

Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region

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HIGHLIGHTS

- ▶ We measured aromatic hydrocarbons at four contrasting sites in the PRD region.
- ▶ Diagnostic ratios were used to imply sources of aromatic hydrocarbons.
- ▶ Sources of aromatic hydrocarbons were apportioned by PMF receptor model.
- ▶ Solvent use, vehicle exhaust and biomass burning contributed over 89% AHs.
- ▶ Biomass burning contributed to AHs, particularly for Benzene in the rural.

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ABSTRACT

Aromatic hydrocarbons (AHs) are both hazardous air pollutants and important precursors to ozone and secondary organic aerosols. Here we investigated 14 C₆–C₉ AHs at one urban, one suburban and two rural sites in the Pearl River Delta region during November–December 2009. The ratios of individual aromatics to acetylene were compared among these contrasting sites to indicate their difference in source contributions from solvent use and vehicle emissions. Ratios of toluene to benzene (T/B) in urban (1.8) and suburban (1.6) were near that of vehicle emissions. Higher T/B of 2.5 at the rural site downwind the industry zones reflected substantial contribution of solvent use while T/B of 0.8 at the upwind rural site reflected the impact of biomass burning. Source apportionment by positive matrix factorization (PMF) revealed that solvent use, vehicle exhaust and biomass burning altogether accounted for 89–94% of observed AHs. Vehicle exhaust was the major source for benzene with a share of 43–70% and biomass burning in particular contributed 30% to benzene in the upwind rural site; toluene, C₈-aromatics and C₉-aromatics, however, were mainly from solvent use, with contribution percentages of 47–59%, 52–59% and 41–64%, respectively.

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1. Introduction

Aromatic hydrocarbons (AHs) are emitted to the Earth's troposphere mainly from anthropogenic sources including vehicle exhausts and solvent usage [1–5]. They contribute an important fraction (~20–30%, mass percent) of total nonmethane hydrocarbons (NMHCs) in the urban atmosphere [6]. Some AHs, like benzene, toluene, ethylbenzene and xylenes, are hazardous air pollutants; and for benzene, a known human carcinogen causing

leukaemia [7], its ambient levels has been regulated in many countries or regions. As important precursors of ozone [8–10], AHs contribute substantially to ambient ozone particularly in polluted urban environments, and photooxidation of AHs was estimated to contribute up to ~30% of photochemically produced ozone in the boundary layer over Europe [11]. AHs are also most important anthropogenic precursors of secondary organic aerosols (SOA) [12–17]. Although estimated SOA from biogenic sources substantially exceeds that from anthropogenic sources on the global scale [18,19], AHs have been identified as dominant SOA precursors in some highly industrialized and densely populated regions, like the Pearl River Delta (PRD) region (Fig. 1) in south China [20].

In the PRD region, the rapid growth in economy has resulted in fast increase in anthropogenic emissions of air pollutants [21], and as an important class of anthropogenic volatile organic

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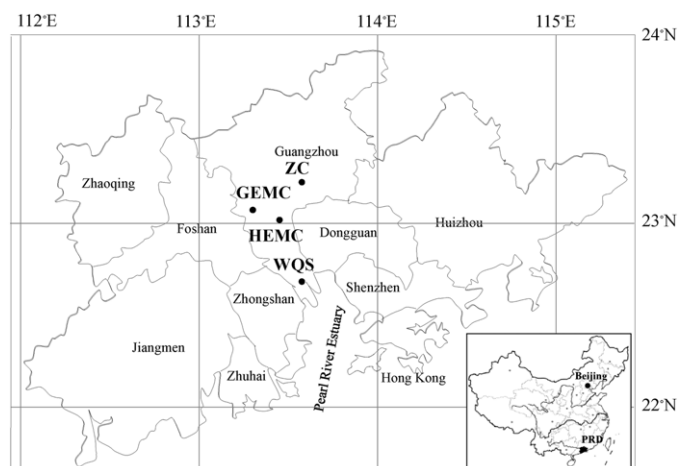


Fig. 1. Locations of four sampling sites in the PRD region.

compounds (VOCs), AHs were found to have comparatively higher ambient levels [3,5,22–26] with tremendous impacts on air quality in the region. Studies showed that in the PRD region ozone formation was largely VOC-limited with AHs among the most important precursors [26–29], and AHs alone were responsible for over 75% secondary organic carbon in fine particles [20]. Therefore, emission control of AHs is vital to lower regional ozone pollution and SOA in the region.

Bottom-up emission inventories of air pollutants in the PRD region were developed with 2006 as the base year [30], and VOCs emission inventory with 10 speciated species including four aromatics (toluene, m,p-xylene, o-xylene and 1,2,4-trimethylbenzene) was further established [31]. Nevertheless, –75% to 150% uncertainties still existed for the anthropogenic VOC emission sources [30]. Based on observed data, receptor models including principal component analysis/absolute principal component scores (PCA/APCS) [32,33] and positive matrix factorization (PMF) have been previously applied to explore VOC emission sources based on VOCs measured at four stations with different environments in Hong Kong (HK) during two sampling campaigns [34], at a Hong Kong urban site and a rural site in inland PRD during October–December 2007 [35], and at 84 sites in a grid study with four campaigns during 2008–2009 over the PRD region [36]; and in the inner PRD region sources of VOCs was apportioned by chemical mass balance (CMB) with ambient VOC data observed at fall-winter 2004 [37]. As CMB receptor model are based on the well-known source profiles [38,39], available emission source profiles in the PRD region are neither sufficient nor representative to cover the complicated emission sources in this region. Therefore PMF, a new receptor model technique limiting all the elements in the source profiles and the source contributions matrix to be positive, is an alternative choice to explore sources of AHs. It has been applied extensively in identifying VOC contributing sources at different locations in the world, such as Los Angeles [40], New Jersey and California [41], Boston [42], Ontario [43], Brisbane [44], Shanghai [45], and Beijing [46,47].

In the study, we collected whole air samples during November to December in 2009 at representative urban, suburban, and rural sites in the PRD region. The objectives were to obtain extensive data about exposure levels of the hazardous AHs in the region, to explore their sources at urban, suburban, and rural sites qualitatively by typical diagnostic ratios and quantitatively by the PMF receptor model, and to compare our source attribution results with those previously obtained by bottom-up compiling or other receptor models like CMB.

2. Sampling and chemical analysis

2.1. Sites description and field sampling

Four sampling sites were selected during this campaign, namely Guangzhou Environmental Monitoring Center (GEMC) (23.13°N, 113.27°E) in the urban, Guangzhou Higher Education Mega Center (HEMC) (23.04°N, 113.37°E) in the suburban, Zengcheng College of South China Normal University (ZC) (23.31°N, 113.56°E) in the upwind rural, and Wanqingsha (WQS) (22.71°N, 113.55°E) in the downwind rural. Their geographical locations are showed in Fig. 1. These four sites are all among the air quality monitoring stations established by the local governmental environmental monitoring center.

GEMC is situated in the center of Guangzhou city and surrounded by intensive residential buildings and business offices. The sampling site is about 23 meters above ground at the rooftop of an eight-story building. This site can represent a typical urban site in the PRD region, which is influenced by traffic-related and residential emission sources.

HEMC is a mega center for ten universities in Guangdong province, which is located in an island and surrounded by the Pearl River in the southern part of Panyu district. It is about 17 km to the southeast of urban Guangzhou, 40 km to the northwest of Dongguan. This suburban site is about 20 m above the ground on the rooftop of an eight-story teaching building.

ZC is in the northeast of urban Guangzhou and is surrounded by farmlands. This rural sampling site is about 15 m above ground at the top of an eight-story teaching building and was in the upwind of urban Guangzhou during our sampling period.

WQS, a small town in the center of the PRD region, is surrounded by farmlands and has very few textile and clothing workshops, so the local anthropogenic emissions are not remarkable and pollutants are mainly from the surrounding cities. The site is 50 km to the southeast of Guangzhou urban center, 40 km to the southwest of Dongguan, which is a developed industrial city. The sampling site there is about 15 m above the ground on the rooftop of a teaching building in a middle school. With the prevailing northeast/north winds during our sampling, WQS acted as a good rural receptor sites downwind Dongguan and/or Guangzhou.

Ambient air samples were collected using pre-evacuated 2-L electro-polished stainless steel canisters from November 8 to December 7, 2009. Samples were collected only on sunny/cloudy days. During field sampling a flow restrictor (Part No. 39-RS-3, Entech Instruments Inc., CA, USA) was adopted to allow each canister to be filled in about 60 min. During this campaign, altogether 233 air samples were collected including 67 samples from GEMC, 51 samples from HEMC, 41 samples from ZC and 74 samples from WQS.

2.2. Lab analysis

Air samples were analyzed using a Model 7100 preconcentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973 N gas chromatography–mass selective detector/flame ionization detector (GC–MSD/FID, Agilent Technologies, USA). Detailed cryogenically concentration steps are described elsewhere [26,48]. 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 H₂O and CO₂ 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 a HP-1 capillary column

Table 1

The mixing ratios, ranges and 95% confidence intervals (95% C.I.) of AHs at GEMC, HEMC, ZC and WQS (in parts per trillion by volume, pptv).

Species	MDL	GEMC (n = 69) ^b		HEMC (n = 52)		ZC (n = 41)		WQS (n = 74)	
		Range	Mean (95% C.I.)	Range	Mean (95% C.I.)	Range	Mean (95% C.I.)	Range	Mean (95% C.I.)
Benzene	14	1020–5899	2642 (265)	331–8828	1919 (429)	243–3035	1093 (196)	473–5834	1914 (247)
Toluene	9	983–8773	4644 (544)	378–14615	2965 (821)	136–4945	911 (295)	564–15693	5935 (800)
Ethylbenzene	6	127–3426	786 (165)	39–3657	572 (182)	31–905	203 (54)	119–2932	1089 (145)
m,p-Xylene	9	97–1982	518 (93)	26–3059	402 (151)	13–725	103 (43)	70–1860	740 (97)
o-Xylene	4	55–678	226 (38)	11–1314	173 (62)	8–211	50 (14)	87–813	309 (42)
i-Propylbenzene	4	ND–137	43 (7)	ND–113	23 (6)	ND–39	16 (3)	5–76	28 (4)
n-Propylbenzene	4	ND–118	32 (6)	ND–109	27 (6)	ND–40	13 (3)	4–96	32 (5)
1,3,5-TMB ^a	3	ND–211	33 (5)	ND–79	17 (5)	ND–50	11 (4)	ND–379	130 (21)
1,2,4-TMB	6	ND–259	75 (15)	ND–237	47 (14)	ND–159	24 (9)	ND–121	39 (7)
1,2,3-TMB	5	ND–344	52 (14)	ND–107	24 (6)	ND–101	23 (6)	ND–57	20 (3)
m-Ethyltoluene	3	22–768	131 (40)	18–733	189 (51)	7–253	47 (15)	19–101	28 (5)
p-Ethyltoluene	3	ND–133	57 (11)	ND–119	25 (7)	ND–60	13 (4)	ND–200	61 (10)
o-Ethyltoluene	3	13–134	50 (9)	ND–127	27 (7)	ND–55	14 (4)	ND–92	34 (5)

^a 1,3,5-TMB, 1,3,5-trimethylbenzene.^b Number in parentheses indicates the total number of samples at each site.

(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; another is to a 65 cm × 0.10 mm I.D. stainless steel line followed by MSD detection. The GC oven temperature was programmed to be initially at –50 °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 selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). The fine particle (PM_{2.5}) samples were also collected during this campaign for the analysis of organic aerosols, including the biomass burning marker levoglucosan. The detailed description can be found elsewhere [20].

2.3. 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.

Target compounds were identified based on their retention times and mass spectra, and quantified by external calibration method. C₄–C₁₁ hydrocarbons and were determined based on MSD signals, while C₂ and C₃ hydrocarbons were determined based on FID signals. The calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 NMHCs including 15 AHs) and TO-14 standard mixture (39 compounds) from Spectra Gases Inc., NJ, USA 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 ±10% of the initial calibration curve, recalibration was performed. The method detection limits (MDLs) for each aromatic hydrocarbon were presented in Table 1.

2.4. Source apportionment with Positive Matrix Factorization (PMF)

USEPA PMF 3.0 model (<http://www.epa.gov/head/products/pmf/pmf.html>) was applied to explore the sources of observed NMHCs in the present study. The detailed method description can be found elsewhere [49,50]. The approaches for replacing and

developing uncertainty values for missing and below-detection-limit data were drawn from previous works [51,52]. Briefly, data values below the method detection limit (MDL) were substituted with MDL/2; missing data values were substituted with median concentrations [40]. Uncertainties were treated the same way as [53,54]. If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using the following equation, $Unc = 5/6 \times MDL$; If the concentration is greater than the MDL provided, the calculation is $Unc = [(Error\ fraction \times mixing\ ratios)^2 + (MDL)^2]^{1/2}$. The number of factors in the PMF model was chosen based on the result from PCA/APCS model [55].

3. Results and discussion

3.1. General characteristics of AHs at urban, sub-urban and rural sites

A total of 57 anthropogenic NMHCs species including AHs, alkanes, alkenes, and acetylene were identified during this campaign. The average mixing ratios, ranges, and 95% confidence intervals (95% C.I.) of AHs observed during the sampling period are listed in Table 1. The total mixing ratios of AHs at GEMC, HEMC, ZC and WQS averaged 9.26 ± 1.04 , 6.40 ± 1.63 , 2.50 ± 0.71 , and 10.4 ± 1.33 pptv, accounting for 12%, 14%, 11%, and 28% of the total NMHCs, respectively. Toluene was the most abundant compound among the AHs at all sampling sites except ZC, where benzene exhibited higher mean mixing ratios (1919 ± 429 pptv) than that of toluene (911 ± 295 pptv). The levels of benzene, toluene, C₈-aromatics (including ethylbenzene, m,p-xylene, and o-xylene) and C₉-aromatics (including i-propylbenzene, n-propylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, m-ethyltoluene, p-ethyltoluene, and o-ethyltoluene) at urban GEMC, suburban HEMC and downwind rural WQS were all significantly higher ($p < 0.001$, two tails *t*-test) than those at upwind rural ZC. The urban site GEMC showed significantly higher benzene levels (2642 ± 265 , mean ± 95% C.I., pptv) than the suburban site HEMC or rural sites ZC and WQS ($p < 0.01$); the highest mean mixing ratios of toluene (5935 ± 2800 pptv) and C₈-aromatics (3207 ± 422 pptv), however, were observed at WQS.

Frequently high concentrations of AHs were observed in other mega cities in China, such as Beijing [46,47,56], Shanghai [45], Hangzhou [57]. When compared to ambient levels of AHs observed in urban Guangzhou in autumn 2004 [58], our measurement in the similar period in 2009 revealed decreased mixing ratios for toluene, ethylbenzene and xylenes. Benzene, on the contrary, showed increased mixing ratios from 2.39 ± 1.99 ppbv in 2004 to 2.64 ± 1.08 ppbv in 2009. At the downwind rural site WQS, levels

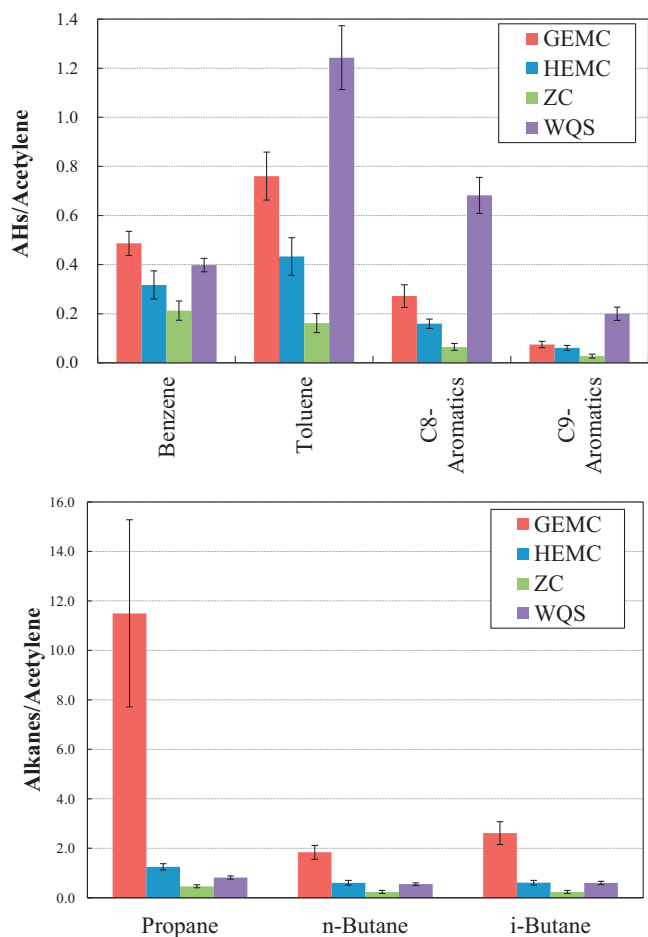


Fig. 2. Ratios of AHs (a) and alkanes (b) to acetylene and their standard errors (95% C.I.) at GEMC, HEMC, ZC, and WQS in the PRD region. C₈-aromatics: including ethylbenzene, m,p-xylene and o-xylene; C₉-aromatics: including i-propylbenzene, n-propylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, m-ethyltoluene, p-ethyltoluene, and o-ethyltoluene.

of benzene also increased from 0.89 ± 0.13 ppbv in 2007 [26] to 1.91 ± 1.09 ppbv in 2009; While average levels of toluene and C₈-aromatics decreased from 6.64 and 9.09 ppbv in 2007 [26] to 5.94 and 2.14 ppbv in 2009 as observed in the present study. For the leukaemia-causing benzene, its average levels observed at the four sampling sites in this study ranged 1093–2642 pptv, more than twice that of 60–480 pptv monitored in 28 cities in the United States [59].

3.2. Diagnostic ratios

Some VOCs or their combination are valuable tracers to indicate their sources as well as photochemical and atmospheric transport processes. Acetylene, for example, had been used extensively as a tracer for combustion [4,28,60–65], and the ratios of hydrocarbons to acetylene were widely used to examine the impact of other emissions sources relative to combustion emissions. The ratios of propane, n-butane and i-butane to acetylene, for example, have been used to indicate their contribution from LPG leakage [28,60]. Ratios of AHs as well as propane, n-butane, and i-butane to acetylene at the four sites were showed in Fig. 2. Among the four sites, except for benzene, the highest ratios of AHs to acetylene occurred at WQS; while the largest ratios of benzene/acetylene were observed at urban GEMC (0.49 ± 0.05). These ratios consistent with the ratio observed in urban Guangzhou in 2005 (0.41 , [5]), but lower than the ratio from boreal forest fire (0.80) [66]. Benzene,

as a carcinogenic compound forbidden to be used in industry, were mainly from automobile exhausts in urban areas [5,24,64], so dominant contribution from vehicle exhausts in the urban site GEMC explained the higher benzene/acetylene ratio than at other sites [5,28]. As toluene, C₈-aromatics and C₉-aromatics were widely used as solvents in painting, coating, printing and cleaning processes in the highly industrialized PRD region [3,26,33,67], their high ratios to acetylene at WQS suggested substantial contribution of AHs from industrial emissions in the upwind city of Dongguan, a world-known manufacturing center in the region. Moreover, the ratios of toluene, C₈-aromatics and C₉-aromatics to acetylene at WQS were 1.24 ± 0.13 , 0.68 ± 0.07 and 0.20 ± 0.03 , consistent with ratios of 1.19, 0.68 and 0.22 previously reported in Dongguan, respectively [5], indicating substantial impacts of emissions from Dongguan on air pollutants occurring at WQS during fall-winter with northeast prevailing winds. The comparatively lower ratios of AHs to acetylene at ZC were attributed to less industry in the upwind and/or aged air masses with depleting unstable AHs relatively to acetylene after long range transport from initial emission sources. The ratios of propane/acetylene, n-butane/acetylene and i-butane/acetylene at GEMC were 11.49 ± 3.79 , 1.84 ± 0.28 and 2.61 ± 0.46 , significantly higher ($p < 0.01$, two tails *t*-test) when compared to that of 1.24 ± 0.13 , 0.60 ± 0.09 and 0.61 ± 0.10 at HEMC; 0.46 ± 0.06 , 0.24 ± 0.06 and 0.23 ± 0.06 at ZC; and 0.82 ± 0.07 , 0.55 ± 0.06 and 0.60 ± 0.07 at WQS, respectively, suggesting more significant influence of LPG-related sources in the urban areas, such as LPG-driven vehicles as well as home-use town gases for cooking. The ratios in urban GEMC were also higher when compared to that of 2.93, 1.05 and 0.56, respectively, observed at roadside in urban Guangzhou in 2005 [28]. This increase might be explained by the increased consumption of LPG for domestic cooking and LPG-driven vehicles. The number of LPG-driven buses and taxis in Guangzhou, for example, increased from 5000 in 2005 to 9300 in 2009 for buses, and from 9200 in 2006 to 15,500 in 2009 for taxis (<http://www.gzstats.gov.cn/>).

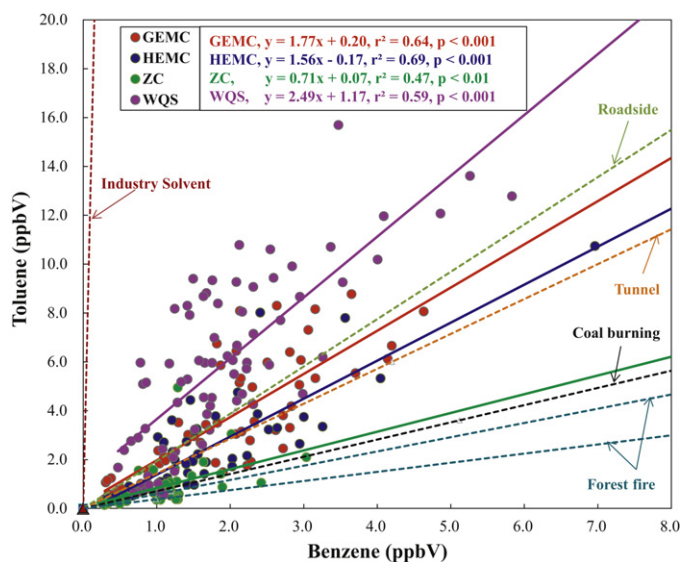


Fig. 3. Scatter plots of toluene to benzene at GEMC, HEMC, ZC, and WQS in the PRD region. T/B slopes are also showed for typical sources including industry solvent emission in the PRD region (dark violet dash line) [28], vehicle exhausts measured in tunnel air (orange dash line, slope = 1.43) [23] and roadside air (Tang et al., 2007; olive green dash line, slope = 1.94) [28] in Guangzhou, biomass burning (Karl et al., 2007, aqua dash line, slope = 0.58; Simpson et al., 2011, slope = 0.37) [67,71], and coal burning study (Liu et al., 2008, black dash line, slope = 0.71) [72]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 4. Factor profiles (% of species) for NMHCs.

Since toluene is widely used as solvent and benzene's use is forbidden in industry, very high toluene to benzene ratios (T/B) were observed in typical industry emissions [28,68]; and T/B ratios in industrial cities [3,5] were comparatively higher than that in vehicle exhausts and roadside air samples [23,28,69,70] in which traffic-related emissions had dominant contributions. Biomass burning or coal burning showed much lower T/B ratios [66,71,72]. Reaction with OH radical was the major pathway for the removal of aromatics in ambient air [73]. As our samples were collected in wintertime with OH radical typically much lower than in summertime, even using a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3} , with the rate constants in [73], we can obtain the life times for benzene and toluene as 114 and 25 h, respectively. Since average transport time from major source regions to the sampling sites in the daytime was within

3 h during sampling periods, loss due to photochemistry for benzene and toluene should be less than 10% and thus were negligible. So T/B ratios could be used for diagnosing sources in the present study. Fig. 3 presents the scatter plots of benzene and toluene from our studies along with T/B slopes of typical emission sources from previous studies. Significant correlations ($p < 0.01$) were observed between toluene and benzene at all sites. The T/B slopes at WQS, GEMC and HEMC were 2.49 ± 0.12 , 1.77 ± 0.08 and 1.56 ± 0.08 , respectively, which were between that observed in industry city Dongguan (T/B = 4.82 and 4.87) [3,5] and that of vehicle exhausts (T/B = 1.43 for tunnel and 1.94 for roadside) [23,28], and were also consistent with those previously reported at various locations in the PRD region [5,25,26,28,72]. T/B slopes closer to that of vehicle exhausts at GEMC and HEMC in fact reflected the fact that vehicle exhausts were the sources much more important in the urban

commercial/business/dwelling areas like GEMC and its downwind areas like HEMC. Higher T/B at WQS, on the other hand, reflected more contribution from industry solvents from upwind Dongguan as previously observed [26]. Much lower T/B slope at the upwind rural site ZC (0.77 ± 0.06) implicated the important role of biomass burning, the T/B of which were reported around 0.5 (T/B = 0.58; [71]) or even lower (T/B = 0.37; [66]).

3.3. Source attribution by PMF

As the atmospheric lifetimes of isoprene, α -pinene and other biogenic VOC species is very short [74], they were not included in receptor models. In the present study only the most abundant 33 NMHCs with fairly long atmospheric lifetimes were selected

for PMF modeling. Five anthropogenic emission sources, namely vehicle exhausts, industrial processes losses/solvent use, oil evaporation, biomass burning and LPG/LNG, were extracted. The PMF reconstructed mass matched the measured mass very well, with slopes (predicted to observed) in the range of 0.91–0.97 and r^2 of 0.90–0.96 for the whole dataset. The typical factor profiles are showed in Fig. 4. The first source is solvent use which is characterized by a significant amount of aromatics species and n-hexane which are major components in various solvents commonly used in manufacturing industries, such as n-hexane in electronics industry particularly the PRD region [3,67]. Source 2 is considered to be LPG/LNG related emissions with a dominance of propane, isobutene, n-butane and ethane, which are typical tracer of emission from LPG/LNG [5,64]. Vehicle exhaust is identified as source 3

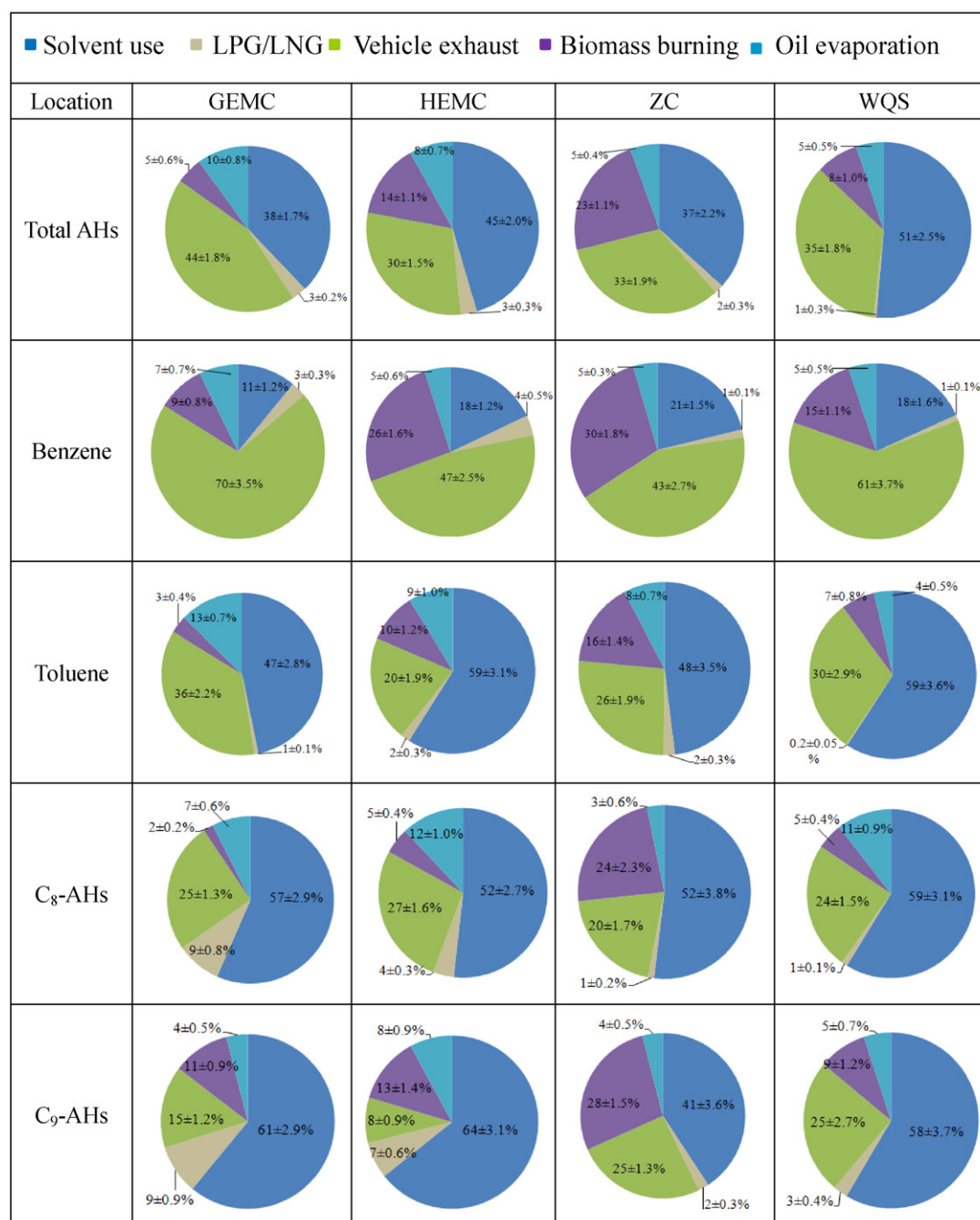


Fig. 5. Source contributions to total AHs as well as benzene, toluene, C₈-AHs and C₉-AHs at GEMC, HEMC, ZC and WQS.

by a significant presence of acetylene, C₃–C₄ alkanes, and aromatics [36]. Source 4 is rich in acetylene, ethene, and C₃–C₄ alkenes, indicating its relation to biomass burning [2]. Source 6 is oil evaporation, which is characterized by the abundance of isopentane, and C₅–C₆ alkanes [75].

Contributions of different sources to total AHs, benzene, toluene, C₈-AHs and C₉-AHs based on PMF at the four sites were presented in Fig. 5. Solvent usage, vehicle exhaust and biomass burning were three major sources that altogether accounted for 89–94% of observed AHs; they individually contributed 30–44%, 37–51% and 5–23% to total AHs, respectively. Vehicle exhausts topped among the sources of AHs at the urban site GEMC with a share of 44 ± 1.8% (mean ± 95% C.I.), and also contributed over 30% to AHs at suburban and rural sites. Solvent use ranked first at the suburban HEMC (45 ± 2.0%), the rural ZC (37 ± 2.2%) and the rural WQS (51 ± 2.5%). Biomass burning, however, shared larger parts at ZC (23 ± 1.1%), which was consistent with the above analysis by diagnostic ratios. In fact, ZC as a site surrounded by farm lands and hills in upwind of urban Guangzhou and Dongguan was probably much more influenced by burning of agricultural residues during the harvest seasons as our sampling periods. This was further confirmed by the higher average level of levoglucosan, a typical biomass burning tracer in particulates [76], at ZC (252 ± 57 ng m⁻³) than at other three sites (142 ± 17 ng m⁻³). The oil evaporation took up more percentages in urban GEMC (10 ± 0.8%) and suburban HEMC (8 ± 0.7%) than at rural sites (5 ± 0.4% in ZC and 5 ± 0.5% in WQS), largely due to more gas stations and heavier traffic in urban and suburban areas. Since the major species from LPG/LNG leakage are C₃ and C₄ alkanes [60], they had very minor contributions to AHs.

As showed in Fig. 5, vehicle exhausts were the major contributors of benzene, from 43 ± 2.7% at the rural ZC to 70 ± 3.5% at the urban GEMC. This was consistent with a contribution of ~65% from vehicle exhausts by CMB model in urban Guangzhou during the fall of 2004 [37], but the contribution of vehicle exhausts to benzene at WQS (61 ± 3.7%) was higher than that (~40%) also resolved by CMB in Xinken, a rural site quite near WQS, in the fall 2004 [37]. The shares of biomass burning in benzene, on the contrary, were higher at rural ZC (30 ± 1.8%) and suburban HEMC (26 ± 1.6%) than that at the urban GEMC (9 ± 0.8%) or rural WQS 15 ± 1.1%. These were significantly different from the study in urban Guangzhou and in Xinken [37] based on CMB model which resolved near zero contribution of biomass burning to benzene. As benzene was forbidden to use in industrial processes, contributions from industry solvents ranging from 11 ± 1.2% to 21 ± 1.5% became less important than from combustion sources. These shares of solvent contributions to benzene largely differed that of about 57% in Xinken from the CMB model [37]. The sum of oil evaporation and LPG/LNG contributed less than 10% to benzene at all sites as benzene is allowed in very limited amount in gasoline oils. In recent years, vehicle numbers in the PRD region increased rapidly with annual growth rates over 20% [77]. This would inevitably aggravate citizens' exposure to traffic-related hazardous chemicals like benzene in urban microenvironments [23,24,78] as well as in region-scale background ambient air. Therefore with the fast increase of vehicle numbers imposing more strict emission standards would be a plausible way to reduce exposure of benzene in the region. It is worth noting that biomass burning contributed 30% of benzene observed at the rural site ZC, suggesting that biomass burning is an important source of benzene particularly in the rural areas.

Unlike benzene, toluene was mainly coming from solvent uses with shares of 47 ± 2.8%, 59 ± 3.1%, 48 ± 3.5% and 59 ± 3.6% at GEMC, HEMC, ZC and WQS, respectively (Fig. 5), and vehicle exhaust ranked second with contributions of 20–36%. Previous studies in the region had reported contributions of solvent use to toluene as about 35% in urban Guangzhou and 61% in rural Xinken based on CMB model [37], and about 66% in the whole PRD region from a

bottom-up emission inventory [31]. Contributions of biomass burning to toluene at ZC (16%) were also higher than that of 3–10% at other sites. This contribution of biomass burning to toluene in the PRD region, however, was not resolved by the CMB study [37] or the bottom-up estimation [31]. Oil evaporation contributed more to toluene at the urban GEMC (13 ± 0.7%) and the suburban HEMC (9 ± 1.0%) than at rural ZC (8 ± 0.7%) and WQS (4 ± 0.5%), consistent with the fact that toluene is a significant component in gasoline. These percentages were higher than that of 1–2% from oil evaporation based on CMB and bottom-up studies [31,37]. For C₈-aromatics (Fig. 5), industrial emissions contributed more than 50% at all sites, and vehicle exhausts ranked the second at all sites except ZC, where C₈-aromatics also had much higher input from biomass burning (24 ± 2.3%) than at other sites. Industry solvents, vehicle exhausts and biomass burning contributed 41–64%, 8–25% and 9–28%, respectively, to C₉-aromatics (Fig. 5).

4. Conclusions

In the present study, we collected ambient air samples at four sites (one urban, one suburban and two rural sites) during November–December 2009 in the PRD region and got 14 hazardous AHs and other NMHCs analyzed. Sources of AHs are primarily diagnosed by ratios like VOCs-to-acetylene and toluene-to-benzene, and further apportioned by the PMF receptor model.

The urban site GEMC showed significantly higher benzene levels than other suburban and rural sites ($p < 0.01$); however, the levels of toluene and C₈-aromatics widely used as industry solvents were much higher at WQS, the rural site downwind the industry zones, than that at other sites ($p < 0.05$). The highest average ratios of AHs to acetylene occurred at WQS except for benzene, and the largest average ratios of benzene to acetylene were observed at urban GEMC. Higher T/B ratios at WQS were resulted from input of industry solvents in its upwind, while T/B ratios were near that of vehicle exhausts in the urban and suburban sites, and much lower T/B ratios were observed at upwind rural ZC due to the influence of biomass burning. The PMF receptor model results showed that solvent use, vehicle exhausts and biomass burning contributed 37–51%, 30–44% and 5–23% of total AHs and these three major sources altogether accounted for 89–94% of observed AHs. Oil evaporation and LPG/LNG-related sources only contributed a minor fraction.

For the carcinogenic benzene, PMF resolved a burden ranging from 43% to 70% for vehicle exhausts. Biomass burning is an important source of benzene particularly in rural areas, such like 30% of benzene from biomass burning at ZC from our study. Toluene and xylenes, as most important precursors to ozone and SOA in the PRD region, were mainly from solvent use and vehicle exhausts. The two sources altogether could explain about 80% of toluene or xylenes observed at the four sites. Solvent use alone contributed 47–59% and 52–59%, respectively, to toluene and xylenes. Therefore reducing their industrial emission or getting them replaced by environmentally friendly chemicals are of vital importance in the control of ozone and SOA precursors in the region.

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