Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China

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HIGHLIGHTS

- We present VOC species profiles for China's gasoline evaporation.
- Refueling vapor compositions were compared with vapor recovery systems on/off.
- More alkenes in China's gasoline vapor cause higher ozone formation potential.
- Ratios like i-pentane to benzene or toluene are distinctive for gasoline vapors.

ARTICLE INFO

ABSTRACT

In China, fast increase in passenger cars and gasoline consumption with yet quite limited vapor recovery during gasoline distribution has procured growing concern about gasoline evaporation as an important emission source of volatile organic compounds (VOCs), particularly in megacities hard-hit by air quality problems. This study presents VOC species profiles related to major pathways of gasoline evaporative loss in China, including headspace displacement, refueling operations and spillage/leakage. Apart from liquid gasoline and headspace vapors, gasoline vapors emitted when refueling cars in service stations or tank trucks in oil marketing depots were also sampled in situ with vapor recovery units (VRUs) turning on/off. Alkanes, alkenes and aromatic hydrocarbons accounted for 55–66, 21–35 and 4–8% in refueling vapors, 59–72, 18–28 and 4–10% in headspace vapors and 33–51, 8–15 and 38–48% in liquid gasoline samples, respectively. During refueling with VRUs turning on, total VOCs in vapors were less than one fifth of that with VRUs turning off, and aromatic hydrocarbons had higher weight percentages of about 8% in contrast with that of about 4% during refueling with VRUs turning off. Refueling vapors, especially for that with VRUs turning off, showed a larger fraction of light hydrocarbons including C_3–C_5 light alkenes when compared to headspace vapors, probably due to splashing and disturbance during filling operation. In refueling or headspace vapors the ratios of i-pentane/benzene, i-pentane/toluene, and MTBE (methyl tert-butyl ether)/benzene ranged 8.7–57, 2.7–4.8, and 1.9–6.6, respectively; and they are distinctively much higher than those previously reported in vehicle exhausts. Calculated normalized reactivity or ozone formation potential of the gasoline vapors in China ranged 3.3–4.4 g O_3 g^{-1} VOC, about twice that of gasoline headspace vapors reported in USA as a result of larger fractions of alkenes in China's gasoline vapors. The results suggested that reducing VOC emission from gasoline distribution sector would particularly benefit ground-level ozone control in China.

1. Introduction

Volatile organic compounds (VOC) are precursors of secondary pollutants like ozone (Carter, 1994; Bowman et al., 1995) and secondary organic aerosols (SOA) (Odum et al., 1997). Chemical

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characterization of emission sources, such as vehicle exhausts (Schauer et al., 1999, 2002; Ho et al., 2009) and biomass burning (Andreae and Merlet, 2001; Schauer et al., 2001), is essential for complete bottom-up compiling of VOC emission inventories, or for top-down interpretation of VOC emission sources with measured ambient data. Fuel distribution systems are among important evaporative VOC emission sources. As diesel fuel contains heavier hydrocarbons with relatively lower vapor pressures, evaporative loss from diesel fuel is considered to be negligible compared to that from gasoline fuel.

Gasoline is a mixture of VOC, mostly C_4–C_9 hydrocarbons that can freely evaporate at ambient temperatures. Evaporation of gasoline during its distribution not only causes economic loss, but also contributes substantially to VOC in ambient air. Two air pollution concerns from gasoline dispensing facilities are the amounts of VOC and toxic compounds that are emitted into the atmosphere. According to the *European Emission Inventory Guidebook (EEIG) 2009* (updated July 2012, http://eea.europa.eu/emep-eea-guidebook), the contribution of evaporative emissions to total non-methane VOC from road transport ranged from 2.9% to 16.5% for various European countries in 2006. Meanwhile, some compounds contained in gasoline, like benzene, have adverse impacts on human health, and therefore gasoline evaporation would also induce extra exposure to hazardous air pollutants especially for related employees, such as workers in service stations (Brugnone et al., 1999; Wu et al., 2006; Karakitsios et al., 2007; de Oliveira et al., 2007).

As summarized in USEPA's *AP-42* or above mentioned *EEIG*, in many studies have been conducted on emission factors during gasoline distribution from refinery to tanks of passenger cars. These emission factors have also been adopted in estimating national and regional VOC evaporative emission of gasoline in China or in Asia (Klimont et al., 2002; Streets et al., 2003; Wei et al., 2008; Bo et al., 2008; Zhang et al., 2009). In the developed world wide application of gasoline vapor recovery technologies in gasoline dispensing facilities, including Stage I and Stage II vapor recovery systems in service stations, vapor recovery units in storage tanks and onboard refueling vapor recovery (ORVR) in newly manufactured cars, have greatly reduced gasoline evaporation in distribution facilities and processes (Wu et al., 2006). As for China, fossil-fuel use in recent decades increased rapidly and meanwhile curbing air pollution is becoming a challenge particularly in large cities (Shao et al., 2006; Chan and Yao, 2008; Zhang et al., 2012a), oil evaporative loss has therefore gradually become a concern. However, till 2002 Stage I recovery in service stations was only available in Beijing among China's large cities and economic loss due to evaporative loss of gasoline in China then was estimated to reach about 750 millions RMB (about 120 millions USD), with an emission factor of 2.2 kg t^{-1} in Beijing and 4.2 kg t^{-1} in the other China cities (Shen et al., 2006). These emission factors by Shen et al. (2006) were also adopted very recently for the estimation of gasoline evaporative loss in Beijing (Su et al., 2011) and in the Pearl River Delta region (Yu et al., 2011). As addressed in GB 20950-2007, implementation of emission control in China's bulk gasoline terminals had been just required since May 1st 2008, January 1st 2010 and January 1st 2012, respectively, for the Beijing–Tianjian region, the Pearl River Delta region and the Yangtze River Delta region, which are three major densely populated and economically developed city clusters or megacities in China. Receptor modeling based on observed data had revealed that VOCs from oil evaporation contributed 7–30% in Beijing (Yuan et al., 2009; Wang et al., 2010), 15% in Shanghai (Cai et al., 2010), 4.3–7.6% in Hong Kong (Lau et al., 2010) and 5–10% in the Pearl River Delta region (Liu et al., 2008b; Ling et al., 2011; Zhang et al., 2012b, 2013) to the total man-made VOC emission.

Gasoline evaporation mainly occurs during refueling operations (transferring from bulk storage tanks into transport vehicles like road tankers and dispensing from service station tanks into cars) and escaping of vapors from storage tanks (bulk storage tanks, service station storage tanks and vehicle fuel tanks). Emission from storage tanks includes displacement emissions due to displacement of headspace vapor by the incoming gasoline, withdrawal emissions due to intake of air via the pressure/vacuum relief valves followed by further evaporation into diluted vapor space to restore the equilibrium, and breathing emissions caused by temperature variations and changes in the barometric pressure which in turn cause expansion and contraction of both liquid and vapor within the tank. Other minor gasoline evaporative emissions include spillage when transferring gasoline from one form of container to another, leakage from storage and handling equipment, and seepage of gasoline liquid through parts of handling equipment. Although focus has been always put on estimating VOC emission rates, species profiles are also very important for studying the health/ecological effects and atmospheric activity of VOCs emitted. To obtain species profiles for VOC emission from gasoline distribution, we should mainly consider three categories of emissions: headspace vapor typical of storage tanks' loss as measured previously by Na et al. (2004) and Liu et al. (2008a); gasoline compositions typical of spillage/leakage loss as measured previously by Schauer et al. (2002); and more importantly vapor evolved as a result of splashing and turbulence during filling vehicle tanks. Till present the speciation of VOCs from oil evaporation is quite limited in China (Liu et al., 2008a). The present study was designed to chemically characterize the above-mentioned three types of evaporative emissions related to current gasoline distribution in China, in order to check if these species profiles are consistent with those in other regions, to obtain measured gasoline evaporation source profiles necessary for source attribution and apportioning using receptor models such as chemical mass balance (CMB) (Watson et al., 2001; Borbon et al., 2003), and to assess related hazardous effects and potentials to form secondary pollutants like ozone (Harley et al., 2000).

2. Sampling and chemical analysis

In China, oil refining and distribution facilities are predominately shared by the two large state-owned companies, PetroChina and Sinopec. Quite a small portion of gas stations are private with their gasoline supplied only from bulk storage tanks or marketing depots owned by the two companies. In the present study we conduct our measurements in Guangzhou, which is a central city in the Pearl River Delta, one of the most economically developed region in south China. As one of the pollution control measures to guarantee good air quality during the 2010 Asian Games in Guangzhou, Stage I and Stage II recovery systems in service stations and vapor recovery units (VRU) in bulk storage tanks were installed just before 2010.

2.1. Vapor sampling during refueling operations

In Guangzhou three service stations belonging to PetroChina, Sinopec and a private enterprise, respectively, were randomly chosen for gasoline vapor sampling during refilling the car tanks. These stations all had Stage I recovery for storage tanks and Stage II recovery during refueling cars. Vapors were collected using 2-L stainless steel evacuated canister about 2 cm above the car tank vents when refueling with the self-closing oil filler (SOF). In each service station five samples were collected when the vacuum assisted Stage II recovery systems were turned on and another five samples were collected when the recovery systems were turned off.

Three oil marketing depots with bulk gasoline storage tanks, where gasoline is dispensed to service stations by tank trucks, were

selected for vapor sampling when refueling tank trucks. The three oil marketing depots respectively belong to PetroChina, Sinopec and Southernpec, a reformed subordinate enterprise of Sinopec. Similar to vapor sampling in service stations, in each marketing depots five samples were collected when filling gasoline to tank trucks when VRU was turned on and another five samples when VRU was turned off.

To check the interference of ambient air on the VOC compositions of gasoline vapors during refueling, two ambient air samples upwind each of the service stations and the oil marketing depots were also collected for comparison.

2.2. Gasoline and headspace vapor

In each service stations we fully filled two 10-L steel oil cans for Grade 93# gasoline and another two for Grade 97# gasoline. These two grades were the most widely used particularly in developed regions in China. These oil cans were tightly capped, transported back to lab and then stored at 0 °C before used for the analysis of headspace vapors and gasoline compositions.

Reid vapor pressure (RVP) is used to measure gasoline's inherent tendency to evaporate at 38 °C with vapor/liquid ratio of 4/1 (EMEP/CORINAIR Emission Inventory Guidebook-2007; Harley et al., 2000). Since headspace vapor pressure varies with temperature, in the present study we measured gasoline headspace vapor when vapor and liquid equilibrated at 25 °C, which is about the annual average temperature in Guangzhou. As indicated by Harley et al. (2000), the relative composition of headspace vapors is less variable than loss rate under different temperatures, because the vapor pressures of all compounds present in gasoline are affected similarly by changes in temperature. 10 ml liquid gasoline were drawn from the gasoline cans and transferred to a 50 ml amber VOA glass vial with a plastic screw cap and a Teflon-lined septum. The vial was capped immediately after introducing gasoline and then kept at room temperature (25 °C) for at least 3 h for vapor–liquid equilibrium. A 3 L Tedlar bag fitted with a Teflon QuickConnect connector was pre-filled with 2 L pure nitrogen and 20 μL headspace vapor from each vial was injected to the bag using a 100 μL gas-tight syringe.

2.3. Lab instrumental analysis

Samples collected in canisters or prepared in Tedlar bags were analyzed for speciated hydrocarbons using a Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). Detailed cryogenically concentration steps are described elsewhere (Wang and Wu, 2008; Zhang et al., 2012b). Briefly, VOCs inside the canisters were initially concentrated using liquid-nitrogen cryogenic trap at −160 °C. The trapped VOCs were then transferred by pure helium to a secondary trap at −40 °C with Tenax-TA as adsorbent. Majority of H_2O and CO_2 were removed during these two steps. The secondary trap was then heated to get target VOCs transferred by helium to a third cryo-focus trap at −170 °C. After the focusing step, the trap was rapidly heated and the VOCs were transferred to the GC-MSD/FID system. The mixture was firstly separated by an HP-1 capillary column (60 m × 0.32 mm × 1.0 μm, Agilent Technologies, USA) with helium as carrier gas, and then split into two ways: one is to a PLOT-Q column (30 m × 0.32 mm × 2.0 μm, Agilent Technologies, USA) followed by FID detection of C_2–C_3 hydrocarbons; another is to a 65 cm × 0.10 mm I.D stainless steel line followed by MSD detection of C_4–C_{12} hydrocarbons. The GC oven temperature was programmed to be initially at 10 °C, holding for 3 min; increasing to 10 °C at 15 °C min^{-1}, then to 120 °C at 5 °C min^{-1}, and then to 250 °C at 10 °C min^{-1} and holding for 10 min. The MSD was used in SCAN mode with m/z ranges from 25 to 225 amu and the ionization method was electron impacting (EI). For gasoline composition, instead of pre-concentration by the Entech 7100, 1 μL liquid gasoline was injected to the GC in split mode and determined by the same GC-MSD/FID system as canister samples. The total ion chromatographs for liquid gasoline, headspace vapors, and vapors during refueling were showed in Fig. 1.

2.4. Quality control and quality assurance

Before sampling, all canisters were flushed at least five times by repeatedly filling and evacuating humidified zero air. In order to check if there was any contamination in the canisters, all canisters were evacuated after the cleansing procedures, re-filled with pure nitrogen, stored in the laboratory for at least 24 h, and then analyzed the same way as field samples to make sure that all the target VOC compounds were not present. Tedlar bags were also flushed and checked before use similar to the canisters.

Target compounds were identified based on their retention times and mass spectra, and quantified by external calibration method. C_4–C_{11} hydrocarbons were determined based on MSD signals, while C_2 and C_3 hydrocarbons were determined based on FID signals. For ambient air samples, the calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixtures (Spectra Gases Inc., NJ, USA) of 57 non-methane hydrocarbons (NMHCs) to 0.5, 1, 5, 15 and 30 ppbv. The calibration curves were obtained by running the five diluted standards plus humidified zero air the same way as the field samples. The analytical system was challenged daily with a one-point (typically 1 ppbv) calibration before running air samples. If the response was beyond ± 5% of the initial calibration curve, recalibration was performed. For analysis of refueling vapor samples in canisters or diluted headspace samples in Tedlar bags, 50 ml air samples were introduced and the calibration standards were prepared by dynamically diluting the 1.0 ppmv PAMS standard mixture to 0.10, 0.25, 0.50 ppmv plus 1.0 ppmv (original without dilution) and running them the same as the vapor samples. The precision of VOCs measurements varied by groups, and was within 5% for alkanes, alkenes and alkynes, 3% for aromatics, and 6% for MTBE. The measurement accuracy was determined by the difference between the measured and true values of the standard gases. The measurement accuracy also varied by group and was within 7% for alkanes, alkenes and alkynes, 5% for aromatics, and 8% for MTBE.

As indicated by the study of Harley et al. (2000), headspace vapor from different grades of gasoline had quite similar hydrocarbon compositions or normalized activities; previously study about gasoline headspace vapors (Na et al., 2004; Liu et al., 2008a) or emission inventories did not make a discrimination of different grades of gasoline. Therefore, for the convenience of the use of our measured results, in the present study vapors or liquid gasoline compositions for grade 97# and 93# gasoline were pooled together and we report average weight percentages and their ranges (Table 1).

3. Results and discussion

3.1. Species profiles

Mass concentrations of total and individual NMHCs observed just above the tank vent when filling cars in the service station or filling tank trucks in the marketing depots were about 39–242 times that in ambient air upwind the service stations or bulk
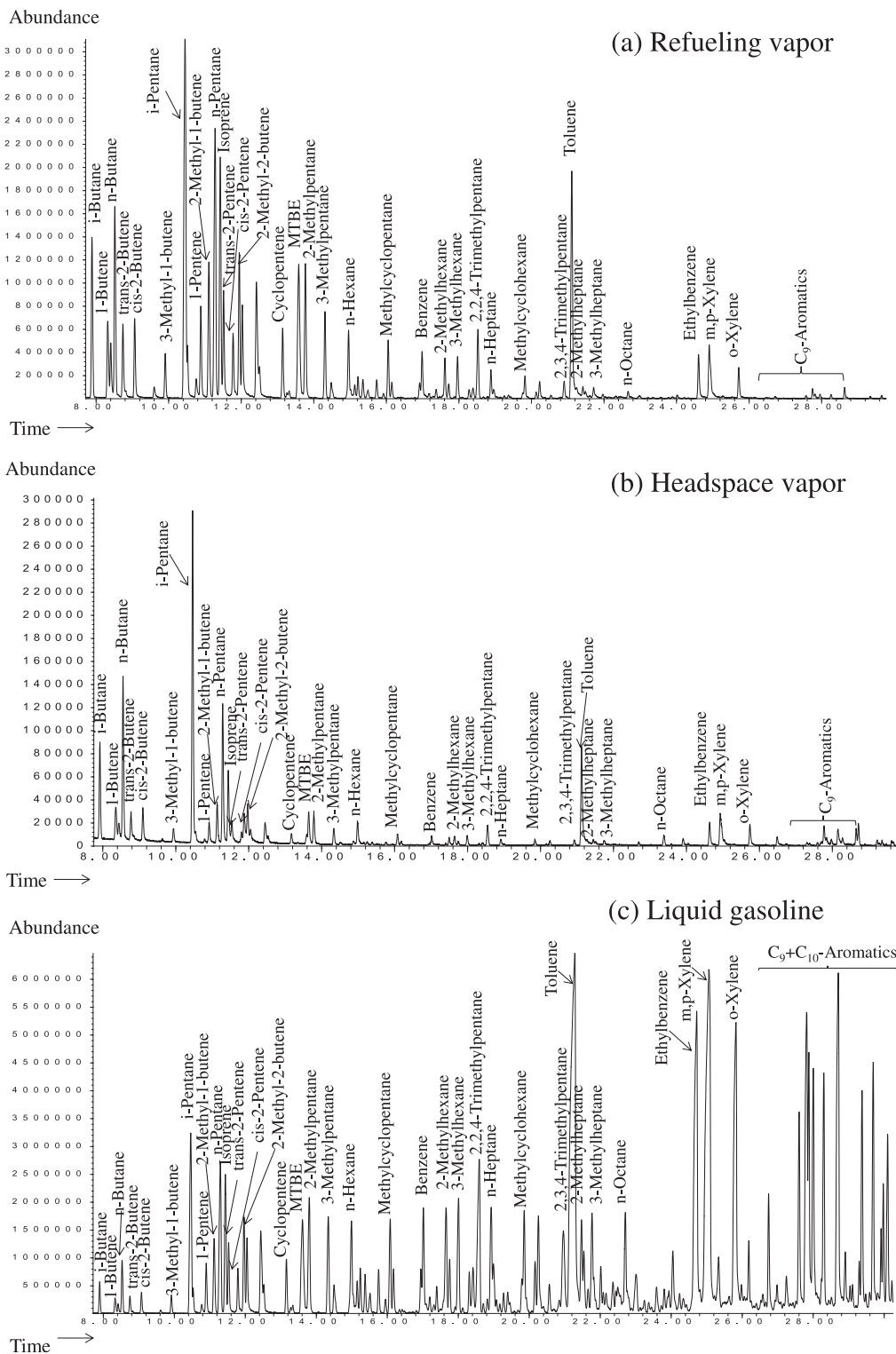
Fig. 1. Typical total ion chromatographs of VOC species in: (a) refueling vapors, (b) headspace vapors and (c) liquid gasoline.

storage tanks, thus during field sampling the impact of VOCs in ambient air on the compositions of the refueling vapors was negligible. Table 1 presents the group weight percentages of VOCs detected in refueling vapors with VRUs turning on/off. Although headspace vapor compositions can be theoretically predicted following vapor–liquid equilibrium relationships (Harley et al., 2000), it is more straightforward to directly measure the

compositions at a fixed temperature as we did at 25 °C in the present study, particularly during refueling operation when vapor–liquid equilibrium is not attained due to splashing and disturbance. Detailed species compositions of vapors and gasoline samples were presented in Table A.1 as supporting materials. Compositions of gasoline and headspace vapors in the present study or investigated previously in South Korea (Na et al., 2004), the United States

Table 1
Group weight percentages of VOCs in refueling vapors, headspace vapors and liquid gasoline from this study in comparison with those from previous studies.

Category	Vapor/refueling cars[a]		Vapor/refueling tank trucks[a]		Headspace vapor[a]	Liquid gasoline[a]	Headspace vapor[b]	Headspace vapor[c]	Headspace vapor[d]	Liquid gasoline[e]
	VRU on mean (range)	VRU off mean (range)	VRU on mean (range)	VRU off mean (range)	Mean (range)	Mean (range)	Mean	Mean	Mean	mean
n-Alkanes	27.69(17.77−40.56)	24.40(17.05−35.27)	22.61(9.25−32.77)	17.15(11.42−25.13)	29.95(24.00−34.15)	10.61(10.12−11.92)	23.76	31.68	8.11	6.74
Branched alkanes	35.46(26.95−42.94)	35.28(27.59−45.08)	40.62(27.58−53.47)	34.58(24.86−43.16)	37.91(35.70−47.30)	26.55(22.03−39.34)	60.22	46.47	22.87	44.29
n-Alkenes	19.35(10.97−28.14)	23.45(12.78−32.37)	19.48(11.16−27.41)	31.72(20.16−45.98)	15.34(9.11−19.25)	6.34(4.72−8.80)	0.28	14.74	15.3	1.62
Branched alkenes	1.46(0.79−2.47)	2.52(1.24−3.24)	3.23(1.63−5.28)	3.75(2.73−5.00)	6.20(5.74−11.98)	4.12(3.18−6.37)	0.03	3.88	10.19	1.71
Alkyne	0.21(0.06−0.37)	0.01(ND−0.05)	0.11(0.04−0.18)	ND	0.02(ND−0.07)	0.02(ND−0.04)	ND	ND	ND	ND
Cycloalkanes	2.01(1.42−2.74)	3.17(1.63−4.45)	2.59(1.73−4.12)	3.60(1.80−5.27)	1.00(0.85−1.88)	3.92(3.18−5.37)	5.29	1.61	2.79	5.93
Cycloalkenes	ND	ND	ND	ND	0.62(0.54−0.66)	0.55(0.36−0.72)	0.02	ND	0.49	0.14
Aromatic hydrocarbons	8.03(4.36−12.65)	3.98(2.55−5.53)	8.18(2.74−16.51)	3.57(2.38−4.69)	8.09(7.03−11.93)	41.36(37.90−47.51)	2.86	1.62	32.32	26.12
MTBE	5.78(2.60−8.56)	7.19(5.16−8.61)	3.18(1.98−4.45)	5.63(4.86−6.13)	0.87(0.73−1.25)	6.53(3.77−8.81)	0.21	ND	ND	13.46

ND: not detected.
[a] This study.
[b] Harley et al., 2000.
[c] Na et al., 2004.
[d] Liu et al., 2008a.
[e] Schauer et al., 2002.

(Harley et al., 2000) and China (Liu et al., 2008a) were also summarized in Table 1 for comparison.

Alkanes, alkenes and aromatic hydrocarbons accounted for 55−66, 21−35 and 4−8% in refueling vapors, 59−72, 18−28 and 4−10% in headspace vapors and 3351, 8−15 and 38−48% in liquid gasoline samples, respectively (Table 1). Aromatic hydrocarbons with comparatively higher molecular weights and less volatility were present much more in liquid gasoline than in vapors, as can be seen by their weight percentages of about 42% in liquid gasoline and <10% in vapors (Fig. 1, Table 1). Light alkanes/alkenes, mainly C_3−C_5, were instead much more enriched in the vapors (Table 1). C_3−C_5 alkanes/alkenes were the dominant hydrocarbons in vapors. Headspace vapors, for example, had more than 50% of their total VOC mass contributed from i-pentane, n-butane, n-pentane and i-butane (Table A.1). For vapors emitted during refueling, saturated hydrocarbons including n-alkanes, branched alkanes and cyclo-alkanes accounted for 55.3−65.8% in total VOCs, while alkenes shared 20.8−35.5% and contributions of aromatic hydrocarbons, MTBE and alkynes were all within 10%. In headspace vapors light alkanes and alkenes shared about 68.9% and 22.2% of total VOCs, respectively. Alkanes' percentages in headspace vapor from this study, however, were still lower than that of 89.3% reported in USA by Harley et al. (2000), 79.8% in South Korea by Na et al. (2004), but much higher than that of 33.8% previously reported in China by Liu et al. (2008a). Aromatic hydrocarbons in vapors (3.6−8.2%) from this study instead were much higher than those by Harley et al. (2000) (2.9%) or by Na et al. (2004) (1.6%), but much lower than that of 32.3% by Liu et al. (2008a). The C4+ alkanes were reported to occupy 89.2% among VOCs of gasoline terminal air samples in Western Europe (Edwards et al., 1986). This was comparatively much higher than that of 49.6−58.0% in vapors from this study, and vapors we measured instead had much larger parts of alkenes and aromatics.

Although detected total VOCs mass concentrations in refueling vapors with VRUs off were over 5 times of their counterparts with VRUs on, in the service stations no obviously differences were found if we compare group percentages for vapors with VRUs on or off except for aromatic hydrocarbons, which accounted for ~8.0% with VRUs on and ~4.0% with VRUs off. When refilling tank trucks, however, n-alkenes shared relatively larger fraction (31.7%) with VRUs off than that of 19.5% with VRUs on, and conversely n-alkanes, branched alkanes and aromatic hydrocarbons had relatively larger portions of 22.6%, 40.6% and 8.2% with VRUs on than those of 17.1%, 34.6% and 3.6% with VRUs off, respectively. With VRUs on group compositions of vapors during refilling were quite similar to that of headspace vapor, particularly in aromatic hydrocarbons, which all shared about 8%. A probable explanation is that splashing and disturbance during filling would induce more evaporation of the light alkanes/alkenes, particularly when refueling tank trucks with much larger flow rates; and with the VRUs on the immediate removal of the splashing-induced vapors would result in the vapors emitted from the tank vent approaching the headspace vapors in their chemical compositions.

If comparing group compositions of gasoline vapors with that of other VOC sources, like vehicle exhausts and biomass burning, we found that aromatic hydrocarbons were much higher in gasoline vehicle exhausts (19.3−49.2%, Schmitz et al., 2000; Schauer et al., 2002; Liu et al., 2008a; Guo et al., 2011) or in pine combustion (16.5%, Schauer et al., 1999), while alkanes had relatively larger weight percentages in gasoline vapors (55.3−65.8%) than those of 29.0−62.2% in vehicular emission (Schauer et al., 1999, 2002; Liu et al., 2008a). Alkenes (47.9%) in pine combustion (Schauer et al., 1999) showed an even larger percentage than that of 20.8−35.5% in gasoline vapors from this study. In Fig. 2 these species profiles were also grouped according to the carbon numbers. C_4- and C_5-
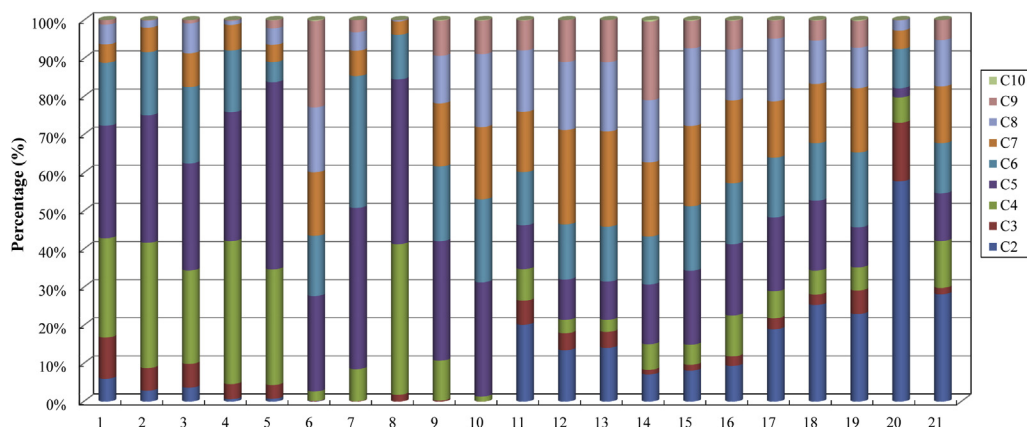
Fig. 2. VOC grouping according to their carbon numbers in different emission sources. 1. Refueling cars, VRU on; 2. Refueling cars, VRU off; 3. Refueling tank trucks, VRU on; 4. Refueling tank trucks, VRU off; 5. Headspace vapor; 6. Liquid gasoline (1–6, this study); 7. Headspace vapor (Harley et al., 2000); 8. Headspace vapor (Na et al., 2004); 9. Headspace vapor (Liu et al., 2008a); 10. Liquid gasoline (Schauer et al., 2002); 11. Tailpipe exhaust (Schauer et al., 2002); 12. Tailpipe exhaust, warm start (Schmitz et al., 2000); 13. Tailpipe exhaust, cold start (Schmitz et al., 2000); 14–18. Tailpipe exhaust, with speeds of 0, 25, 50, 70, 100 km h^{-1}, respectively (Guo et al., 2011); 19. Tailpipe exhaust (Liu et al., 2008a); 20. Pine combustion (Schauer et al., 2001); 21. Diesel exhaust (Schauer et al., 1999).

VOCs dominate in gasoline vapors, with weight percentages of 52.6–71.3% in gasoline vapors during refueling cars or tank trucks and 79.5% in headspace vapors.

As a typical marker to identify oil evaporation source when applying receptor models like PCA or PMF for source attribution and apportioning (Zhang et al., 2012b), i-pentane was observed as the most abundant in majority of vapor samples and also as the most abundant non-aromatic hydrocarbons in liquid gasoline (Table A.1). MTBE, as a gasoline additive to enhance octane rating and combustion efficiency, shared about 10–15% by volume in gasoline in the US (Schauer et al., 2002) and 11% by volume in Taiwan (Chang et al., 2003). Detected MTBE weight percentages in gasoline from this study were much lower, with an average weight percentage of 6.5% (or 6.47% by volume) in gasoline (Table 1). In vapors during refueling cars or tank trucks, MTBE had weight percentages of 3.2–7.2%, much higher than that of 0.8% observed in headspace vapors, which was in the same magnitude as 0.21% reported by Harley et al. (2000) for gasoline headspace vapors in the US. Benzene had an average weight percentage of 1.33% (or 1.12% by volume) in gasoline, and the contents were near that of 0.93% reported by Schauer et al. (2002), but higher than benzene content standard of 1.0 vol% in China (GB17930-2011), and much higher than the annual average gasoline benzene content standard of 0.62 vol% beginning in 2011 in the US. In the present study, benzene ranged 0.71–1.37% in refueling vapors and averaged 0.44% in headspace vapors; the latter was comparable to that of 0.37% reported by Harley et al. (2000) or 0.56% by Na et al. (2004) in headspace vapors, but much lower than that of 4.49% previously reported in China by Liu et al. (2008a).

3.2. Comparison of diagnostic ratios among sources

Table 2 presents ratios of paired VOCs that have been widely used to indicate relative contributions from different emission sources (Barletta et al., 2002,2008; Jobson et al., 2004; Chan et al., 2006; de Gouw et al., 2006; Karl et al., 2007; Simpson et al., 2011). Toluene to benzene (T/B) ratios ranged 2.0–5.8 in refueling vapors from the present study, and ranged 1.5–6.5 in headspace vapors from this study and previous works (Harley et al., 2000; Na et al., 2004; Liu et al., 2008a). These T/B ratios were overlapping with those of 1.1–4.3 for gasoline-powered vehicle exhausts (Schmitz et al., 2000; Schauer et al., 2002; Wang et al., 2002; Liu et al., 2008a; Guo et al., 2011) and of 2.7 for tunnel air in Hong Kong (Ho et al., 2009), but substantially higher than that of 0.4 measured for biomass burning from Schauer et al. (2001) or 0.2–0.8 for biomass burning studied by Andreae and Merlet (2001). Therefore T/B ratios can be used to distinguish gasoline evaporation from biomass burning sources instead of from vehicular emissions.

MTBE as gasoline additive is a marker specific to gasoline-related sources and it can be present in both gasoline vapors and gasoline-powered vehicle exhausts due to incomplete combustion (Poulopoulos and Philippopoulos, 2000). The MTBE/B and MTBE/T ratios in refueling vapors from this study ranged 4.1–6.6 and 0.7–3.3, respectively, much higher than that of 0.5 and 0.1, respectively, in tailpipe exhausts reported by Schauer et al. (2002). Since refueling operation is a major pathway among evaporative loss in gasoline distribution sector, higher MTBE/B and MTBE/T ratios in gasoline vapors might be indicators to differentiate between gasoline evaporation and gasoline vehicle exhausts.

Ratios of i-pentane to benzene (i-pentane/B) and i-pentane to toluene (i-pentane/T) ranged 8.7–15.8 and 2.7–4.3 in refueling vapors, and 45–57 and 8.8–29.9 in headspace vapors, respectively (Table 2). These ratios were much higher than their counterparts ranging 0.7–4.2 and 0.3–1.9, respectively, in vehicular emissions (Schauer et al., 1999; Schmitz et al., 2000; Schauer et al., 2002; Liu et al., 2008a; Ho et al., 2009; Guo et al., 2011). The ratios of benzene (B), toluene (T), ethylbenzene (E) and xylenes (X) to 2,2-dimethylbutane (2,2-diMB) were once used to be characteristic ratios for vehicular sources (Chang et al., 2006). Except for headspace vapor tested by Liu et al. (2008a), gasoline vapors in the present study as well as headspace vapors tested by Harley et al. (2000) and Na et al. (2004) had ratios of B, T, E, m,p-X, and o-X to 2,2-diMB ranged 0.4–1.5, 0.9–4.8, 0.03–1.0, 0.1–1.3, and 0.04–0.8, significantly lower than that of 2.9–22.5, 7.3–60.0, 1.0–6.5, 1.6–18.5, and 0.6–8.0, respectively in vehicle exhausts (Schauer et al., 1999, 2002; Schmitz et al., 2000; Liu et al., 2008a; Ho et al., 2009; Guo et al., 2011). So like the MTBE/B and MTBE/T ratios, the ratios of i-pentane and 2,2-dimethylbutane to aromatic species like benzene and toluene were suitable to make a distinction between gasoline evaporation and vehicle exhausts.

3.3. Assessment of ozone formation potential (OFP)

Species profiles from gasoline vapors and liquid gasoline from this study and previous studies were presented in Table A.1 for comparing their reactivity. As illustrated by Harley et al. (2000),

Table 2
Typical ratios related to gasoline evaporation compared to those in other sources.

Source types	T/B	i-P/B	i-P/T	MTBE/B	MTBE/T	B/2,2-diMB	T/2,2-diMB	E/2,2-diMB	m,p-X/2,2-diMB	o-X/2,2-diMB
Vapor/refueling cars, VRU on[a]	2.1	8.7	4.2	4.2	2.0	1.5	3.0	1.0	1.3	0.8
Vapor/refueling cars, VRU off[a]	2.0	8.7	4.3	6.6	3.3	1.2	2.4	0.3	0.3	0.1
Vapor/refueling tank trucks, VRU on[a]	5.8	15.8	2.7	4.1	0.7	0.8	4.8	1.0	1.2	0.5
Vapor/refueling tank trucks, VRU off[a]	3.2	13.6	4.3	4.9	2.5	0.8	2.4	0.1	0.3	0.1
Headspace vapor[a]	6.5	57	8.8	1.9	0.3	0.5	3.1	1.0	1.7	0.7
Liquid gasoline[a]	7.6	5.2	0.7	6.0	0.8	1.2	8.87	3.7	6.2	2.9
Headspace vapor[b]	4.9	67	13.8	0.6	0.1	0.4	1.9	0.1	0.4	0.1
Headspace vapor[c]	1.5	45	29.9	NA	NA	0.6	0.9	0.03	0.1	0.04
Headspace vapor[d]	2.1	1.9	0.9	NA	NA	4.8	10.2	2.0	6.9	2.7
Tailpipe exhaust[e]	4.3	1.4–1.5	0.3	NA	NA	4.6–4.7	19.9–20.8	4.1–4.3	8.8–9.3	3.5–3.7
Tailpipe exhaust[f]	1.8	0.9	0.5	0.5	0.3	5.2	9.3	1.8	6.2	2.4
Tailpipe exhaust[d]	1.1	0.7	0.7	NA	NA	9.4	10.3	1.5	5.2	2.5
Tailpipe exhaust[g]	2.0–3.8	2.2–4.2	0.8–1.9	NA	NA	2.9–5.7	7.3–14.6	1.0–1.6	1.6–6.6	0.6–2.3
Pine combustion[h]	0.4	0.01	0.03	NA	NA	10.6	4.4	0.6	1.7	0.5
Diesel exhaust[i]	1.5	1.0	0.7	NA	NA	6.3	9.2	1.1	5.4	1.9
Tunnel[j]	2.7	1.2	0.5	NA	NA	22.5	60	6.5	18.5	8.0

T: toluene; B: benzene; E: ethylbenzene; m,p-X: m,p-xylenes; o-X: o-xylene; i-P: i-pentane; MTBE: methyl tert-butyl ether; 2,2-diMB: 2,2-dimethylbutane; NA: not available.
 [a] This study.
 [b] Harley et al., 2000.
 [c] Na et al., 2004.
 [d] Liu et al., 2008a.
 [e] Schmitz et al., 2000.
 [f] Schauer et al., 2002.
 [g] Guo et al., 2011.
 [h] Schauer et al., 2001.
 [i] Schauer et al., 1999.
 [j] Ho et al., 2009.

maximum incremental reactivity (MIR) from Carter (1994) can be used together with species profiles to calculate normalized reactivity R (g O_3 g^{-1} VOCs emitted) to indicate ozone formation potential (OFP) for VOCs from a specific emission source:

$$R = \sum_i w_i \times (MIR)_i \qquad (1)$$

where w_i is the weight percentage of species i present in the refueling/headspace vapors or in fuels. As showed in Fig. 3, refueling vapors or headspace vapor had R values from 3.26 to 4.42 g O_3 g^{-1} VOC, and liquid gasoline had an average R value of 4.07 g O_3 g^{-1} VOC. For VOCs in liquid gasoline, 63% of their reactivity or OFPs was explained by the aromatic hydrocarbons; On the contrary, the reactivity or OFPs for headspace vapors or refilling vapors was largely explained by their light n-alkenes, which share 56–64%

OFPs in refueling vapors at service stations, 54–70% of OFPs in vapors emitted when refueling tank trucks, 43% of OFPs in headspace vapors, and 12% of OFPs in liquid gasoline. These results were consistent with that by Harley et al. (2000), with aromatic hydrocarbons responsible for 62–64% of OFP for liquid gasoline but only 5–6% of OFP for headspace vapors. For VOCs in headspace vapors, total OFP was 3.42 g O_3 g^{-1} VOC in this study, lower than that of 4.32 g O_3 g^{-1} VOC calculated based on species profiles from another study in China by Liu et al. (2008a), but higher than that of 2.92 g O_3 g^{-1} VOC in Korea (Na et al., 2004) and of 1.61 g O_3 g^{-1} VOC in USA (Harley et al., 2000). VOCs in liquid gasoline also showed much higher reactivity (4.07 g O_3 g^{-1} VOC) in this study than that of 3.33 g O_3 g^{-1} VOC in Korea (Na et al., 2004) and that of 2.46 g O_3 g^{-1} VOC (Harley et al., 2000) or 2.82 g O_3 g^{-1} VOC (Schauer et al., 2002) in USA. During refueling operations, vapors emitted when VRUs were
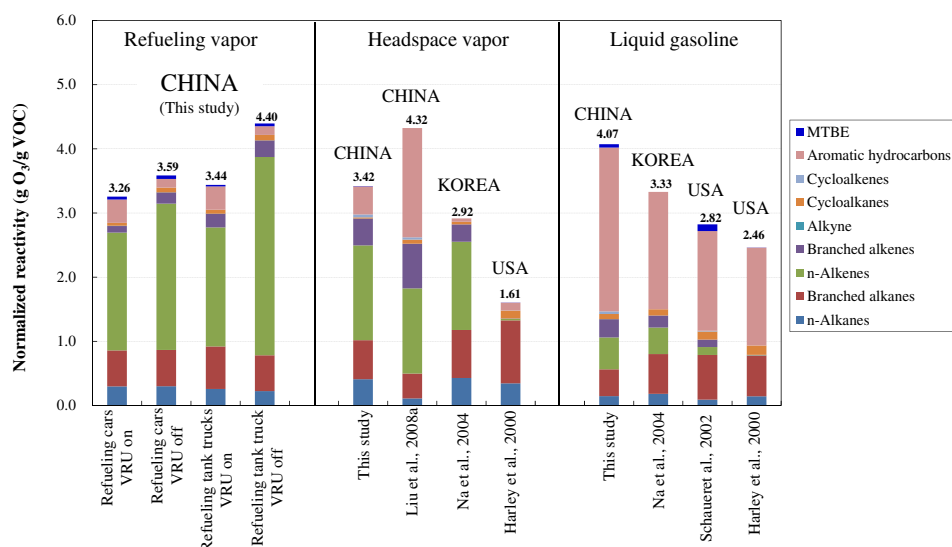
Fig. 3. Normalized reactivity or ozone formation potential (OFP) of VOCs in gasoline vapors and liquid gasoline.

turned on had *R* values 9–22% lower than those when VRUs were turned off (Fig. 3). Nonetheless, vapors emitted during refueling had OFPs quite near that of headspace vapors. It is worth noting that both liquid gasoline and gasoline vapors in China, as investigated by the present study, had normalized reactivity over 3.2 g O_3 g^{-1} VOC, much higher when compared to those reported by Harley et al. (2000) in USA with <2.0 g O_3 g^{-1} VOC for headspace vapors and <3.0 g O_3 g^{-1} VOC for different grades of gasoline. Detailed comparison revealed that a larger portion of alkenes, which are more reactive with much bigger MIRs, was responsible for the higher reactivity of gasoline vapors in China than that in USA from the study by Harley et al. (2000). Alkenes also explained much larger fraction of reactivity (∼20%) in liquid gasoline in this study than those (0.6–8.8%) in USA (Harley et al., 2000; Schauer et al., 2002). Previous studies already revealed that gasoline evaporation contributed substantially to ambient VOCs in China's megacities (Liu et al., 2008a; Yuan et al., 2009; Cai et al., 2010; Lau et al., 2010; Wang et al., 2010; Ling et al., 2011; Zhang et al., 2012b), if gasoline vapor in China are much more enriched in reactive alkenes, gasoline evaporation would be an emission source quite important to regional ozone pollution in these megacities and their surrounding areas. Application of VRUs would greatly reduce the amount of gasoline evaporative loss and also lower the alkenes percentages in the refueling vapors, and therefore would benefit ambient ozone control in China; but fundamentally limiting alkenes in gasoline would help to lower the OFPs of gasoline vapor in China. In California, for example, alkenes in gasoline are limited to less than 4% by volume, which was comparatively much lower than the limit of 30% by volume in China's gasoline (GB17930-2011).

4. Conclusions

In the present study, apart from updating VOC species profiles for gasoline headspace vapor in China, we also measured VOC compositions of vapors emitted during refueling cars in service stations and refueling tank trucks from bulk storage tanks. The profiles of refueling vapors were also compared when the VRUs were turning on or turning off. These species profiles plus the gasoline compositions can cover major pathways of evaporative loss, including refueling operation, headspace displacement, and spillage/leakage during gasoline distribution, and thus can be used when studying the contribution of gasoline evaporation to ambient VOCs, particularly ozone precursors and hazardous air pollutants. The ratios of i-pentane, MTBE and 2,2-dimethylbutane to benzene or toluene are distinctive for gasoline evaporation, and can be used to differentiate gasoline evaporation from vehicle exhausts.

Based on calculated normalized reactivity or ozone formation potentials, one big concern is that gasoline vapors in China showed about doubled ozone formation potentials when compared to that reported by Harley et al. (2000) for gasoline headspace vapors in USA. This unusually higher ozone formation potential for gasoline vapors in China was largely explained by a larger fraction of reactive light alkenes. Since VURs can substantially lower evaporative loss and, to a less degree, the ozone formation potential of gasoline vapors from refueling operations, to mitigate negative impacts of gasoline evaporation on air quality in China, gasoline vapor recovery should be enhanced from a few megacities to more densely-populated regions be set with ambient ozone pollution (Chan and Yao, 2008). On the other hand, a lower limit should be set for alkenes in China's gasoline.

Acknowledgments

The authors would like to thank Mr. Zhengyue Li for his help in sample collection. This study was supported by National Natural Science Foundation of China (NSFC, Project No. 41025012/41121063) and NSFC-Guangdong Joint Funds (U0833003) and Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB05010200).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.06.029.

References

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochemical Cycles 15, 955–966.
Barletta, B., Meinardi, S., Simpson, I.J., Haider, A.K., Blake, D.R., Rowland, F.S., 2002. Mixing ratios of volatile organic compounds (VOCs) in the atmosphere of Karachi, Pakistan. Atmospheric Environment 36, 3429–3443.
Barletta, B., Meinardi, S., Simpson, I.J., Zou, S.C., Rowland, F.S., Blake, D.R., 2008. Ambient mixing ratios of nonmethane hydrocarbons (NMHCs) in two major urban centers of the Pearl River Delta (PRD) region: Guangzhou and Dongguan. Atmospheric Environment 42, 4393–4408.
Bo, Y., Cai, H., Xie, S.D., 2008. Spatial and temporal variation of historical anthropogenic NMVOCs emission inventories in China. Atmospheric Chemistry and Physics 8, 7297–7316.
Borbon, A., Fontaine, H., Locoge, N., Veillerot, M., Galloo, J.C., 2003. Developing receptor-orientated methods for non-methane hydrocarbon characterisation in urban air Part I: source identification. Atmospheric Environment 37, 4051–4064.
Bowman, F.M., Pilinis, C., Seinfeld, J.H., 1995. Ozone productivity of reactive organics. Atmospheric Environment 29, 579–589.
Brugnone, F., Perbellini, L., Romeo, L., Cerpelloni, M., Bianchin, M., Tonello, A., 1999. Benzene in blood as a biomarker of low level occupational exposure. The Science of the Total Environment 235, 247–252.
Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. Journal of Air and Waste Management Association 44, 881–899.
Cai, C.J., Geng, F.H., Tie, X.X., Yu, Q., An, J.L., 2010. Characteristics and source apportionment of VOCs measured in Shanghai, China. Atmospheric Environment 44, 5005–5014.
Chan, C.K., Yao, X.H., 2008. Air pollution in mega cities in China. Atmospheric Environment 42, 1–42.
Chan, L.Y., Chu, K.W., Zou, S.C., Chan, C.Y., Wang, X.M., Barletta, B., Blake, D.R., Guo, H., Tsai, W.Y., 2006. Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial-urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China. Journal of Geophysical Research – Atmospheres 111, D11304. http://dx.doi.org/10.1029/2005JD006481.
Chang, C.C., Lo, S.J., Lo, J.G., Wang, J.L., 2003. Analysis of methyl tert-butyl ether in the atmosphere and implications as an exclusive indicator of automobile exhaust. Atmospheric Environment 37, 4747–4755.
Chang, C.C., Wang, J.L., Liu, S.C., Lung, S.C.C., 2006. Assessment of vehicular and non-vehicular contributions to hydrocarbons using exclusive vehicular indicators. Atmospheric Environment 40, 6349–6361.
de Gouw, J.A., Warneke, C., Stohl, A., Wollny, A.G., Brock, C.A., Cooper, O.R., Holloway, J.S., Trainer, M., Fehsenfeld, F.C., Atlas, E.L., Donnelly, S.G., Stroud, V., Lueb, A., 2006. Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada. Journal of Geophysical Research – Atmospheres 111, D10303. http://dx.doi.org/10.1029/2005JD006175.
de Oliveira, K.M.P.G., Martins, E.M., Arbilla, G., Gatti, L.V., 2007. Exposure to volatile organic compounds in an ethanol and gasoline service station. Bulletin of Environment Contamination and Toxicology 27, 237–241.
Edwards, A.H., Campobasso, A., Camps, R., Cremer, G., Long, M.D., 1986. Volatile Organic Compound Emissions: an Inventory for Western Europe. Report No.PB-86–241189/XAB. CONCAWE-2/86.
European Environment Agency, EMEP/CORINAIR Emission Inventory Guidebook-2007/Group 5: Extraction and Distribution of Fossil Fuels and Geothermal Energy. http://www.eea.europa.eu/publications/EMEPCORINAIR5/page014.html.
Guo, H., Zou, S.C., Tsai, W.Y., Chan, L.Y., Blake, D.R., 2011. Emission characteristics of nonmethane hydrocarbons from private cars and taxis at different driving speeds in Hong Kong. Atmospheric Environment 45, 2711–2721.
Harley, R.A., Coulter-Burke, S.C., Yeung, T.S., 2000. Relating liquid fuel and head-space vapor composition for California reformulated gasoline samples containing ethanol. Environmental Science and Technology 34, 4088–4094.
Ho, K.F., Lee, S.C., Ho, W.K., Blake, D.R., Cheng, Y., Li, Y.S., Ho, S.S.H., Fung, K., Louie, P.K.K., Park, D., 2009. Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong. Atmospheric Chemistry and Physics 9, 7491–7504.
Jobson, B.T., Berkowitz, C.M., Kuster, W.C., Goldan, P.D., Williams, E.J., Fesenfeld, F.C., Apel, E.C., Karl, T., Lonneman, W.A., Riemer, D., 2004. Hydrocarbon source signatures in Houston, Texas: influence of the petrochemical industry. Journal of Geophysical Research - Atmospheres 109, D24305. http://dx.doi.org/10.1029/2004JD004887.

Karakitsios, S.P., Papaloukas, C.L., Kassomenos, P.A., Pilidis, G.A., 2007. Assessment and prediction of exposure to benzene of filling station employees. Atmospheric Environment 41, 9555—9569.

Karl, T.G., Christian, T.J., Yokelson, R.J., Artaxo, P., Hao, W.M., Guenther, A., 2007. The tropical forest and fire emissions experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR, and GC from tropical biomass burning. Atmospheric Chemistry and Physics 7, 5883—5897.

Klimont, Z., Streets, D.G., Gupta, S., Cofala, J., Fu, L., Ichikawa, Y., 2002. Anthropogenic emissions of non-methane volatile organic compounds in China. Atmospheric Environment 36, 1309—1322.

Lau, A.K.H., Yuan, Z., Yu, J.Z., Louie, P.K.K., 2010. Source apportionment of ambient volatile organic compounds in Hong Kong. Science of the Total Environment 408, 4138—4149.

Ling, Z.H., Guo, H., Cheng, H.R., Yu, Y.F., 2011. Sources of ambient volatile organic compounds and their contributions to photochemical ozone formation at a site in the Pearl River Delta, southern China. Environmental Pollution 159, 2310—2319.

Liu, Y., Shao, M., Fu, L.L., Lu, S.H., Zeng, L.M., Tang, D.G., 2008a. Source profiles of volatile organic compounds (VOCs) measured in China: part I. Atmospheric Environment 42, 6247—6260.

Liu, Y., Shao, M., Lu, S.H., Chang, C.C., Wang, J.L., Fu, L.L., 2008b. Source apportionment of ambient volatile organic compounds in the Pearl River Delta (PRD), China: part II. Atmospheric Environment 42, 6261—6274.

Na, K., Kim, Y.P., Moon, I.1, Moon, K.C., 2004. Chemical composition of major VOC emission sources in the Seoul atmosphere. Chemosphere 55, 585—594.

Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1997. The atmospheric aerosol-forming potential of whole gasoline vapor. Science 276, 96—99.

Poulopoulos, S., Philippopoulos, C., 2000. Influence of MTBE addition into gasoline on automotive exhaust emissions. Atmospheric Environment 34, 4781—4786.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C_2 through C_{30} organic compounds from medium duty diesel trucks. Environmental Science and Technology 33, 1578—1587.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C_1—C_{29} organic compounds from fireplace combustion of wood. Environmental Science and Technology 33, 1716—1728.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C_1—C_{32} organic compounds from gasoline-powered motor vehicles. Environmental Science and Technology 36, 1169—1180.

Schmitz, T., Hassel, D., Weber, F.J., 2000. Determination of VOC-components in the exhaust of gasoline and diesel passenger cars. Atmospheric Environment 34, 4639—4647.

Shao, M., Tang, X.Y., Zhang, Y.H., Li, W.J., 2006. City clusters in China: air and surface water pollution. Frontiers in Ecology and the Environment 4, 353—361.

Shen, J., Hao, J.M., Wang, L.T., 2006. VOC emission situation and control measures of gas station in China. Environmental Science 27, 1473—1478 (in Chinese with English abstract).

Simpson, I.J., Akagi, S.K., Barletta, B., Blake, N.J., Choi, Y., Diskin, G.S., Fried, A., Fuelberg, H.E., Meinardi, S., Rowland, F.S., Vay, S.A., Weinheimer, A.J.,

Wennberg, P.O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R.J., Blake, D.R., 2011. Boreal forest fire emissions in fresh Canadian smoke plumes: C_1—C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN. Atmospheric Chemistry and Physics 11, 6445—6463.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.-H., Yarber, K.F., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. Journal of Geophysical Research - Atmospheres 108, D21. http://dx.doi.org/10.1029/2002JD003093.

Su, J.H., Shao, M., Lu, S.H., Xie, Y.Y., 2011. Non-methane volatile organic compound emission inventories in Beijing during Olympic Games 2008. Atmospheric Environment 45, 7046—7052.

Wang, B., Shao, M., Lu, S.H., Yuan, B., Zhao, Y., Wang, M., Zhang, S.Q., Wu, D., 2010. Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008. Atmospheric Chemistry and Physics 10, 5911—5923.

Wang, X.M., Sheng, G.Y., Fu, J.M., Chan, C.Y., Lee, S.C., Chan, L.Y., Wang, Z.S., 2002. Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. Atmospheric Environment 36, 5141—5148.

Wang, X.M., Wu, T., 2008. Release of isoprene and monoterpenes during the aerobic decomposition of orange wastes from laboratory incubation experiments. Environmental Science and Technology 42, 3265—3270.

Watson, J.G., Chow, J.C., Fujita, E.M., 2001. Review of volatile organic compound source apportionment by chemical mass balance. Atmospheric Environment 35, 1567—1584.

Wei, W., Wang, S.X., Chatani, S., Klimont, Z., Cofala, Z., Hao, J.M., 2008. Emission and speciation of non-methane volatile organic compounds from anthropogenic sources in China. Atmospheric Environment 42, 4976—4988.

Wu, B.Z., Hsieh, L.L., Sree, U., Chiu, K.H., Lo, J.G., 2006. Determination and impact of volatile organics emitted during rush hours in the ambient air around gasoline stations. Journal of the Air and Waste Management Association 56, 1342—1348.

Yu, Y.F., Lu, Q., Zheng, J.Y., Zhong, L.J., 2011. VOC emission inventory and its uncertainty from the key VOC-related industries in the Pearl River Delta Region. China Environmental Science 31, 195—201 (in Chinese with English abstract).

Yuan, Z.B., Lau, A.K.H., Shao, M., Louie, P.K.K., Liu, S.C., Zhu, T., 2009. Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing. Journal of Geophysical Research — Atmospheres 114. http://dx.doi.org/10.1029/2008JD011190.

Zhang, Q., Streets, D.G., Carmichael, G.R., He, K.B., Huo, H., Kannari, A., Klimont, Z., Park, I.S., Reddy, S., Fu, J.S., Chen, D., Duan, L., Lei, Y., Wang, L.T., Yao, Z.L., 2009. Asian emissions in 2006 for the NASA INTEX-B mission. Atmospheric Chemistry and Physics 9, 5131—5153.

Zhang, Q., He, K.B., Huo, H., 2012a. Clean China's air. Nature 484, 161—162.

Zhang, Y.L., Wang, X.M., Blake, D.R., Li, L.F., Zhang, Z., Wang, S.Y., Guo, H., Lee, F.S.C., Gao, B., Chan, L.Y., Wu, D., Rowland, F.S., 2012b. Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China. Journal of Geophysical Research — Atmospheres. http://dx.doi.org/10.1029/2011JD017356.

Zhang, Y.L., Wang, X.M., Blake, D.R., Barletta, B., Meinardi, S., Zhang, Z., Fu, X.X., He, Q.F., Liu, T.Y., Ding, X., Zhao, X.Y., 2013. Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region. Journal of Hazardous Materials 250, 403—411.