3.80	5.70	1.50	1.29	5.71
<i>n</i> -Hexane	15.22	9.74	5.61	0.98	3.25	9.54
2,3-Dimethylpentane	15.67	9.99	N.A.	1.31		13.09
Methylcyclopentane	1.94	1.21	N.A.	2.80		3.39
2,4-Dimethylpentane	1.95	1.24	4.77	1.50	0.35	1.87
Cyclohexane	4.10	2.56	7.49	1.28	1.17	3.28
2-Methylhexane	3.37	2.15	N.A.	1.08		2.32
3-Methylhexane	1.08	0.69	N.A.	1.40		0.97
2,2,4-Trimethylpentane	6.61	4.21	3.34	0.93	0.84	3.92
<i>n</i> -Heptane	7.49	4.78	7.15	0.81	2.04	3.87
Methylcyclohexane	3.51	2.20	10.4	1.80	1.39	3.95
2-Methylheptane	2.42	1.54	N.A.	0.96		1.48
3-Methylheptane	1.81	1.15	N.A.	0.99		1.14
<i>n</i> -Octane	10.49	6.68	8.68	0.60	3.46	4.01
<i>Alkenes</i>						
Ethene	41.15	25.72	8.52	7.40	13.33	190.32
Propene	20.52	12.82	26.30	9.40	20.52	120.53
1-Butene	7.73	4.83	31.40	8.90	9.23	43.02
<i>trans</i> -2-Butene	2.46	1.54	64.00	10.00	5.99	15.39
<i>cis</i> -2-Butene	1.86	1.16	56.40	10.00	3.99	11.63
1-Pentene	3.45	2.16	31.40	6.20	4.12	13.39
Isoprene	1.78	1.08	101.00	9.10	6.83	9.83
<i>trans</i> -2-Pentene	1.44	0.90	67.00	8.80	3.68	7.94
<i>cis</i> -2-Pentene	1.32	0.83	65.00	8.80	3.26	7.27
1-Hexene	2.76	1.72	37.00	4.40	3.88	7.58
Ethyne	46.76	27.13	0.90	0.50	1.60	13.57
<i>Aromatic hydrocarbons</i>						
Benzene	24.29	14.10	1.23	0.42	1.14	5.92
Toluene	76.88	45.11	5.96	2.70	17.42	121.79
Ethylbenzene	19.53	11.55	7.10	2.70	5.27	31.19
<i>m/p</i> -Xylene (average)	11.07	6.55	19.00	7.40	8.00	48.46
Styrene	2.18	1.27	58.00	2.20	4.81	2.78
<i>o</i> -Xylene	6.18	3.66	13.70	6.50	3.22	23.76
1,2,4-Trimethylbenzene	2.27	1.35	32.5	8.80	2.81	11.90

N.A.: data were not available in the respective reference.

^a Rate constant of NMHCs react with OH at 298 K ($\text{cm}^3/\text{molecule}/\text{s}$) (Atkinson, 1989, 1997; Atkinson and Arey, 2003).

^b MIR denotes maximum incremental reactivity ($\text{g O}_3/\text{g NMHCs}$) (Carter, 1994, 1997).

^c $[\text{NMHC}] \times \text{MIR}$ ($\mu\text{g}/\text{m}^3$).

Table 5. Ozone production of abundant hydrocarbons during wintertime in Foshan and other regions (units: $\mu\text{g}/\text{m}^3$).

	Winter in Foshan, China (This study)	November in Los Angeles (Gorham et al., 2010)	Tradière in French (Sauvage et al., 2009)	Nagoya in Japan (Saito et al., 2009)	Beijing in China (Duan et al., 2008)	Valderejo Park in Spain (Navazo et al., 2008)	Guangzhou in China (Tang et al., 2007)	Urban site in Hong Kong (Guo et al., 2007)	43 cities in China (Barletta et al., 2005)	Downtown site in Ulsan Korea (Na et al., 2001)
Ethane	6.20	0.75	0.59	1.29	0.61	0.48	1.31	0.61	1.2–5.7	0.54
Propane	12.23	1.99	0.69	3.15	9.92	0.44	10.64	1.50	1.4–19.7	4.71
n-Butane	8.94	1.78	0.69	6.32	20.70	0.48	15.00	3.47	1.4–34.6	8.32
i-Pentane	46.70	3.00	0.71	4.75	41.91	0.32	13.61	1.86	1.1–67.5	7.15
Ethene	190.37	6.94	6.29	26.73	56.70	2.22	79.55	13.60	19.5–323.3	63.83
Propene	80.37	1.53	1.65	8.23	65.33	1.06	27.73	3.64	2.4–96.8	24.68
Ethyne	13.57	0.51	0.28	1.15	3.52	0.15	5.69	1.13	1.7–34	1.10
Benzene	5.92	0.39	0.22	0.76	12.24	0.10	4.02	0.61	1–15.3	1.61
Toluene	121.76	6.21	2.99	28.17	126.53	1.11	111.11	30.61	4.5–124.8	43.25

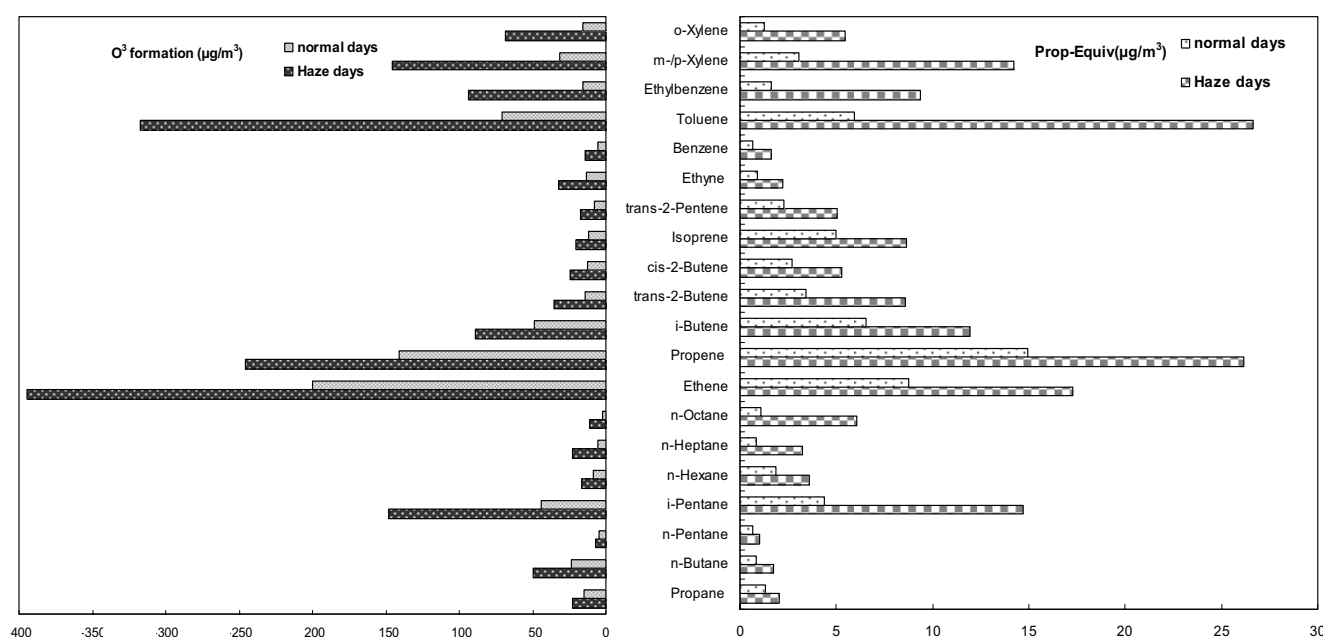


Fig. 5. Twenty most important NMHCs in terms of ozone production and Prop-Equiv for the ambient samples in haze and normal days.

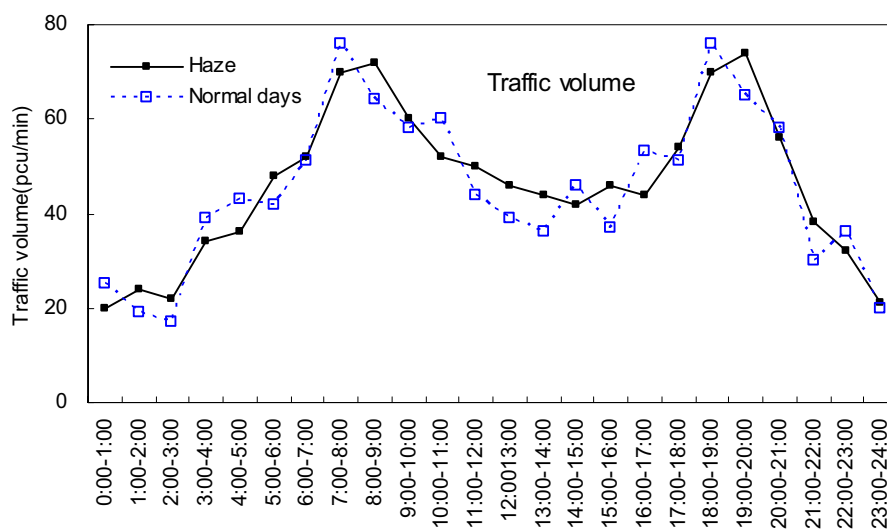


Fig. 6. Variations of traffic volume during sampling periods.

The measured mean B/T ratio (0.45 ± 0.24) further supported this conclusion. In addition, diurnal variations in the mass ratios of toluene and *m/p*-xylene to benzene implied that aromatic hydrocarbons mainly came from solvent evaporation. On average, total Prop-Equiv and OFP reached 153.0 ppbc and $863.4 \mu\text{g}/\text{m}^3$ during the study period. Ranking by Prop-Equiv, propene, toluene, ethene, *1*-butene, *i*-pentane, *m/p*-xylene, isoprene, 2,3-dimethylbutane, *trans*-2-butene and ethylbenzene were the top 10 contributors, accounting for 66% of the total Prop-Equiv as a whole. Ethene, toluene, propene, *i*-pentane, *m/p*-xylene, *1*-butene, ethylbenzene, *o*-xylene, 2,3-dimethylbutane and *trans*-2-butene were the top 10 contributors to O₃ formation, explaining 77% of the total OFP. Thus, alkenes played the most important role in O₃ formation, followed by aromatic hydrocarbons and alkanes.

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