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Volatile organic compounds in 43 Chinese cities

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Abstract

Whole air samples were collected in 43 Chinese cities in January and February 2001, and methane and nonmethane hydrocarbon (NMHC) concentrations for those samples are here discussed. In order to identify the main sources of the hydrocarbons in these cities, cross-correlations with the general combustion tracer ethyne and the gasoline marker *i*-pentane were investigated. Most of the identified NMHCs correlated with ethyne or *i*-pentane suggesting that their primary source is combustion or gasoline evaporation. To differentiate between vehicular and other combustion sources, the benzene to toluene ratio characteristic of the Chinese vehicular fleet was calculated using roadside samples (collected in 25 cities). Cities where the main source of the NMHCs was traffic related were identified. The slope resulting from the correlation of selected gases was used to identify the likely sources of the NMHCs measured. Vehicular emissions were found to be an important source of isoprene in some cities. Different VOC mixing ratio distributions throughout the country were also investigated. This paper gives a general overview of urban VOCs in many Chinese cities. Future more rigorous studies will be necessary to further characterize VOC sources in China.

Keywords: VOCs; Vehicular emissions; Urban air; Combustion; Gas-chromatography

1. Introduction

Volatile organic compounds (VOCs) are emitted from both anthropogenic and biogenic sources (Hewitt, 1999 and references therein). The most important anthropogenic sources are stationary fuel related (combustion from power plants, extraction and handling of fossil fuels, service stations), transport related (combustive and evaporative emissions from cars) and industrial (mainly solvent use, storage and transport). Biogenic compounds are emitted by vegetation (e.g. isoprene, monoterpenes, sesquiterpenes and oxygenated compounds), by oceans (e.g. methyl iodide, methyl nitrate, dimethyl sulfide), or by soils (e.g. carbonyl sulfide). In some regions biogenic sources can substantially contribute to the total amount of VOCs present, while in urban atmospheres this contribution is usually minor compared to anthropogenic emissions.

Among the different VOCs, nonmethane hydrocarbons (NMHCs) represent a major sub-class. The source of NMHCs in urban environments is often dominated by vehicular emissions involving gasoline distribution,

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evaporation and automobile exhaust (Watson et al., 2001). Alkenes and alkynes, particularly ethene and ethyne, are characteristic products of internal combustion engines, while C_5–C_8 saturated NMHCs are generally associated with unburned vehicular emissions (Mayrsohn and Crabtree, 1976). Alkanes are emitted from gasoline evaporation, liquefied petroleum gas (LPG) leakage, and natural gas leakage (Blake and Rowland, 1995; Chen et al., 2001; Barletta et al., 2002). Aromatic hydrocarbons, usually representing a significant fraction of total NMHCs, are emitted by fuel combustion and evaporation of fuels and solvents. Characterization of hydrocarbons has been carried out in several cities around the world (Haszpra, 1991; Mohan et al., 1997; Sharma, 1997; Singh et al., 1997; Grosjean et al., 1998a, 1998b, 1999; Padhy and Varshney, 2000; Sharma et al., 2000; Barletta et al., 2002). However, relatively few data are available for China.

The People's Republic of China is the world's third largest country in area, but the most populated with 1.3 billion people (21% of the world total in 2001; EIA, 2005a). The country is divided into 23 provinces, five autonomous regions, four municipalities, and two special administrative regions. The transition to a market economy, which began in the 1980s, makes China one of the world's fastest growing economies. China's most developed regions are urban costal areas, in particular the Pearl River Delta (PRD) situated in the southern province of Guangdong, and the Yangtse River Delta (YRD) in the eastern provinces of Zhejiang, Jiangsu, Fujian and Shanghai.

Several environmental issues are associated with rapid development including a severe degradation of the air quality. By 2020 emissions of VOCs in China are expected to increase by about 60% compared to 1990 (Klimont et al., 2002). Different emission sources are responsible for the increased amount of pollutants, the most important being vehicular emissions, industrial emissions and coal combustion.

The number of vehicles in China has grown enormously since the 1980s. Because of the expected growth in the use of vehicles for personal transport and the subsequent increased demand for liquid fuel, VOC emissions from fuel processing, distribution, and storage are also expected to increase significantly within China. Vehicular emissions were found to be a major contributor of pollutants in cities like Beijing, Shanghai, and Guangzhou (Fu et al., 2001). The average emission factors of Chinese vehicles in their study were several times higher than those in developed countries. Moreover, NO_x, CO, particulate matter, and ozone levels exceeded the Chinese air quality standard in several roadside and traffic areas of many Chinese cities (Fu et al., 2001).

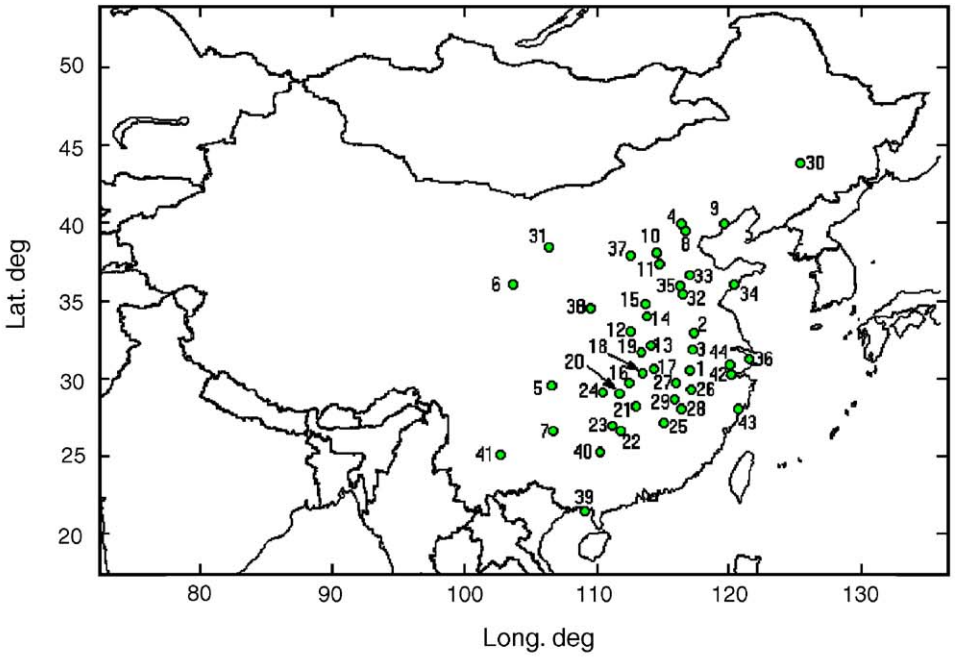
Another possible source of VOCs in China can be related to coal combustion. China is the world's largest consumer of coal (1422 million tons annually, corresponding to 27% of the total global consumption; EIA, 2005b) but also the world's largest producer (1610 million tons annually, or 29% of the global total; EIA, 2005b). In addition to industrial applications (mainly for industrial boilers and furnaces), coal is used throughout the country in household cooking stoves and for heating purposes. Because the combustion of coal for domestic purposes is less efficient than in industrial applications, emissions from coal combustion in the residential sector comprise a significant portion of the total emissions from coal burning. Coking plants are also very common around China. The production of coke accounted for 45% in the world in 2003 (Association of China Coke Industry, 2003). Many coking plants are privately run and therefore the emissions due to the lower production efficiency should not be overlooked.

Despite the increasing international attention devoted in the last years to characterize pollutant emissions from China, a comprehensive characterization of the VOC distribution in China is still lacking. Only a few studies of VOC emissions from China have been published (e.g. Piccot et al., 1992; Tonooka et al., 2001; Klimont et al., 2002; T. Wang et al., 2002; Streets et al., 2003). However, some of these studies were not based on actual measurements. Instead, emission factors were developed to produce an inventory of emissions from China. The main limitation of this approach is the lack of information about the major emitting sectors in China. In some cases, VOC emission factors used for China were derived from western sources and thus are likely not very accurate.

VOC measurements available today are restricted to particular regions of China such as Hong Kong (Lee et al., 2002; Ho and Lee, 2002; Ho et al., 2002; Chan et al., 2002), the PRD (X. Wang et al., 2002), Guangzhou (Bi et al., 2003; Chan et al., 2003), and Changchun (Liu et al., 2000). In this study the composition of C_2–C_{10} NMHCs in the urban atmospheres of 43 different Chinese cities is presented and discussed.

2. Experimental

In collaboration with the Hong Kong Polytechnic University (HKPU), and Zhongshan University, ground-level whole air samples were collected in China in January/February 2001. Students from the Zhongshan University collected a total of 158 canisters in 43 different cities covering 15 out of 23 total provinces, two out of five autonomous regions, and three out of four municipalities (Fig. 1). The majority of samples (131 canisters in 43 different cities) were collected at an approximate height of 1.5 m ($\pm$1 m) in different urban locations (mainly residential, commercial, and industrial areas), paying attention not to take samples near



Province		City		Population (in $\times 10^3$) Urban	Total	Province		City		Population (in $\times 10^3$) Urban	Total
Anhui	1	Anqing (0-3)		570	6010	Jiangxi	25	Ji'an (2-1)	B	420	4390
	2	Bengbu (3-0)		760	3360		26	Jingdezhen (2-1)	T	410	1440
	3	Hefei* (4-1)	T[a]	1425	4455		27	Jiujiang (2-1)	T	510	4460
Beijing**	4	Beijing (2-1)	T	10590	11280		28	Linchuan (3-0)	B	233	976
Chongqing**	5	Chongqing (3-0)	B[b]	9890	30900		29	Nanchang* (3-1)	T	1700	4320
Gansu	6	Lanzhou* (3-1)		1810	2900	Jilin	30	Changchun* (3-1)	B	2950	6990
Guizhou	7	Guiyang* (4-1)		1870	3320	Ninxia	31	Yinchuan* (3-1)		807	1177
Hebei	8	Langfang (1-1)		710	3810	Shandong	32	Jining (2-1)	B	1030	6850
	9	Qinghuangdao (2-1)	B	700	2680		33	Jinan* (5-0)	T	3170	5630
	10	Shijiazhuang* (4-1)	B	1940	8960		34	Qingdao (2-1)		2350	7070
	11	Tangshan (2-1)	B	2920	7000		35	Zoucheng (2-1)	B	250	1100
Henan	12	Nanyang (2-1)	B	1650	10400	Shanghai**	36	Shanghai (5-0)		1608	16740
	13	Xinyang (3-0)		1350	771	Shanxi	37	Taiyuan* (5-1)	B	2390	3150
	14	Xuchang (3-0)	T	360	4400	Shaanxi	38	Weinan (3-0)		880	5280
	15	Zhengzhou* (4-1)	T	2190	6270	Guangxi	39	Beihai (2-0)	B	510	1430
Hubei	16	Shishou (3-0)	B	141	660		40	Guilin (4-0)		610	4830
	17	Wuhan* (5-0)		4310	7490	Yunnan	41	Kunming* (5-0)		2110	4810
	18	Xiantao (3-0)	T	300	1590	Zhejiang	42	Hangzhou* (5-0)		3730	6220
	19	Suizhou (3-0)		1660	2570		43	Wenzhou (2-1)		1300	7370
Hunan	20	Changde (3-0)		1340	5950	Jiangsu	44	Wuxi (3-0)		2100	4330
	21	Changsha* (5-0)	T	1710	5820						
	22	Qiyang (2-1)	B	79	944						
	23	Shaoyang (2-1)	B	600	7160						
	24	Zhangjiajie (2-1)		450	1550						

*Capital of Province or Autonomous Region, usually with the highest density of population in the area.
** Municipality
[a] T = traffic related (see text); [b] B = high B/T ratio (see text)

Fig. 1. Sampling sites for ground-level whole air samples collected in China in January/February 2001. The first and the second number in parenthesis next to each city refer, respectively, to the number of ambient samples and roadside samples collected in that particular city. The population data by 2000 are from the official website of Ministry of Civil Affair of PR China: http://www.xzqh.org.cn/quhua/index.htm.

obvious VOC sources such as busy streets. Those samples are considered "ambient samples" because they are representative of the particular urban area where they were collected. A total of 27 samples (in 25 different cities) were collected next to streets with heavy traffic, and are therefore considered "roadside samples" (see Fig. 1 for details about the sampling distribution).

Two-liter electropolished, stainless-steel, evacuated canisters were used for sampling. To collect each whole air sample, a stainless-steel bellows valve was slightly

opened and the canister was filled to ambient pressure in about 2 min. The canisters were then shipped to our laboratory at the University of California, Irvine (UCI) and analyzed for carbon monoxide, methane, NMHCs, halocarbons, and alkyl nitrates. However, in this paper only methane and NMHCs will be discussed. The gas chromatographic system is extensively described in Colman et al. (2001) and Barletta et al. (2002). Briefly, for the NMHCs, 790 cm^3 of air were cryogenically preconcentrated at −196 °C in liquid nitrogen, and subsequently vaporized and split into five different column/detector combinations, the detectors being two Flame Ionization Detectors (FIDs), two Electron Capture Detectors (ECDs) and a Mass Spectrometer Detector (MSD). Our analytical accuracy ranges from 1% to 10%. The precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision is 2% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. Careful calibration procedures are used, whereby new standards are referenced to older certified standards, with appropriate checks for stability, and interlaboratory comparisons are routinely performed. The limit of detection (LOD) is 5 pptv for the NMHCs, and all the gases reported in this paper were present at mixing ratios above their detection limits.

3. Results and discussion

Methane and a total of 39 C_2–C_{10} NMHCs were quantified (Table 1). Although we recognize that the number of samples collected in each city is limited, for each city the average value of the samples was calculated. The lowest and highest mixing ratio for the 43 Chinese cities, expressed in part per billion by volume (ppbv), are reported in Table 1. To make a comparison with other Asian cities, NMHC data from one Chinese city (Changchun; Liu et al., 2000), Karachi (Pakistan; Barletta et al., 2002), Seoul (Korea; Na et al., 2003), Taipei (Taiwan; Ding and Wang, 1998) and Khatmandu (Nepal; Sharma et al., 2000) are also reported. In Changchun samples were collected at five different locations: roadside, downtown, industrial, residential, and comparison areas. The average mixing ratio for downtown, industrial, and residential locations was calculated and is reported in Table 1. In Seoul the average of the morning, afternoon and evening sampling was used. For some of the hydrocarbons, the concentration difference between the cleanest of the 43 Chinese cities and the dirtiest city was quite large. In general, the city with the lowest mixing ratio for a particular gas among the 43 Chinese cities was also cleaner than the comparison cities (although we recognize that comparison between sampling campaigns carried out in different season and different years must be carefully done). However, for combustion related compounds (ethyne and the majority of alkenes and aromatic compounds), the highest mixing ratios measured for the 43 Chinese city is also higher than Changchun and the other Asian cities. In Karachi, where the dominant source of short chain alkanes was found to be natural gas leakage, the mixing ratios of ethane, propane, and the butanes were higher than the maximum level measured in any of the 43 Chinese cities sampled in this study.

The maximum 1,3-butadiene and benzene mixing ratios (2.5 and 10.4 ppbv, respectively) exceed the Environmental Protection Agency Reference Concentration for Chronic Inhalation Exposure limit (RfC) of 0.9 ppbv for 1,3-butadiene and the Inhalation Minimal Risk Level (MRL) of 4.0 ppbv for benzene (US EPA, 2004a, b). Seven of the 43 cities had an average mixing ratio higher than the EPA RfC for 1,3-butadiene while eight cities were higher for benzene. Beijing, Changsha, Hefei, Kunming, and Suizhou show high average levels for both of these gases (Table 2). Thus, this study suggests a potential health risk in several Chinese cities.

The different distributions in mixing ratios for benzene, ethyne, toluene, and ethane in China are shown in Fig. 2. The average mixing ratio of these gases, together with standard deviations, is reported in Table 2 for each city. These gases are representative of different emission sources. Ethyne and benzene are usually associated with combustion processes (mainly from automobile exhaust in urban areas); toluene is emitted from vehicles, but painting and industrial processes (solvent application) are likely additional sources; and ethane is mainly related to leakage from LPG or natural gas. The cities where the highest mixing ratios for ethyne were observed (Kunming, Hefei, Beijing, Changsha, Guiyang and Suizhou) were also high for benzene and toluene confirming a general common source for those gases. Also, the toluene distribution showed high mixing ratios in Changde and in Shanghai, Hangzhou and Wenzhou along the eastern coast of China suggesting additional sources there. Although some of the cities with high levels of combustion related compounds were also high for ethane (Beijing, Suizhou, Changsha, and Guiyang), the mixing ratio distribution of ethane showed high levels in the northern area where Shijiazhuang, Taiyuan and Changchun are located (in those three cities, high levels of methane and, to a lesser extent, propane were also measured).

Correlations between the individual hydrocarbons were used to identify different sources of NMHCs. Ethyne is a characteristic product of combustion processes, while *i*-pentane is a marker for gasoline evaporation (although also emitted during combustion processes, but in much smaller amounts). In order to

Table 1
Minimum and maximum mixing ratios for 43 Chinese cities (part per billion by volume—ppbv; unless otherwise specified)

	This study Min–Max	Changchun[a]	Kathmandu[b]	Taipei[c]	Seoul[d]	Karachi[e]
Methane (ppmv)	1.889–2.356					6.3
Ethane	3.7–17.0		7.7	8.3	4.3	93
Ethene	2.1–34.8		48.4	14.1	5.2	19.0
Ethyne	2.9–58.3		36	15.1	7.0	18.0
Propane	1.5–20.8		6	6.4	9.8	35
Propene	0.2–8.2		12.8	4.6	1.1	5.5
i-Butane	0.4–4.6		16.4	2.4	5.2	11.0
n-Butane	0.6–14.5		42.2	5.2	7.8	19.8
1-Butene	0.07–2.4		2.5	0.9		1.1
i-Butene	0.1–4.0			2.7		1.2
trans-2-Butene	0.01–3.4					0.3
cis-2-Butene	0.02–2.7					0.2
i-Pentane	0.3–18.8	8.8	25.9	12.8	3.5	12.1
n-Pentane	0.2–7.7		24.8	4.3	3.2	13.4
1,3-Butadiene	0.02–2.5					0.8
Isoprene	0.04–1.7		0.3			0.8
trans-2-Pentene	0.02–5.3					
cis-2-Pentene	0.02–9.4					
2,2-Dimethylbutane	0.009–0.4					0.6
2,3-Dimethylbutane	0.01–5.0				1.3	0.5
2-Methylpentane	0.08–5.6	4.0	16.1		1.4	4.7
3-Methylpentane	0.1–3.6		13.4	2.3		3.1
n-Hexane	0.1–3.2	1.5	13.8		1.3	7.5
n-Heptane	0.06–3.4	1.5			1.2	3.9
n-Octane	0.04–1.3					1.1
n-Nonane	0.04–0.7				1.4	0.7
n-Decane	0.03–0.4					0.7
Benzene	0.7–10.4	9.0			1.6	5.2
Toluene	0.4–11.2	17.5			12.8	7.1
Ethylbenzene	0.1–2.7	2.9			1.8	
m-Xylene	0.2–10.1					2.1
p-Xylene	0.2–5.2					1.0
o-Xylene	0.1–6.9				1.5	1.1
i-Propylbenzene	0.007–0.2					0.05
n-Propylbenzene	0.02–0.3					0.2
3-Ethlytoluene	0.05–1.7					
4-Ethyltoluene	0.02–0.7					0.4
2-Ethyltoluene	0.01–0.5					0.4
1,3,5- Trimethylbenzene	0.04–1.1					0.4
1,2,4-Trimethylbenzene	0.1–2.9				1.5	1.0

[a]Liu et al. (2000).
[b]Sharma et al. (2000).
[c]Ding and Wang (1998).
[d]Na et al. (2003).
[e]Barletta et al. (2002)

determine the impact of combustion and gasoline evaporation on VOC concentrations, correlation coefficients (R^2) of the different hydrocarbons with ethyne and *i*-pentane were calculated for the 43 Chinese cities (Table 3). Short chain alkenes (ethene, propene, 1-butene, *i*-butene and 1,3-butadiene) and aromatic compounds showed a good correlation with ethyne ($R^2 > 0.6$; benzene being an exception with a correlation coefficient of 0.5) suggesting that their primary source is combustion. The majority of aromatic compounds also correlated well with *i*-pentane indicating that gasoline evaporation is likely an additional source. The lack of correlation of long chain alkanes (C_6–C_{10}) with ethyne together with their very good correlation with *i*-pentane

Table 2
Average mixing ratio expressed in part per billion by volume (ppbv) of ethane (C_2H_6), ethyne (C_2H_2), 1,3-butadiene, benzene (C_6H_6), and toluene (C_7H_8), measured in the 43 Chinese cities (see Figure 1). The one-sigma standard deviation (SD) is also reported

	C_2H_6	SD	C_2H_2	SD	1,3-Butadiene	SD	C_6H_6	SD	C_7H_8	SD
Beihai	4.8	0.08	4.0	1.1	0.05	0.05	0.8	0.2	0.5	0.3
Beijing	16.4	3.0	34.7	3.6	1.4	0.08	5.9	1.4	7.5	2.7
Bengbu	5.4	2.0	6.9	8.0	0.3	0.5	1.1	0.9	1.2	1.2
Changchun	15.7	15.3	13.4	6.9	0.7	0.7	2.9	2.7	2.1	1.3
Changde	6.3	1.4	5.2	2.6	0.2	0.2	3.4	4.2	7.9	12.3
Changsha	10.0	2.7	33.4	25.7	2.5	2.1	5.3	2.9	11.2	7.6
Chongqing	12.3	4.0	22.7	14.4	0.8	0.8	7.0	5.0	5.3	3.0
Guilin	5.8	0.3	4.5	1.2	0.08	0.06	1.0	0.3	3.7	4.5
Guiyang	8.3	3.5	27.0	26.2	0.8	1.3	10.4	14.5	7.5	7.2
Hangzhou	5.5	0.8	18.4	11.2	0.4	0.4	2.4	0.8	7.0	3.3
Hefei	7.4	4.4	39.8	62.7	1.9	3.2	4.9	5.6	8.1	9.2
Ji'an	4.4	0.8	4.3	1.3	0.1	0.2	1.4	0.8	0.8	0.2
Jinan	6.4	2.9	23.6	38.8	0.5	0.8	2.3	2.7	5.1	4.6
Jingdezhen	4.7	1.2	4.9	0.9	0.1	0.09	1.1	0.2	1.1	0.03
Jining	8.2	1.6	7.9	1.4	0.2	0.008	2.3	1.0	1.5	0.6
Jiujiang	4.3	0.9	4.8	3.1	0.2	0.3	1.1	0.7	1.3	0.9
Kunming	8.1	8.5	59.3	114.7	2.1	3.7	5.2	7.1	8.6	13.5
Langfang	6.1		5.1		0.1		1.4		1.1	
Lanzhou	6.1	4.8	9.6	14.1	0.3	0.5	1.9	2.5	4.7	4.6
Linchuan	5.3	1.1	10.3	8.8	0.6	0.8	2.5	1.4	2.0	1.5
Nanchang	4.9	1.4	19.8	23.3	0.8	1.0	2.2	1.9	3.4	3.5
Nanyang	6.6	2.5	5.5	3.7	0.06	0.03	2.0	1.0	1.1	0.1
Qingdao	8.3	4.9	3.5	0.3	0.1	0.1	1.4	1.1	1.3	0.7
Qinghuangdao	4.9	0.7	2.9	0.4	0.05	0.003	0.8	0.3	0.7	0.3
Qiyang	5.4	0.01	3.5	0.1	0.02	0.01	0.8	0.05	0.5	0.2
Shanghai	3.7	0.6	9.3	7.6	0.2	0.2	1.2	0.7	5.1	5.8
Shaoyang	5.2	2.1	3.2	0.6	0.05	0.007	0.9	0.3	0.5	0.06
Shijiazhunag	17.0	2.6	21.0	5.3	0.4	0.1	4.6	0.5	3.8	1.2
Shishou	5.6	1.2	4.9	1.2	0.1	0.08	1.0	0.04	0.8	0.1
Suizhou	10.6	3.2	26.1	27.8	1.1	1.1	4.0	2.7	7.6	6.6
Taihu (Wuxi)	6.8	0.4	11.9	7.2	0.7	0.5	2.3	0.9	3.2	1.9
Taiyuan	16.9	8.0	15.0	14.7	0.3	0.4	3.7	2.4	3.5	3.4
Tangshan	5.9	0.9	8.6	6.8	0.2	0.02	2.0	0.2	1.4	0.4
Weinan	5.4	3.0	6.6	3.6	0.1	0.08	1.4	0.8	1.2	0.7
Wenzhou	4.6	0.8	16.1	16.1	0.6	0.7	2.6	0.5	6.1	2.2
Wuhan	7.6	2.9	22.9	35.2	1.1	1.9	2.7	2.1	3.4	4.2
Xiantao	5.9	1.4	15.5	16.1	1.0	1.0	2.1	1.7	4.7	4.1
Xinyang	6.6	2.4	6.5	4.0	0.2	0.2	1.3	0.7	1.5	1.1
Xuchang	7.5	1.3	11.2	9.0	0.6	0.6	2.1	1.2	2.4	1.5
Yinchuan	4.4	2.8	5.2	3.6	0.1	0.09	0.7	0.4	0.9	0.6
Zhangjiajie	4.8	0.3	3.5	0.7	0.06	0.02	0.8	0.1	1.2	1.0
Zhengzhou	6.4	3.6	16.0	15.9	0.6	0.8	1.8	1.6	2.2	2.2
Zoucheng	3.9	0.7	3.5	0.5	0.1	0.1	0.9	0.2	0.5	0.2

indicates that solvent evaporation is more likely the main source for those gases. Finally, short chain (C_2–C_4) linear alkanes showed a lack of correlation with either ethyne or *i*-pentane suggesting additional sources for these gases.

Although the compounds that correlated well with ethyne (Table 3) are associated with combustion, several types of combustion processes should be considered. In urban environments, vehicular emissions are by far the most important combustion source (Watson et al., 2001). However, as mentioned earlier, the widespread use of coal and biofuel for a variety of applications throughout China must be considered as an additional source of combustion emitted compounds in urban areas.

In an attempt to differentiate between vehicular emissions and other combustion sources, the benzene to toluene ratio (B/T) was considered. Studies on

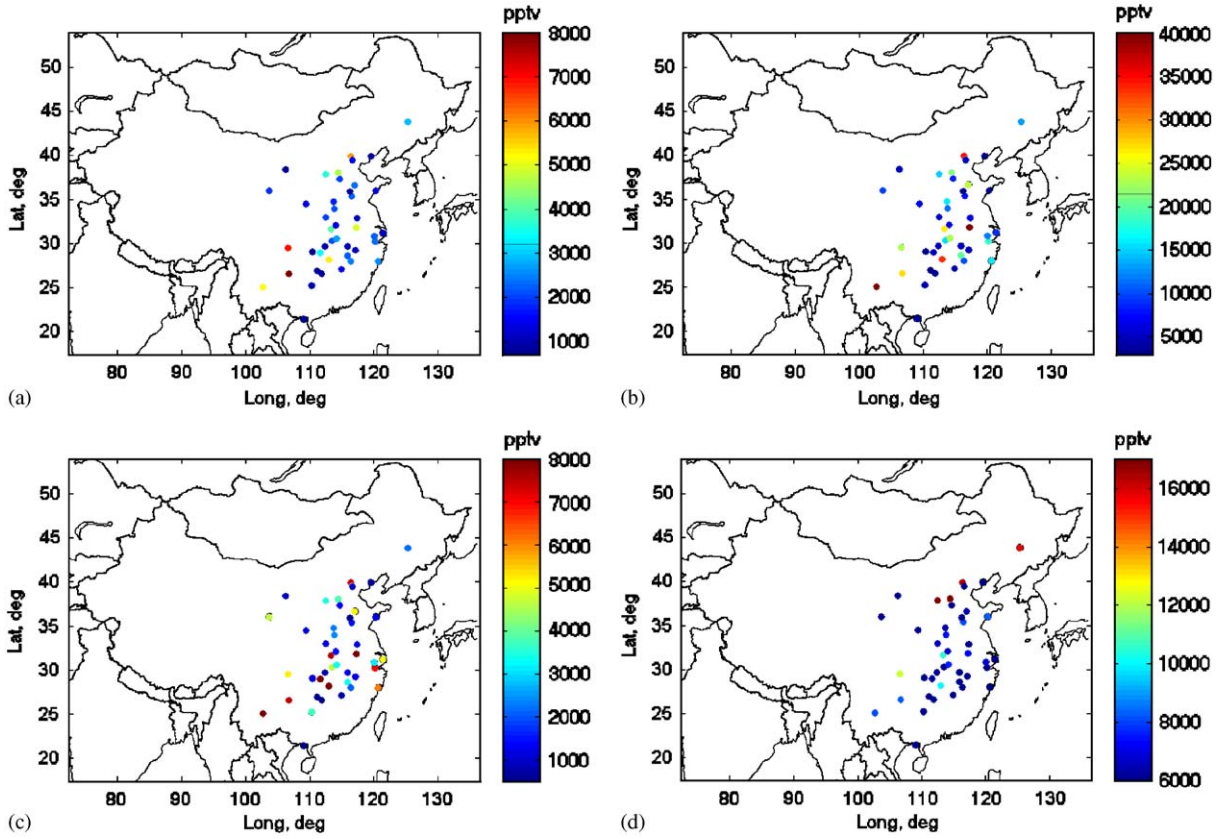


Fig. 2. Spatial distribution of (a) benzene, (b) ethyne, (c) toluene, (d) ethane mixing ratios.

vehicular exhaust suggest that the ratio of different aromatic compounds (particularly benzene and toluene) can be useful in identifying VOC sources, and a B/T ratio of around 0.5 (wt/wt) has been reported to be characteristic of vehicular emissions (Perry and Gee, 1995; Brocco et al., 1997). In order to verify if this ratio could be applied to the Chinese vehicular fleet, 27 roadside samples were collected in 25 different cities (see Fig. 1 for the sampling location). The samples were collected close to very busy streets and therefore are considered representative of the VOC composition of vehicular emissions in China. The B/T ratio was calculated and an average value of 0.6 (wt/wt) ($\sigma = 0.2$) was found.

The B/T ratio for the different Chinese cities in this study ranged from 0.2 to 2.2. To identify the cities with a B/T ratio characteristic of vehicular emission, the ratios were calculated for the individual samples collected in each city. Only cities with an average B/T ratio between 0.4 and 0.8, and a 1 σ value of 0.2 were considered. Hefei, Beijing, Xiantao, Changsha, Nanchang, Jingdezhen, Jiujiang, Xuchang, Zhengzhou and Jinan had a B/T ratio close to 0.6, suggesting vehicular emissions as the main source of VOCs for these ten cities (''traffic related cities''). Moreover, the slopes resulting from the plot of selected hydrocarbons (benzene, toluene and 1,3-butadiene) with ethyne and ethene for the 27 traffic samples and for the cities with a B/T ratio of 0.6 was not significantly different (Table 4). This is an additional indication that for the ten ''traffic related cities'' vehicular combustion is the main source of combustion related hydrocarbons.

Some of the remaining Chinese cities had a relatively high B/T ratio. The benzene mixing ratio was equal or higher than toluene in fifteen Chinese cities (Beihai, Changchun, Chongqing, Ji'an, Jining, Linchuan, Nanyang, Qinghuangdao, Qiyang, Shaoyang, Shijiazhuang, Shishou, Taiyuan, Tangshan, and Zoucheng). Higher benzene emissions with respect to toluene have been reported for biofuel and charcoal burning (Andreae and Merlet, 2001), and a B/T ratio higher than 1 has also been reported for coal burning (Moreira dos Santos et al., 2004). The correlation of some hydrocarbons can highlight other differences between these 15 cities (B/T ratio >1.0) and the 10 traffic related cities (B/T$\sim$0.6). The emission of benzene and ethene with respect to ethyne was higher in the 15 cities where the B/T ratio was greater than 1. The relatively good

Table 3
Correlation coefficient (R^2) of the identified NMHCs with ethyne and *i*-pentane for the 43 Chinese cities sampled. The number in parenthesis is the R^2 resulting after one city was removed (Qingdao for *n*-butane, *n*-pentane and *n*-hexane; Jiujiang for trans-2-butene; Changsha for 2,3-dimethylbutane; Changde for *n*-heptane)

	R^2			R^2	
	Ethyne	*i*-Pentane		Ethyne	*i*-Pentane
Ethane	0.20	0.14	2-Methylpentane	0.48	0.89
Ethene	0.86	0.54	3-Methylpentane	0.46	0.85
Ethyne	—	0.45	*n*-Hexane	0.19 (0.34)	0.50
Propane	0.06	0.07	*n*-Heptane	0.14 (0.43)	0.27 (0.76)
Propene	0.79	0.58	*n*-Octane	0.47	0.72
i-Butane	0.21	0.38	*n*-Nonane	0.48	0.76
n-Butane	0.01 (0.28)	0.14 (0.37)	*n*-Decane	0.51	0.83
1-Butene	0.56	0.60	Benzene	0.53	0.34
i-Butene	0.71	0.73	Toluene	0.63	0.56
trans-2-Butene	0.37	0.55 (0.77)	Ethylbenzene	0.61	0.56
cis-2-Butene	0.41	0.63	*m*-Xylene	0.70	0.75
i-Pentane	0.45	—	*p*-Xylene	0.65	0.76
n-Pentane	0.15 (0.51)	0.52 (0.86)	*o*-Xylene	0.70	0.75
1,3-Butadiene	0.81	0.69	*i*-Propylbenzene	0.62	0.69
Isoprene	0.47	0.55	*n*-Propylbenzene	0.76	0.78
trans-2-Pentene	0.47	0.89	3-Ethlytoluene	0.70	0.79
cis-2-Pentene	0.37	0.83	4-Ethyltoluene	0.72	0.79
2,2-Dimethylbutane	0.47	0.52	2-Ethyltoluene	0.71	0.72
2,3-Dimethylbutane	0.30 (0.53)	0.70	1,3,5-TMB[a]	0.69	0.78
			1,2,4-TMB[b]	0.60	0.73

[a]1,3,5-Trimethylbenzene.
[b]1,2,4-Trimethylbenzene.

Table 4
Correlation of selected combustion related compounds with ethyne and ethene for the traffic samples and for the 10 cities with a B/T ratio of about 0.6 (“traffic related cities”)

	Traffic samples		“Traffic-related” Cities	
	Slope	R^2	Slope	R^2
Benzene/ethyne	0.11	0.8	0.13	0.9
Benzene/ethene	0.17	0.8	0.17	0.9
Toluene/ethyne	0.24	0.7	0.24	0.8
Toluene/ethene	0.34	0.7	0.31	0.9
1,3-Butadiene/ethyne	0.04	0.7	0.05	0.7
1,3-Butadiene/ethene	0.06	0.7	0.07	0.9

correlation found between benzene and ethyne when all the 43 cities were grouped together ($R^2 = 0.53$), substantially improves if the two groups of cities are separated (Fig. 3a). A slope of 0.13 ($R^2 = 0.86$) is obtained for the “traffic related cities” while a slope of 0.26 ($R^2 = 0.93$) for the high B/T ratio 15 cities is obtained. The plot of ethene versus ethyne shows the same behavior, where higher ethene emissions correspond to the city with a high B/T ratio (Fig. 3b). In a previous study benzene versus ethylbenzene had a very good correlation in biomass combustion samples with a slope significantly higher than for vehicular traffic (Monod et al., 2001). Our benzene versus ethylbenzene plot has a slope of 4.9 ($R^2 = 0.81$) for the 15 cities, and a slope of 2.0 ($R^2 = 0.82$) for the “traffic related” cities (Fig. 3c). These findings, the higher emission of benzene with respect to toluene (B/T ratio > 1) and benzene with respect to ethylbenzene, suggest that the main combustion source responsible for the emission of the NMHCs for the 15 selected cities is likely not vehicular combustion, but possibly biofuel and/or coal burning.

Finally, the analysis of the relative abundance of a selected hydrocarbon (or a selected fraction of hydrocarbons) can help highlight the different distributions of NMHCs in different areas of China (Table 5). Ethyne and the alkenes’ fraction were not significantly different in the three groups of cities (“traffic related”, cities with a B/T ratio > 1, and other cities). The fractional importance of benzene in BTEX (benzene, toluene, ethylbenzene and xylenes) was higher in the cities with a B/T ratio > 1. The abundance of the light alkane fraction (ethane, propane and the butanes) relative to the total NMHCs was also significantly higher in the cities with a B/T ratio > 1. Propane and butanes are generally associated with LPG leakage while natural gas leakage is responsible for methane and ethane emissions. The

ethane fraction of the short chain alkanes was almost double in the cities with a B/T ratio > 1 relative to the other Chinese cities, while no significant differences were observed for the others light alkanes.

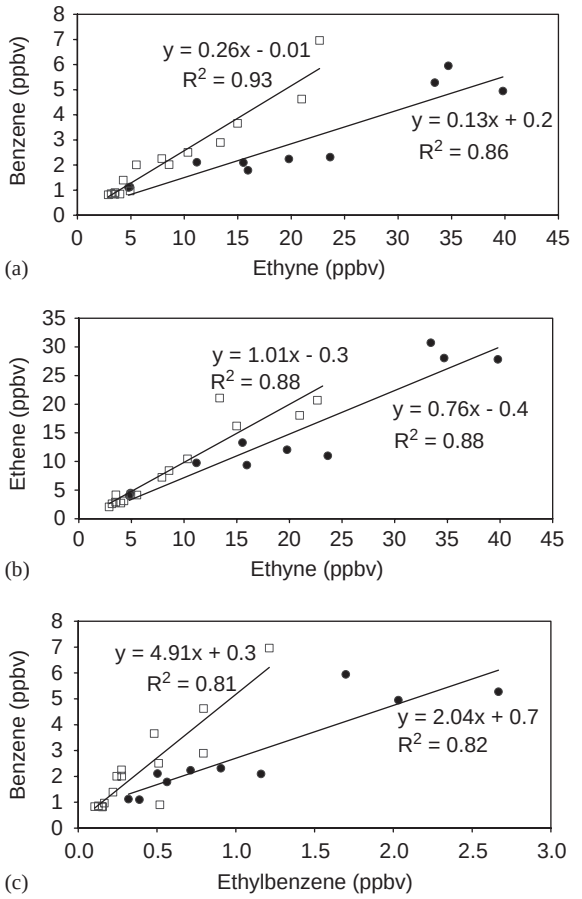


Fig. 3. Correlation between (a) benzene and ethyne, (b) ethene and ethyne and (c) benzene and ethylbenzene for the cities showing a B/T ratio of about 0.6 (solid circles) and the cities showing a B/T ratio > 1 (open squares).

When the 43 Chinese cities are grouped together, the overall average methane mixing ratio was 1.998 ppmv, compared to a background concentration in northern mid-latitudes of 1.820–1.850 in December 2001 (Simpson, 2004, personal communication). This relatively low enhancement in methane concentration in the urban areas of China does not support a large contribution of natural gas leakage to the light alkane concentrations. However, if the cities are divided in the three groups reported in Table 5, an average methane of 1.981 ppmv was measured for the "traffic related cities" while the average methane mixing ratio measured for the "other cities" was 1.986 ppmv. However, for the cities with B/T ratio > 1, the average methane concentration was 2.044 ppmv suggesting some influence of natural gas leakage. This is consistent with the elevated ethane concentrations relative to other short chain alkanes observed in those 15 cities.

Another interesting aspect is the distribution of isoprene in urban atmospheres. The main source of isoprene is biogenic reaching a maximum during the summer months (Guenther et al., 1993; Jobson et al., 1994). However, vehicular emissions have been reported to be a significant source of isoprene in some urban areas (McLaren and Singleton, 1996; Starn et al., 1998; Barletta et al., 2002). Mixing ratios higher than 0.5 ppbv were measured in 11 Chinese cities even though the sampling campaign took place during winter. Roadside samples had higher isoprene mixing ratios with an average of 857 pptv ($\sigma = 832$), compared to the average mixing ratios for the ambient samples, 384 pptv ($\sigma = 335$). To assess vehicular combustion (or combustion in general) as a source of isoprene during the winter season, correlations between isoprene and selected hydrocarbons, known to be markers of combustion, were investigated. In Table 6, the correlation coefficients and slopes of isoprene versus ethyne, 1,3-butadiene, ethene and ethylbenzene are reported for the roadside samples, the cities where the main VOC source was vehicular emissions, the cities with a high B/T ratio, and the other Chinese cities sampled. The average isoprene

Table 5
Relative abundance of selected hydrocarbons (or group of hydrocarbons) to the total NMHCs, alkanes fraction, or BTEX fraction (benzene, toluene, ethylbenzene, xylenes). SD—Standard Deviation given in parenthesis

% Relative Abundance	Cities with B/T 0.6 (SD)	Cities with B/T > 1 (SD)	Other cities (SD)
Ethyne/NMHCs	19 (5)	18 (2)	18 (6)
Alkenes/NMHCs	29 (4)	25 (6)	24 (6)
Benzene/BTEX	19 (4)	36 (4)	22 (9)
Light alkanes[a]/NMHCs	20 (8)	33 (9)	24 (11)
Ethane/alkanes	24 (8)	44 (7)	31 (10)
Propane/alkanes	16 (9)	18 (4)	16 (4)
Butanes/alkanes	16 (6)	14 (2)	15 (4)

[a]Light alkanes : ethane, propane, *i*-butane, *n*-butane.

Table 6
Isoprene correlation with combustion emitted compounds for the roadside samples, the "traffic related cities", for the cities where a high B/T ratio was measured, and for the other Chinese cities sampled

	Roadside	Traffic related cities	High B/T cities	Other cities
	R^2 (slope)	R^2 (slope)	R^2 (slope)	R^2 (slope)
Isoprene vs. ethyne	0.73 (0.03)	0.35 (0.02)	0.39 (0.02)	0.46 (0.02)
Isoprene vs. ethene	0.75 (0.04)	0.53 (0.03)	0.39 (0.01)	0.53 (0.03)
Isoprene vs. 1,3-butadiene	0.91 (0.66)	0.80 (0.51)	0.40 (0.41)	0.53 (0.44)
Isoprene vs. ethylbenzene	0.83 (0.44)	0.71 (0.48)	0.30 (0.28)	0.28 (0.21)
Average isoprene, pptv (SD)	857 (832)	596 (446)	215 (164)	408 (313)

mixing ratio is also reported. Although, we cannot explain the poor correlation with ethyne (for both the traffic related cities and the high B/T cities), the good correlation between isoprene and the other hydrocarbons (with the exception of ethyne), and the high isoprene levels for the traffic related cities, suggests that vehicular emissions are responsible for about 60% ($R^2 \approx 0.6$) of isoprene observed in these cities, during this winter season. The poor correlation of isoprene with ethyne, for both the traffic related cities and the high B/T cities, is partly the result of the different lifetimes of the two hydrocarbons. Combustion sources are responsible for about 40% of isoprene observed in high B/T cities and in the other Chinese cities but the type of combustion responsible for NMHC emissions was not clearly identified (i.e. coal burning, biofuel burning, vehicular emissions).

4. Conclusions

A sampling campaign was conducted in China in January/February 2001 in order to characterize the distribution of urban VOCs and to identify likely sources of NMHCs.

Using a B/T ratio of 0.6 ± 0.2, two groups of cities were identified: 10 cities with a ratio in the range of 0.4–0.8 and 15 cities with a ratio greater than 1. The B/T ratio of about 0.6 (literature values of 0.5 for western countries have been reported) and the good correlation with *i*-pentane, suggest vehicular emissions (vehicular combustion and gasoline evaporation) are likely the main sources of the identified hydrocarbons for those cities. Combustion is still the main source of NMHCs for the second group of cities, but because of the high B/T ratio and the differences in the slopes when combustion related gases are plotted, the main combustion source is likely coal and/or biofuel usage. Combustion appears to be the source of about half of the winter isoprene observed in the 43 Chinese cities. It also appears that natural gas leakage or some other methane/ethane source impacts NMHC concentrations in the 15 cities that had $B/T > 1$.

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