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Nonmethane Hydrocarbons in Ambient Air of Hazy and Normal Days in Foshan, South China

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Abstract

A first study of nonmethane hydrocarbons (NMHCs) on hazy and normal days was performed in Foshan for providing deep insight into the local deteriorating air quality. Ethane, propane, *i*-pentane, ethene, propene, ethyne, benzene, and toluene were eight most abundant compounds, accounting for 71%–85% of total NMHCs. Most hydrocarbons showed much higher levels on hazy days than normal days together with hydrocarbon/ethyne ratios and diurnal variations, indicating hazy days are more dominated by vehicular emission. Correlation coefficients (R^2) of ethane, propane, ethane, propene, benzene, and total NMHCs with ethyne were 0.62–0.83, indicating these compounds are mainly related to vehicular emission. R^2 analysis indicated that solvent usage is responsible for toluene and other aromatic hydrocarbons (e.g., ethylbezene). Benzene/toluene (B/T) ratio was 0.44 ± 0.23 during whole sampling periods, again indicating vehicular emission is the dominant source. Lower B/T ratio (0.30 ± 0.14) on hazy days than that (0.58 ± 0.21) on normal days suggested that solvent usage emitted toluene.

Key words: air pollution control processes; atmospheric chemistry; air quality; haze

Introduction

Nonmethane hydrocarbons (NMHCs) are the major classes of organic pollutants and the key ozone (O_3) precursors in atmosphere (Poisson *et al.*, 2000; Xiao and Zhu, 2003; Caselli *et al.*, 2010), which can significantly affect the atmospheric photochemical chemistry and human health (Atkinson, 2000; Elbir *et al.*, 2007; Mudliar *et al.*, 2010). Their sources in urban air are usually dominated by anthropogenic emissions including liquefied petroleum gas (LPG) leakage, solvent usage, and vehicular emission (Barletta *et al.*, 2005; Tang *et al.*, 2007; Duan *et al.*, 2008). Recent studies on NMHCs showed that they have frequently exhibited much higher levels in Pearl River Delta (PRD), a rapidly developed region as well as a highly polluted area in south China (Wang *et al.*, 2002; Tang *et al.*, 2007; Shao *et al.*, 2009). Although NMHCs have been widely investigated in PRD (Liu *et al.*, 2008; Shao *et al.*, 2009), for instance, leakage from vehicles fueled by LPG contributed mainly to ambient propane in Guangzhou (Tang *et al.*, 2007); however, much remains unclear about the behaviors of NMHCs under conditions of particular pollution episodes, for example, hazy days, which will provide us deep insight into the local air pollution.

Haze is defined as a weather phenomenon that leads to visibility of < 10 km in China (CMA, 2003), which is formed from moisture, dust, and vapor in the atmosphere. Urban haze generally results from excessive air pollutants emitted by anthropogenic sources and gas-to-particle conversion (Watson, 2002; Fu *et al.*, 2008). Especially, haze is closely related to meteorological conditions and air pollution differing from those in normal days (Sun *et al.*, 2006; Mao *et al.*, 2008), because it is affected by the air contaminants with special characteristics (Wang *et al.*, 2006; Lü *et al.*, 2009). Recently, haze pollution has been an increasing concern among the public, scientific, and governments because of its negative impact on visibility, human health, and even the global climate (Yadav *et al.*, 2003; Kang *et al.*, 2004; Che *et al.*, 2009).

The growing haze and photochemical smog involving NMHCs has now become the major air pollution items in PRD region. Air pollutants such as carbonyls and particles have been studied on hazy days of Guangzhou in PRD (Lü *et al.*, 2009; Tan *et al.*, 2006, 2009); until now, very few studies on atmospheric NMHCs during haze episodes have been conducted, although hazy days often occur in the local region, particularly in winter time (Lü *et al.*, 2009; Tan *et al.*, 2009). Especially, no data on NMHCs are available in the most highly polluted city named Foshan (GDEMC, 2008), an

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intensive industrialization area in PRD. With the rapid economic development of Foshan during the past three decades, large amounts of air pollutants were released into the air and then resulted in a rapid deterioration of the local air quality. Considering that both photochemical smog involving NMHCs and haze pollution in Foshan are becoming more deteriorate now than before, the objectives of this study mainly aim at (1) studying variation characteristics of NMHCs between hazy days and normal days in Foshan and (2) providing original data of NMHCs for local environmental protection agency to manage the rapidly deteriorating air quality in Foshan.

Experimental

Site description

Foshan is the third largest city in central Guangdong province of PRD (the PRD region has a total population of 120 million people) in southern China, which experiences a humid subtropical climate. The prefectural area under the city's jurisdiction covers about 3840 km^2 and a population of 5.9 million, of which 3.6 million reside in the city proper. The city has become relatively affluent compared with other cities in China and is home to many large private enterprises. Foshan has been recently the production base of leathers, ceramics, and plastic products of China, for example, its production of microwave cooker ranks first in the country. The sampling site (longitude 113°06′E and latitude 23°02′N) is located on the roof of a 10-storey building (30 m above the ground) in the urban central of Foshan, which is surrounded by residential buildings, business offices, and roads (Fig. 1).

Air sampling

Hydrocarbon samples on December 6–8, 10–13, and 27–31, 2008, were collected each day at 08:30 (morning), 14:30 (afternoon), and 19:00 (evening). Hazy days (Fig. 2) demonstrated lower visibility (≤10 km), lower wind speed (WS), and higher temperature than that on normal days (Tan *et al.*, 2009). The samples were collected by 2-L commercial stainless steel canisters (Polar Ware Company), inside of which were electrically polished (Lü *et al.*, 2006). All canisters were precleaned five times using ultrapure N_2 (>99.999%) and then preevacuated by a canister cleaner (Entech Instruments, Inc.; Model 3100) before sampling. Sampling was performed according to the USEPA Compendium Method To-14A (Wang *et al.*, 2002). A flow-controlling valve was used to collect 10 min integrated sample by slightly opening the valve, and the sampling inlet was placed at ~1.5 m above the roof of the building, through which air was drawn by opening the valve. During sampling periods, data of traffic volume in Foshan were collected from Foshan Environmental Protection Bureau by our sampling staff to evaluate possible effects of vehicles on hydrocarbons.

Analysis

The analytical method has been reported in our previous studies in detail (Wang *et al.*, 2002; Lü *et al.*, 2006). Briefly, samples were concentrated in the Model 7100 preconcentrator (Entech Instruments, Inc.) and then injected into an HP6890 gas chromatography coupled to an HP5973 mass-selective detector. A RESTEK RTX-1 capillary column (60 m × 0.32 mm × 1.0 μm) was used in 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 isothermal held for 5 min. Compounds were identified by their retention times and mass spectra. Standard gas mixtures (1.0 ppm; Supeclo 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. During analysis, the sample volume for each injection was 250 mL, and the detection limits of the method for

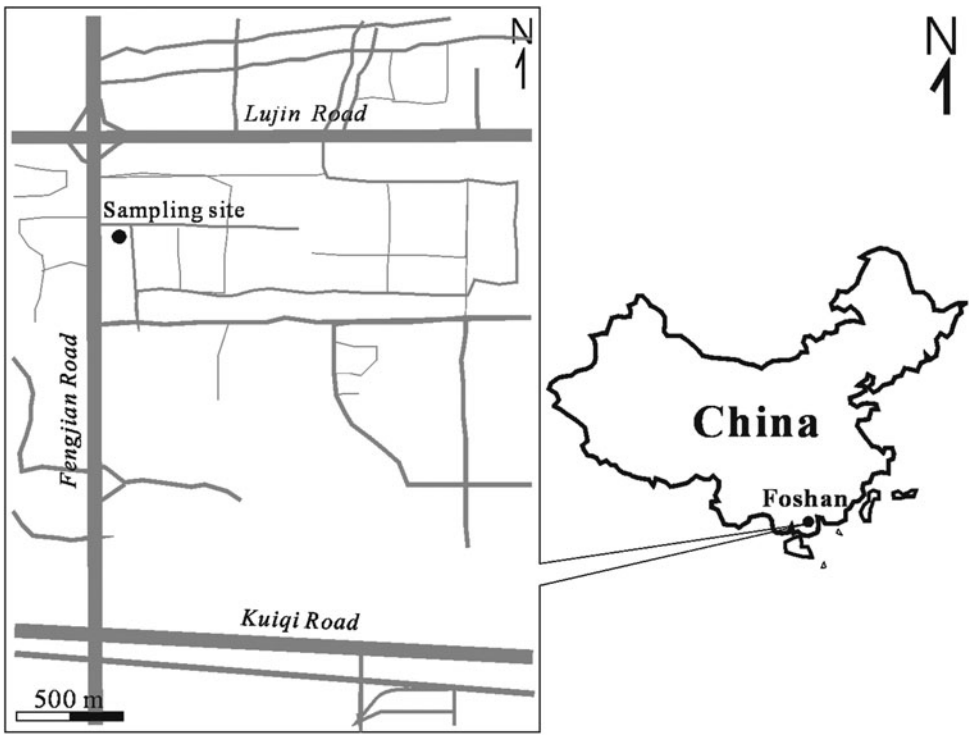

FIG. 1. Location of sampling site during sampling periods in Foshan, China.

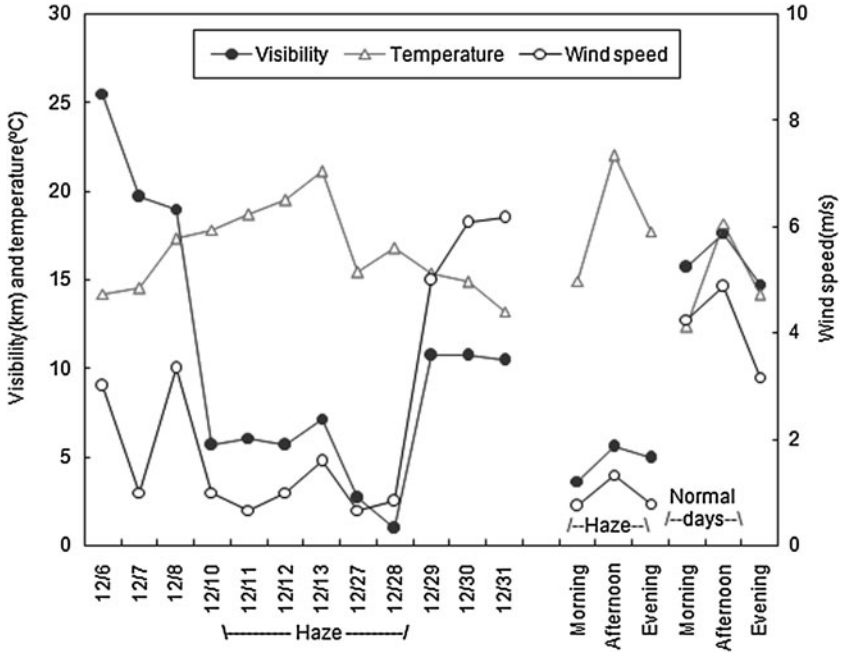

FIG. 2. Averages of visibility, wind speed, and temperature during sampling periods.

all compounds were <0.2 ppb. The relative deviations in the duplicate samples were $\leq 5\%$, for example, it was 2% for alkanes and 5% for alkenes.

Results and Discussion

Concentrations

To evaluate pollution levels of hydrocarbons between hazy days and normal days in Foshan, a total of 24 hydrocarbons were measured for data comparison (hazy days vs. normal days) during sampling periods (Table 1). Total NMHCs ranged from 96 to 342 ppbv with a mean of 175.16 ± 66.97 ppbv on hazy days, whereas it ranged from 39 to 128 ppbv (with a mean of 76.96 ± 21.24 ppbv) on normal days. On both hazy and normal days, ethane, propane, *i*-pentane, ethene, propene, ethyne, benzene, and toluene are the eight most abundant hydrocarbons, accounting for 71%–85% of total NMHCs (Table 1).

As shown in Table 1, the concentrations of most hydrocarbons on hazy days were higher than that on normal days, for example, ethyne increased by $\sim$142% from normal days to hazy days. The variation trends of hydrocarbons have also been observed for other air pollutants such as carbonyls and particles between hazy days and normal days in Guangzhou (Lü *et al.*, 2006; Tan *et al.*, 2009), indicating that hazy days represent more serious pollution of hydrocarbons than normal days. Data of evaluated O_3 levels on hazy days (13.75 ppbv) and normal days (11.38 ppbv) (Table 1) suggested that hazy days are more oxidative, which will likely lead to much more losses of hydrocarbons on hazy days. The observed higher levels of NMHCs on hazy days might be due to accumulation of hydrocarbons under steady weather conditions, for example, lower visibility and WS on hazy days (Fig. 2).

Diurnal patterns

Most hydrocarbons showed higher levels in the morning and evening, especially on hazy days (Table 1), for example, ethyne on hazy days decreased by $\sim$30% from morning to afternoon and then increased by $\sim$37% from afternoon to evening. This diurnal variation pattern (Fig. 3) implied the dominant emission from vehicles, as traffic volume reaches its highest level at rush hours in the morning and evening. The lowest levels in the afternoon are also likely the results of reaction with OH and increased mixing height of the planetary boundary layer (Tang *et al.*, 2007). In addition, the average WS in the afternoon was higher than that in the morning (or evening) (Fig. 2), resulting in stronger ventilation and then diluting the air pollutants. However, *i*-pentane, a marker for gasoline evaporation (Barletta *et al.*, 2005), exhibited the highest levels (30.99 ± 10.67 ppbv) in the afternoon, especially on hazy days. The higher temperature in the afternoon than in the morning (or evening) (Fig. 2) is conducive to evaporation of solvent containing *i*-pentane, which was supported by the highest level of *i*-pentane occurring in the afternoon (Fig. 3).

Averagely, alkanes, alkenes, and aromatic hydrocarbons accounted for 36%–51%, 18%–26%, and 12%–19% of total NMHCs on hazy days (they were 45%–48%, 23%–29%, and 9%–10% on normal days), respectively (Table 1). On hazy days, ethyne contributed first (19%), followed by ethene (15%), *i*-pentane (14%), ethane (10%), toluene (9%), propane (9%), propene (5%), and benzene (3%). On normal days, ethyne contributed first (18%), followed by ethene (17%), ethane (14%), propane (14%), *i*-pentane (9%), propene (6%), toluene (5%), and benzene (3%). Considering that ethyne is a tracer for vehicular exhaust (Barletta *et al.*, 2005), *i*-pentane is a marker for gasoline evaporation, and toluene is emitted from vehicles, painting, and industrial processes (solvent usage) (Barletta *et al.*, 2002), the contribution ranking of these abundant compounds to total NMHCs was closely associated with vehicular emission, gasoline evaporation, and solvent application. Especially, the concentration of toluene in total NMHCs showed the largest distinction between hazy days and normal days compared with other seven abundant compounds. This

Table 1. Concentrations (ppbv) of Hydrocarbons, O_3, and NO_2 During Sampling Periods in Foshan, China

	Hazy days (December 10–13 and 27–28, 2008)						*Normal days (December 6–8 and 29–31, 2008)*					
Hydrocarbons	*Morning*[a]	*Afternoon*[a]	*Evening*[a]	*Mean*[b]	*Min.*[c]	*Max.*[c]	*Morning*[a]	*Afternoon*[a]	*Evening*[a]	*Mean*[b]	*Min.*[c]	*Max.*[c]
Ethane	22.71 ± 9.47	11.95 ± 6.17	16.57 ± 8.31	17.08 ± 8.86	7.61	38.47	11.95 ± 3.14	8.69 ± 1.78	11.67 ± 3.28	10.77 ± 3.05	5.53	17.12
Propane	17.50 ± 7.49	13.14 ± 4.11	16.22 ± 3.69	15.62 ± 5.39	7.57	29.01	10.34 ± 1.21	8.86 ± 1.24	11.33 ± 2.41	10.18 ± 1.92	6.56	14.32
n-Butane	5.68 ± 1.87	3.49 ± 1.17	4.42 ± 1.37	4.53 ± 1.68	2.24	9.00	2.27 ± 0.60	1.83 ± 0.62	2.40 ± 0.98	2.17 ± 0.75	0.74	3.73
i-Butane	5.32 ± 2.24	3.14 ± 1.23	4.39 ± 1.15	4.28 ± 1.78	1.85	8.48	1.97 ± 0.58	1.35 ± 0.65	2.00 ± 1.00	1.77 ± 0.78	0.23	3.81
n-Pentane	1.65 ± 1.24	0.79 ± 0.51	1.61 ± 1.08	1.35 ± 1.02	0.14	4.05	0.71 ± 0.33	0.66 ± 0.50	1.17 ± 0.71	0.85 ± 0.55	0.11	2.48
i-Pentane	14.91 ± 8.37	30.99 ± 10.67	18.49 ± 12.72	21.46 ± 12.33	5.28	43.37	6.11 ± 6.69	6.84 ± 2.99	6.27 ± 3.64	6.41 ± 4.45	1.61	19.20
Cyclopentane	0.35 ± 0.17	0.26 ± 0.10	0.36 ± 0.14	0.32 ± 0.14	0.05	0.56	0.15 ± 0.12	0.15 ± 0.09	0.26 ± 0.11	0.19 ± 0.12	0.05	0.43
n-Hexane	2.09 ± 1.63	3.99 ± 6.09	2.41 ± 1.57	2.83 ± 3.62	0.60	16.26	0.94 ± 0.83	0.79 ± 0.52	2.66 ± 4.46	1.47 ± 2.63	0.23	11.75
Cyclohexane	0.50 ± 0.37	0.27 ± 0.18	0.57 ± 0.50	0.45 ± 0.38	0.08	1.52	0.16 ± 0.09	0.16 ± 0.14	0.77 ± 1.24	0.36 ± 0.74	0.06	3.28
n-Heptane	2.15 ± 2.08	0.55 ± 0.41	2.44 ± 2.40	1.71 ± 1.94	0.18	6.02	0.31 ± 0.16	0.32 ± 0.37	0.66 ± 0.62	0.43 ± 0.43	0.09	1.83
n-Octane	2.34 ± 1.81	1.18 ± 1.00	3.34 ± 2.32	2.29 ± 1.91	0.37	7.01	0.29 ± 0.10	0.31 ± 0.13	0.64 ± 0.44	0.41 ± 0.31	0.20	1.24
Total alkanes[d]	75.18 ± 27.71	69.74 ± 22.63	70.82 ± 23.16	71.91 ± 23.24	38.37	117.81	35.20 ± 3.13	29.95 ± 5.40	39.83 ± 12.55	35.00 ± 8.66	24.22	62.36
Ethene	30.65 ± 18.40	16.59 ± 3.64	32.74 ± 7.56	26.66 ± 13.22	11.21	64.98	13.83 ± 6.61	10.03 ± 4.69	16.66 ± 6.25	13.51 ± 6.21	1.49	26.24
Propene	10.04 ± 5.76	5.20 ± 2.79	10.90 ± 3.10	8.71 ± 4.64	2.02	18.20	5.12 ± 1.65	3.59 ± 1.64	6.24 ± 3.17	4.99 ± 2.41	1.44	10.38
i-Butene	2.65 ± 1.70	1.56 ± 0.66	3.28 ± 1.84	2.50 ± 1.59	0.84	6.10	1.42 ± 0.46	1.10 ± 0.84	1.59 ± 0.93	1.37 ± 0.75	0.46	2.91
trans-2-Butene	0.99 ± 0.73	0.37 ± 0.22	1.29 ± 0.46	0.88 ± 0.62	0.12	2.08	0.32 ± 0.08	0.27 ± 0.09	0.45 ± 0.20	0.35 ± 0.15	0.14	0.70
cis-2-Butene	0.70 ± 0.50	0.28 ± 0.11	0.87 ± 0.45	0.62 ± 0.45	0.12	1.50	0.27 ± 0.09	0.23 ± 0.10	0.44 ± 0.25	0.31 ± 0.18	0.13	0.78
Isoprene	0.37 ± 0.26	0.37 ± 0.11	0.60 ± 0.13	0.45 ± 0.20	0.15	0.81	0.22 ± 0.07	0.26 ± 0.17	0.30 ± 0.16	0.26 ± 0.13	0.06	0.57
trans-2-Pentene	0.55 ± 0.31	0.16 ± 0.08	0.47 ± 0.31	0.39 ± 0.30	0.08	0.90	0.15 ± 0.06	0.14 ± 0.09	0.24 ± 0.18	0.18 ± 0.12	0.03	0.52
Total alkenes[d]	45.95 ± 26.34	24.52 ± 7.02	50.15 ± 11.77	40.21 ± 19.82	15.48	93.75	21.35 ± 7.54	15.62 ± 6.38	25.92 ± 9.71	20.97 ± 8.67	4.94	38.67
Ethyne	36.12 ± 15.74	25.68 ± 8.64	35.30 ± 13.05	32.36 ± 12.99	18.31	64.10	13.51 ± 2.80	11.91 ± 2.91	14.62 ± 3.73	13.35 ± 3.19	7.03	19.76
Benzene	5.61 ± 4.58	3.66 ± 3.38	8.08 ± 2.98	5.78 ± 3.95	1.24	14.29	1.89 ± 0.64	2.18 ± 1.23	2.92 ± 1.06	2.33 ± 1.04	0.44	4.16
Toluene	20.28 ± 10.11	10.29 ± 5.51	19.77 ± 8.90	16.78 ± 9.20	5.13	34.78	3.98 ± 2.43	3.21 ± 1.43	4.02 ± 2.32	3.74 ± 2.02	1.40	7.95
Ethylbenzene	5.60 ± 5.72	1.88 ± 1.75	5.55 ± 4.02	4.34 ± 4.30	0.43	13.06	0.92 ± 1.01	0.45 ± 0.18	0.87 ± 0.69	0.75 ± 0.70	0.21	2.81
m-/p-Xylene	2.71 ± 2.47	1.09 ± 1.43	3.57 ± 1.99	2.46 ± 2.17	0.14	5.97	0.67 ± 0.63	0.29 ± 0.13	0.62 ± 0.45	0.53 ± 0.46	0.13	1.63
o-Xylene	1.69 ± 1.71	0.57 ± 0.63	1.68 ± 1.16	1.31 ± 1.29	0.10	4.31	0.35 ± 0.35	0.22 ± 0.15	0.35 ± 0.28	0.30 ± 0.26	0.06	1.00
Total aromatics[d]	35.89 ± 23.52	17.48 ± 11.97	38.65 ± 16.99	30.67 ± 19.58	7.04	67.29	7.82 ± 4.85	6.35 ± 3.02	8.78 ± 4.57	7.65 ± 4.10	2.90	16.41
Total NMHCs[d]	193.14 ± 90.75	137.42 ± 39.20	194.92 ± 53.96	175.16 ± 66.97	95.97	342.95	77.88 ± 11.34	63.83 ± 15.47	89.16 ± 27.92	76.96 ± 21.24	39.09	128.07
NO_2[e]	13.31 ± 4.00	13.39 ± 6.15	20.05 ± 9.85	15.58 ± 7.41	7.30	32.14	30.92 ± 17.43	27.43 ± 18.15	18.34 ± 18.29	25.57 ± 16.37	6.33	63.30
O_3[e]	4.71 ± 3.70	33.29 ± 14.25	3.27 ± 0.90	13.75 ± 16.32	0.47	46.67	5.68 ± 4.74	25.36 ± 3.93	3.12 ± 0.89	11.38 ± 10.77	1.40	31.27

[a]The arithmetic mean and standard deviation for data collected from the same sampling duration.
[b]The total arithmetic mean and standard deviation for all data on hazy or normal days.
[c]The minimum (Min.) (or the maximum [Max.]) value of data on hazy or normal days.
[d]Total alkanes, total alkenes, total aromatics, and total NMHCs were the sum of the listed alkanes, alkenes, aromatics, and all hydrocarbon concentrations, respectively.
[e]Data of O_3 and NO_2 concentrations were collected from Foshan Environmental Protection Bureau (EPB), Foshan.
NMHC, nonmethane hydrocarbon.

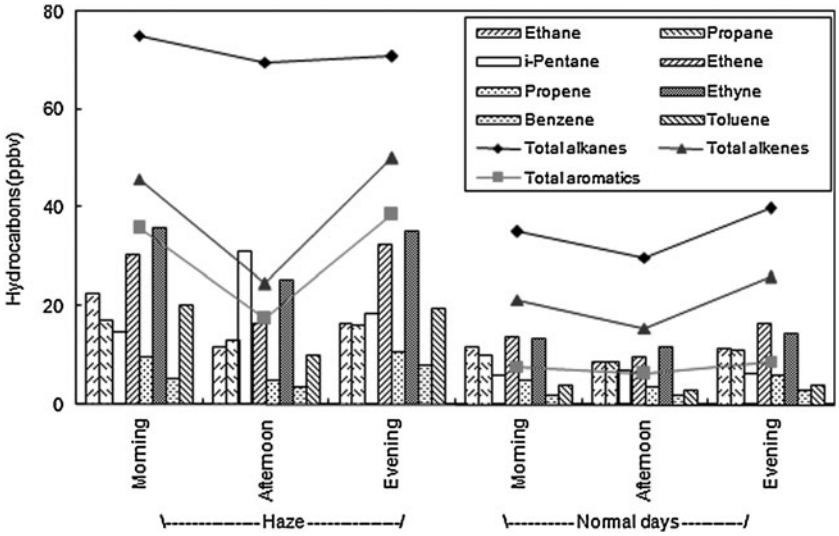

FIG. 3. Mean diurnal variations of abundant hydrocarbons during sampling periods.

might be due to different meteorological conditions (Fig. 2) and different photochemical activities of toluene (Atkinson, 2000) in the two day types.

Levels in relation to meteorology

Meteorological conditions can affect air pollutants and have been long recognized as being associated with the worst air pollution episodes (Lü *et al.*, 2006; Tan *et al.*, 2009). Figure 4 plots the relationships of total NMHCs with visibility and WS. On hazy days, total NMHCs did not show clear variation trends under lower visibility conditions (0–5 km), but it decreased with the increasing of visibility when visibility was 5–10 km. Total NMHCs also showed no statistical variation trend together with WS being ≤ 2 m/s for most samples on hazy days (Fig. 4), indicating that the

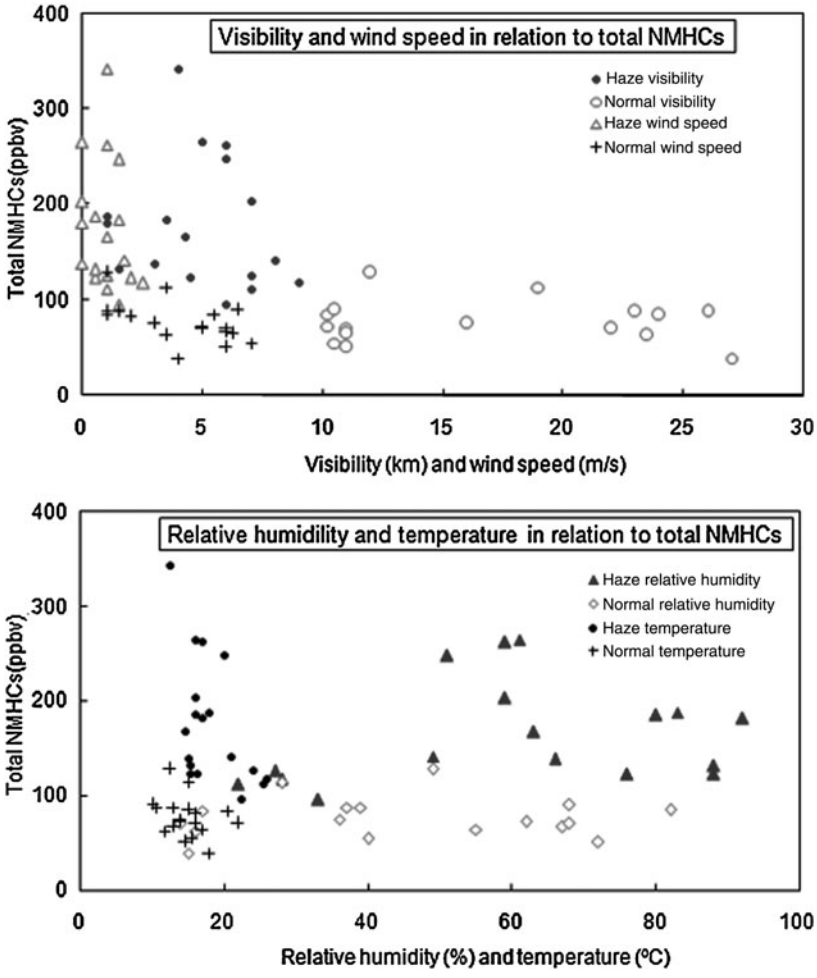

FIG. 4. Meteorological conditions in relation to total NMHCs during sampling periods. NMHC, nonmethane hydrocarbon.

dilution effect of WS on hydrocarbons is negligible on hazy days. In addition, no clear boundaries were observed for both relative humidity (RH) and temperature between hazy days and normal days, and RH ranged from 40% to 90% for most samples during sampling periods (Fig. 4). On the whole, hazy days demonstrated lower visibility, lower WS (≤ 2 m/s), and higher levels of hydrocarbons compared with normal days in this study.

Sources of hydrocarbons

Generally, alkenes and alkynes are characteristic products of combustion engines (Barletta *et al.*, 2005). In urban environments, vehicular emission is by far the most important source (Tang *et al.*, 2007), which has been supported by the highest level of ethyne (a tracer for vehicular emission) in this study (Table 1). To assess the impact of vehicles on hydrocarbon levels, mean hydrocarbon/ethyne ratios were calculated for individual hydrocarbons between hazy days and normal days (Fig. 5). It was expected that the lower hydrocarbon/ethyne ratios mean that air hydrocarbons are more dominated by vehicular emission. For most hydrocarbons, the hydrocarbon/ethyne ratios on hazy days were approximately less than those in normal days, although traffic volume showed no significant differences in the two day types (Fig. 5), indicating vehicular emission is more dominant on hazy days. However, toluene exhibited significant higher ratios on hazy days, likely suggesting additional source differing from vehicles, because toluene is also emitted from solvent usage including painting, printing, and dry cleaning (Na *et al.*, 2003; Yan *et al.*, 2010).

To clearly identify the influence of vehicular emission on ambient hydrocarbons, correlation coefficients (R^2) of abundant hydrocarbons with ethyne are calculated in Table 2. Ethane, propane, ethane, propene, and benzene showed good correlations ($R^2 = 0.62$–0.83) with ethyne, indicating that their sources are mainly vehicular emission; the R^2 of total NMHCs with ethyne was 0.76–0.79, indicating that ambient hydrocarbons are mainly related to vehicles. Especially, R^2 of propane with ethyne ($R^2 = 0.62$) on hazy days were significantly lower than that ($R^2 = 0.83$) on normal days (Table 2), suggesting the more intensive photochemical activity of propane (Atkinson, 2000) on hazy days compared with normal days.

Toluene is emitted from both vehicular emission and solvent usage (painting, printing, dry cleaning, etc.) (Klimont *et al.*, 2002; Na *et al.*, 2003; Yan *et al.*, 2010), and most of the

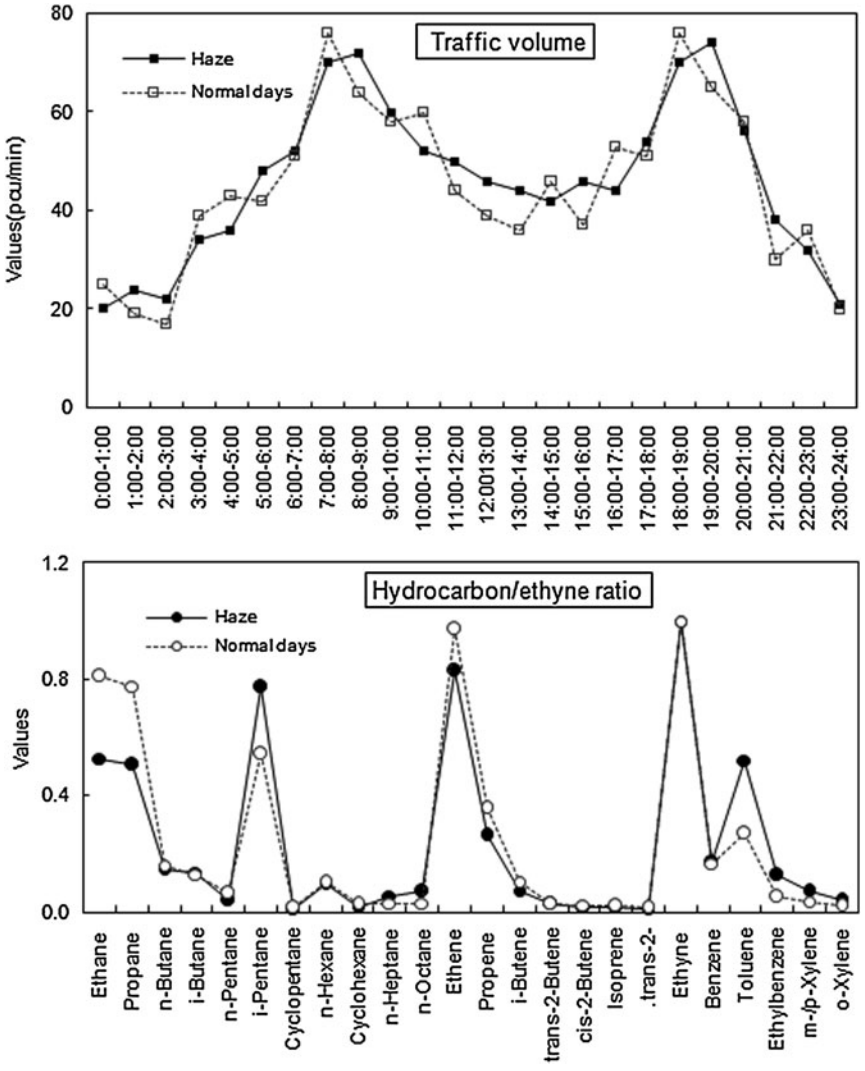

FIG. 5. Variations of traffic volume and mean hydrocarbon/ethyne ratio during sampling periods.

Table 2. Correlation Coefficients (R^2) of Hydrocarbons with Ethyne and Toluene

	R^2 *with ethyne*			R^2 *with toluene*	
Hydrocarbons	*Hazy days*	*Normal days*	*Hydrocarbons*	*Hazy days*	*Normal days*
Ethane	0.62	0.65	Benzene	0.53	0.48
Propane	0.62	0.83	Ethylbezene	0.78	0.84
Ethene	0.66	0.63	*m/p*-Xylene	0.79	0.85
Propene	0.66	0.76	*o*-Xylene	0.70	0.81
Benzene	0.67	0.73	*Total aromatics*	0.93	0.98
Toluene	0.49	0.55			
Total NMHCs	0.76	0.79			

solvents did not contain benzene (Na *et al.*, 2003). In this study, abundant toluene showed weak correlation ($R^2 = 0.48$–0.55) with benzene and ethyne, leading us to believe that ambient toluene could be used as a reliable marker for solvent usage during sampling periods. As can be seen in Table 2, ethylbezene, *m/p*-xylene, and *o*-xylene showed good correlations ($R^2 = 0.70$–0.85) with toluene, indicating they mainly come from a similar source as that of toluene, for example, solvent usage. Especially, R^2 of ethylbezene, *m/p*-xylene, and *o*-xylene with toluene on normal days were higher than that on hazy days. This may be explained by more intensive photochemical activity of toluene on hazy days. Generally, radiation can be weaker because of scattering by haze and oxidants may be titrated by the high concentration of hydrocarbons as well as active nitrogen oxides such as nitric oxide (Atkinson, 2000) on hazy days. In this study, O_3 levels during sampling periods in Foshan were used to evaluate the oxidative activities of toluene between hazy days and normal days, because O_3 is the crucial intermediate species in photochemical reactions of ambient hydrocarbons and represents the major photochemical oxidant in the atmosphere. As can be seen in Table 1, the mean O_3 levels in the morning (or evening) on hazy days were approximately equal to those on normal days. However, in the afternoon, hazy days showed much higher levels of O_3 (33.29 ppbv) than normal days (25.36 ppbv). Therefore, hazy days in this study are considered to be more intensive oxidation than normal days, resulting in weaker correlations of toluene with these aromatic hydrocarbons. Moreover, total aromatics showed rather good correlation with toluene ($R^2 = 0.93$–0.98), indicating ambient aromatic hydrocarbons are mainly related to the same source as that of toluene.

To further differentiate vehicular emission and other combustion sources, the benzene-to-toluene ratio (B/T) was considered. A B/T ratio of ~ 0.5 (wt/wt) was reported to be characteristic of vehicular emission (Barletta *et al.*, 2005), and higher B/T ratios represented the sources from burning of biofuel, charcoal, and coal (Duan *et al.*, 2008). During whole sampling periods, the mean B/T ratio was 0.44 ± 0.23, indicating the dominant emission from vehicles. On hazy days, the B/T ratios (a mean of 0.30 ± 0.14) were 0.23 ± 0.12 in the morning, 0.29 ± 0.17 in the afternoon, and 0.37 ± 0.10 in the evening; on normal days, they were 0.47 ± 0.13 in the morning, 0.57 ± 0.24 in the afternoon, and 0.70 ± 0.22 in the evening (with a mean of 0.58 ± 0.21 on normal days). In this study, ambient hydrocarbons on hazy days are mainly dominated by vehicular emission, which may raise the B/T ratio on hazy days compared with normal days, because benzene was mainly emitted from vehicles as discussed earlier. The rate constants (k_{OH}) for gas-phase reactions of OH radical with benzene and toluene are 1.23×10^{12} and 5.95×10^{12} $cm^{-3} \cdot molecule^{-1} \cdot s^{-1}$, respectively (Yassaa *et al.*, 2006). Then, the faster removal rate of toluene under conditions of more intensive oxidation may also raise the B/T ratios on hazy days. However, the measured mean B/T value (0.30) on hazy days was much lower than that (0.58) on normal days. The observed significant difference of measured mean B/T ratios between hazy days and normal days suggests the following fact. The lower WS, weaker air convection, and weaker atmospheric diffusion on hazy days (Fig. 2) might be more prone to accumulations of toluene with high levels compared with low levels of benzene. The difference was more likely to benefit from solvent usage emitting toluene based on the R^2 analysis above, resulting in the reduction of B/T values on hazy days, because a large amount of trades involving painting, printing, and dry cleaning are very well developed in Foshan.

Conclusions

Ethane, propane, *i*-pentane, ethene, propene, ethyne, benzene, and toluene are eight most abundant hydrocarbons on hazy and normal days of Foshan, accounting for 71%–85% of total NMHCs. Concentrations of most hydrocarbons on hazy days were greater than that on normal days together with diurnal variations and the hydrocarbon/ethyne ratios, indicating that hazy days are more dominated by vehicles than normal days. R^2 analysis indicated that ethane, propane, ethane, propene, benzene, and total NMHCs are mainly related to vehicular emission, whereas solvent usage is responsible for toluene and other aromatic hydrocarbons. The mean B/T ratio was 0.44 ± 0.23 during whole sampling periods, again indicating the dominant vehicular emission. The mean B/T ratio showed a lower value (0.30 ± 0.14) on hazy days than that (0.58 ± 0.21) on normal days, suggesting that solvent usage emitted toluene during sampling periods.

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