

Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China

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[1] In the second half of 2008 China's highly industrialized Pearl River Delta (PRD) region was hard-hit by the financial crisis (FC). This study reports volatile organic compounds measured in the PRD during November–December in both 2007 before the FC and 2008 after the FC. While total mixing ratios of non-methane hydrocarbons (NMHCs) on average were only about 7% lower from 40.2 ppbv in 2007 to 37.5 ppbv in 2008, their ozone formation potentials (OFPs) dropped about 30%, resulting from about 55% plummet of aromatic hydrocarbons (AHs) against a greater than 20% increase of total alkanes/alkenes. The elevated alkanes and alkenes in 2008 could be explained by greater emissions from vehicle exhausts and LPG combustion due to rapid increase of vehicle numbers and LPG consumption; the drop of AHs could be explained by reduced emissions from industries using AH-containing solvents due to the influence of the FC, as indicated by much lower ratios of toluene to benzene and of xylenes/trichloroethylene/tetrachloroethylene to carbon monoxide (CO) in 2008. Source apportionment by positive matrix factorization (PMF) also revealed much less contribution of industry solvents to total anthropogenic NMHCs and particularly to toluene and xylenes in 2008 than in 2007. Based on PMF reconstructed source contributions, calculated OFPs by industrial emissions were responsible for 40.8% in 2007 in contrast to 18.4% in 2008. Further investigation into local industry output statistics suggested that the plummet of AHs in 2008 should be attributed to small enterprises, which contributed largely to ambient AHs due to their huge numbers and non-existent emission treatment, but were much more influenced by the FC.

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1. Introduction

[2] Ozone strongly affects the atmospheric oxidation capacity [Burnett et al., 1994; Warneck, 2000], governs oxidation processes in the Earth's atmosphere through formation

of OH radical [Lelieveld and Dentener, 2000], and as a greenhouse gas contributes to the radiative balance of the upper troposphere and lower stratosphere [Intergovernmental Panel on Climate Change, 1995]. As an air pollutant with strong oxidizing potential, ozone near the ground poses adverse effects on human health [Lippman, 1989], plant growth and crop yields [Krupa et al., 2001; Wang et al., 2007a, 2007b; Feng et al., 2008]. Increased near ground ozone levels have been observed in various areas over the northern hemisphere with growth rates of 0.5–2% per year [Vingarzan, 2004]. In the East Asia, ambient ozone in megacities and their adjacent areas has become an air quality issue of increasing concern. In Japan, observed tropospheric ozone levels increased at stations like Tsukuba during 1969–1990 and Okinawa during 1989–1997 [Akimoto et al., 1994; Lee et al., 1998]. Elevated ozone levels were also observed in the urban area of Hong Kong during 1984–1999 [Chan et al., 2003], in the background atmosphere of Southern China [Wang et al., 2009], in eastern China during 1991–2006 [Xu et al., 2008], and in Taiwan during 1994–2003 [Chou et al., 2006]. In China, surface ozone pollution occurred only in a

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Figure 1. Location of the sampling site, Wanqingsha (WQS), in the Pearl River Delta in south China.

few urban and industrial centers in the 1980s [Tang *et al.*, 1989], but now has spread to many mega-cities, such as Beijing [Wang *et al.*, 2006], Yangtze River Delta [Xu *et al.*, 1999; Cheung and Wang, 2001], and the Pearl River Delta (PRD) including Hong Kong [Chan *et al.*, 1998; Wang *et al.*, 1998; Wang and Kwok, 2003; Zhang *et al.*, 2008].

[3] Aromatic hydrocarbons (AHs) as an important class of volatile organic compounds (VOCs) are not only hazardous air pollutants but also dominant anthropogenic precursors of ozone [Carter, 1994; Bowman *et al.*, 1995] and secondary organic aerosols [Odum *et al.*, 1997; Forstner *et al.*, 1997; Griffin *et al.*, 1999; O'Dowd *et al.*, 2002; Song *et al.*, 2007; Ng *et al.*, 2007; Sato *et al.*, 2010; Ding *et al.*, 2012]. With fuel combustion and industrial emission as AHs' major sources, they often have higher mixing ratios and contribute substantially to secondary pollutants in urban/industry areas and in polluted plumes [Mohamed *et al.*, 2002; Barletta *et al.*, 2005; Qin *et al.*, 2007]. In the PRD region, one of China's most urbanized and industrialized regions, ambient ozone has become an important air quality concern with both high ambient levels and steadily increasing background levels [Chan *et al.*, 1998; Wang *et al.*, 1998, 2003; Chan *et al.*, 2003; Zhang *et al.*, 2008]. Ozone formation in the region so far was found to be VOC-limited [So and Wang, 2003; Huang *et al.*, 2005; Wang *et al.*, 2005; Shao *et al.*, 2009; Zhang *et al.*, 2007, 2008; Chan and Yao, 2008; Wang *et al.*, 2010]. Since relatively higher ambient AHs were observed in PRD region [X. M. Wang *et al.*, 2002; Chan *et al.*, 2006] with substantial contribution to near ground ozone formation [Barletta *et al.*, 2008; Liu *et al.*, 2008a; Cheng *et al.*, 2010b], emission control of AHs is vital to lower regional ozone pollution [Cheng *et al.*, 2010a].

[4] To explore the VOC sources in the PRD region, many receptor models were applied to field measurement data in previous studies, such as principal component analysis / absolute principal component scores (PCA/APCS) by Guo *et al.* [2004, 2006, 2007] in Hong Kong and Wang *et al.* [2008] in the PRD region, positive matrix factorization (PMF) method by Lau *et al.* [2010] to characterize major VOC sources in Hong Kong, and chemical mass balance (CMB) technique by Liu *et al.* [2008b] for the source apportionment of non-methane hydrocarbons (NMHCs) in

PRD region. Compared to emission inventory by Streets *et al.* [2003] for anthropogenic NMHCs in China with 2000 as the base year, a speciated VOC emission inventory recently established by Zheng *et al.* [2009a, 2009b] offered a more detailed knowledge about VOC emission in PRD region. Nevertheless, in addition to the lack of local emission factors, fugitive emission and/or emission from a large number of small enterprises were quite hard to be included in the emission inventory although these emissions might share a considerable fraction.

[5] The rapid growth in economy in the PRD region has resulted in fast increase in anthropogenic emissions of air pollutants in this region [Chan and Yao, 2008]. The financial crisis brought about a sudden and huge blow on export-oriented industries in the PRD region in the second half of 2008, particularly during the 4th quarter. According to the official statistical report, the Entrepreneur Confidence Index (ECI) of major industrial sectors in Guangdong province all showed a turning-down in the second half of 2008 [Guangdong Provincial Bureau of Statistics (GPBS), 2009], and for some industry sectors like textiles and apparels, processing of metals and metal products, computer accessories and furniture, ECI in the 4th quarter was about half those in the 2nd quarter. According to official statistics, near 1,500 factories, mainly producing toys, shoes, furniture and electronics, closed in Dongguan, a manufacturing base in the PRD region [Guo, 2009]. This number did not include much smaller factories that shutdown due to order loss, since official statistics only counts factories with gross product over 20 million RMB Yuan. On the other hand, very unusually, air quality in the PRD region appeared to be improved a lot in 2008, especially in the second half of the year. As an example, in Guangzhou only 14 haze days, defined as those with visibility less than 10 km with relative humidity less than 90%, were observed in the second half of 2008, a significant drop from 47 days in the second half of 2007. With the industry in the PRD region hard-hit due to financial crisis, it is also a unique opportunity to assess the role of industrial emission from ambient monitoring before and after the outbreak of financial crisis. In the present study we report levels, compositions and ozone formation potentials (OFP) of VOCs observed at a rural site in the central PRD region during autumn 2007 and autumn 2008. Tracer methods and the Positive Matrix Factor (PMF) technique were applied to identify the major VOC sources as well as their contribution to ozone formation. The purpose of this study is to better understand anthropogenic ozone precursors emitted from industry in the region for more efficient and accurate control strategies to mitigate regional ozone pollution.

2. Materials and Methods

2.1. Description of Sampling Site

[6] The PRD region, with an area of 41,698 km² and a population of about 42.9 million (2008), is located in the southeast corner of China and middle-southern part of the Guangdong Province (Figure 1). It encompasses nine cities in Guangdong province, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Foshan, Jiangmen, Zhongshan, Zhaoqing and Huizhou, plus Hong Kong and Macau Special Administrative Regions constituting the greater PRD. The

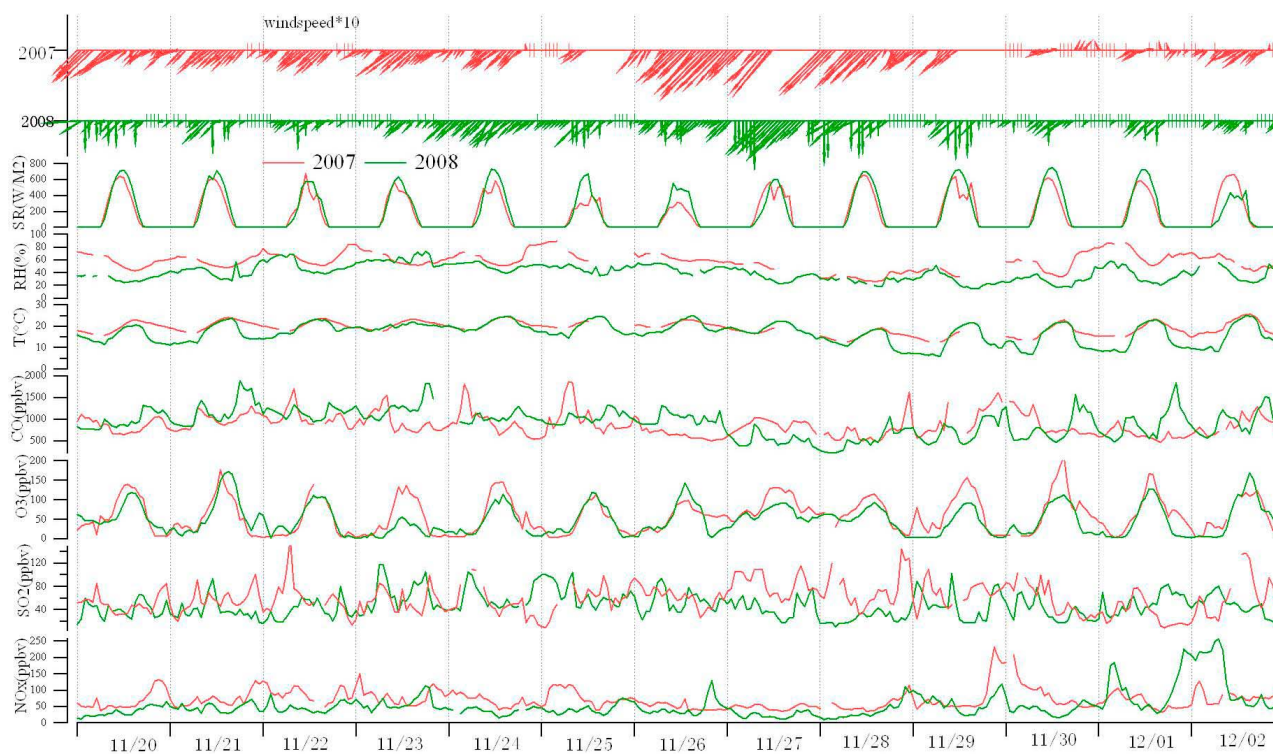


Figure 2. Time series of meteorological factors and trace gases during November 20 to December 1 in 2007 and 2008.

field sampling site (22.711°N, 113.549°E), is located at Wanqingsha (WQS), a small town southernmost of Guangzhou in the center of the PRD (Figure 1). This small town is surrounded by farmlands, and has very few textile and clothing workshops, so the local anthropogenic emissions are not remarkable and air 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, 50 km to the northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good regional monitoring station to characterize the air pollution in inner PRD. The measurement was carried out 15 m above the ground on the rooftop of the teaching building in a middle school.

2.2. Field Sampling

[7] Ambient VOCs samples were collected from November 25 to December 1 both in 2007 and 2008 using cleaned and evacuated 2-Liter electro-polished stainless steel canisters. During field sampling an Entech's restrictive sampler (Part No. 39-RS-3, Entech Instruments Inc., CA, USA) was adopted to allow each canister to be filled in about 60 min. Samples were collected every two hours starting at 00:00, 02:00, 04:00, 06:00, 08:00, 10:00, 12:00, 14:00, 16:00, 18:00, 20:00 and 22:00. A total of 76 samples were collected in 2007 and 84 samples were collected in 2008.

[8] The meteorological parameters were measured by a mini weather station (Vantage Pro2TM, Davis Instruments Corp., USA). Trace gases including O₃, NO-NO₂-NO_x, CO and SO₂ were also monitored online during the two field campaigns in 2007 and 2008. Detailed information about the measurements and quality control and quality assurance can

be found elsewhere [Guo *et al.*, 2009; Zhang *et al.*, 2010]. Time series of wind speed/direction, relative humidity, temperature and global solar radiation were showed in Figure 2.

2.3. Lab Analysis of VOCs and Carbon Monoxide (CO)

[9] Air samples were analyzed using a Model 7100 pre-concentrator (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 [Yi *et al.*, 2007; Wang and Wu, 2008]. Briefly, the VOCs inside the canister were first concentrated in a 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 first separated by an HP-1 capillary column (60 m \times 0.32 mm \times 1.0 μm , Agilent Technologies, USA) with helium as carrier gas, and then split into two ways: one is a PLOT-Q column (30 m \times 0.32 mm \times 2.0 μm , Agilent Technologies, USA) followed by FID detection, another is a 65 cm \times 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 $15^{\circ}\text{C min}^{-1}$, then to 120°C at $5^{\circ}\text{C min}^{-1}$, then to 250°C at $10^{\circ}\text{C min}^{-1}$, and finally

holding for 10 min. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). CO in air samples was also analyzed by a gas chromatography (Agilent 6890 GC) equipped with a FID and a packed column (5A Molecular Sieve 60/80 mesh, 3 m × 1/8 inch). CO was first converted by Ni-based catalyst to CH₄ and then detected by FID after separation by the packed column.

2.4. Quality Control and Quality Assurance

[10] Before sampling, all canisters were cleaned at least five times by repeatedly filling and evacuating of humidified zero air. In order to check if there was any contamination in the canisters, all vacuumed canisters after cleaning procedure were re-filled with humidified zero air and 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.

[11] Target compounds were identified based on their retention times and mass spectra, and quantified by external calibration method. C₄-C₁₁ hydrocarbons and chlorinated solvents 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) 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 (MDL) for each VOCs species were presented in Table 1.

2.5. Positive Matrix Factorization (PMF)

[12] PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices, factor contributions and factor profiles, which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis, and emission inventories. The method is reviewed briefly here and described in greater detail elsewhere [Paatero and Tapper, 1994; Paatero, 1997].

[13] An ambient data set can be viewed as a data matrix X of i by j dimensions, in which i number of samples and j chemical species were measured. The goal of multivariate receptor modeling is to identify a number of sources p that best characterize the VOC composition at a site, with the species profile f of each source, and the amount of mass g contributed by each source to each individual sample, plus the residuals e :

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij}. \quad (1)$$

[14] Results are constrained by a penalty function so that no sample can have a negative source contribution and no

species can have a negative concentration in any source profile. Another strength of PMF is that it can individually weigh each data point. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. By individually weighing data, samples with some species missing or below the detection limit do not need to be excluded as a whole; rather the analyst can adjust the uncertainty so that these missing or below-detection-limit species have little or no impact on the final solution. The PMF solution minimizes the object function Q , based on these uncertainties (u):

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik}f_{kj}}{u_{ij}} \right]^2. \quad (2)$$

[15] USEPA PMF 3.0 model was applied to explore the sources of observed NMHCs. The approaches for replacing and developing uncertainty values for missing and below-detection-limit data were drawn from previous works [Poirot *et al.*, 2001; Hopke *et al.*, 2003]. Briefly, data values below the method detection limit (MDL) were substituted with MDL/2; missing data values were substituted with median concentrations. Uncertainties were treated the same way as Polissar *et al.* [1998] and Reff *et al.* [2007]. 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 $Unc = [(\text{Error Fraction} \times \text{mixing ratios})^2 + (\text{MDL})^2]^{1/2}$. The number of factors in the PMF model was chosen based on the result from PCA/APCS model [Anderson *et al.*, 2001].

3. Results and Discussion

[16] As illustrated in Figure 2, during the identical sampling intervals in both years meteorological conditions were quite similar to each other. Average air temperature was $19.3 \pm 0.3^\circ\text{C}$ (mean ± 95% C.I.) in 2007 and $17.6 \pm 0.5^\circ\text{C}$ in 2008; prevailing wind directions were all NNE; average wind speed was 1.6 m/s in 2007 and 1.3 m/s in 2008. For trace gases, averaged levels of O₃, NO_x, SO₂ and CO were 59 ± 5 , 71 ± 3 , 59 ± 3 and 886 ± 29 ppbv (mean ± 95% C. I.) in 2007, and 48 ± 4 , 53 ± 5 , 47 ± 2 and 917 ± 35 ppbv in 2008, respectively. Maximum O₃ level was 212 ppbv in 2007 and 173 ppbv in 2008. In the present study, since our focus was put on anthropogenic NMHCs, biogenic hydrocarbons like isoprene and monoterpenes were not included although they are very important ozone precursors.

3.1. Changes in Levels, Compositions and Ozone Formation Potentials (OFP) of NMHCs

[17] Average mixing ratios together with the 95% confidence intervals, minimum and maximum values for PAMS targeted NMHCs, expressed in part per trillion by volume (pptv), were summarized in Table 1. During the sampling periods, total NMHC mixing ratios averaged 40.2 ± 0.4 (mean ± 95% C.I.) and 37.5 ± 0.3 ppbv in 2007 and 2008, respectively. Toluene was the most abundant species in both 2007 and 2008, similar to the previous studies in Dongguan

Table 1. The Method Detection Limits (MDL) and Mixing Ratios of 51 NMHCs Measured at WQS in 2007 and 2008^a

Group	Species	MDL	2007				2008			
			Mean	95% C.I.	Min	Max	Mean	95% C.I.	Min	Max
Alkanes	Ethane	39	2659	249	935	6884	3229	342	1034	9326
	Propane	31	1855	239	424	5702	2851	312	784	7210
	Isobutane	17	772	125	80	2794	1489	133	381	3162
	n-Butane	21	1088	159	161	3474	1796	155	765	4050
	1-pentane	14	527	107	60	2498	1835	336	180	8789
	n-Pentane	8	515	106	84	3498	1007	211	145	6614
	2,2-Dimethylbutane	14	47	6	10	144	76	12	ND*	273
	2,3-Dimethylbutane	12	112	20	21	621	349	109	ND	2618
	2-Methylpentane	8	477	68	65	1342	707	110	91	2073
	3-methylpentane	7	284	55	42	1269	671	122	110	3030
	n-Hexane	6	1109	507	8	12996	1102	271	115	7846
	Methylcyclopentane	9	549	294	25	7787	243	45	14	1140
	2,4-Dimethylpentane	4	47	6	11	131	71	13	11	333
	Cyclohexane	6	75	17	8	532	337	75	ND	2223
	2-Methylhexane	6	270	60	16	1411	463	212	ND	5821
	2,3-Dimethylpentane	9	34	7	ND	161	261	71	ND	2181
	3-Methylhexane	6	1600	386	62	9376	631	259	17	9585
	2,2,4-Trimethylpentane	9	102	150	ND	5714	25	5	ND	85
	n-Heptane	10	458	114	20	2941	542	157	ND	3851
	Methylcyclohexane	5	167	40	11	984	303	99	8	2669
	2,3,4-Trimethylpentane	6	18	14	ND	401	47	17	ND	326
	2-Methylheptane	4	79	13	5	365	77	24	ND	538
	3-Methylheptane	5	41	7	5	173	57	20	ND	509
n-Octane	6	295	56	19	1757	683	270	ND	8111	
n-Nonane	6	206	100	12	2963	57	17	6	405	
n-Decane	6	467	220	31	7671	69	24	ND	568	
n-Undecane	7	140	49	7	1309	64	20	ND	350	
Alkenes	Ethene	41	3697	380	571	9091	3554	444	1086	10555
	Propene	31	390	59	150	1980	1258	206	251	4467
	1-Butene	17	166	69	26	2591	790	119	131	2539
	Trans-2-butene	13	50	17	9	358	215	51	24	1261
	Cis-2-butene	11	46	15	ND	311	165	34	10	718
	1-Pentene	20	30	6	6	151	81	17	ND	404
	Isoprene	13	107	35	10	908	139	42	11	1428
	Trans-2-pentene	10	38	17	ND	415	67	17	ND	333
	Cis-2-pentene	6	76	30	7	726	59	18	ND	551
	Aromatics	Benzene	14	890	129	231	3073	1289	248	126
Toluene		9	6635	1377	117	30862	4032	968	147	20480
Ethylbenzene		6	2553	972	46	27554	897	240	32	5226
m/p-Xylene		9	4778	2724	62	84314	850	228	26	5053
o-Xylene		4	1757	925	33	26735	360	94	15	1812
i-Propylbenzene		4	206	100	12	2963	20	6	ND	133
Propylbenzene		4	51	15	10	281	45	14	ND	280
m-Ethyltoluene		3	101	32	7	762	253	153	ND	4781
p-Ethyltoluene		3	134	49	3	1165	183	80	ND	2290
1,3,5-Trimethylbenzene		3	91	36	10	1024	53	20	ND	384
o-Ethyltoluene		3	79	34	3	1021	43	14	ND	293
1,2,4-Trimethylbenzene		6	142	49	11	1146	131	46	ND	936
1,2,3-Trimethylbenzene		5	108	61	5	2015	54	18	ND	446
1,3-Diethylbenzene		4	210	133	10	4580	88	41	ND	1132
Alkynes	Ethyne	57	3814	354	1087	9494	3817	214	1107	5450

^aUnit is parts per trillion by volume, pptv. C. I., confidence interval.

city upwind of WQS [Chan *et al.*, 2006; Barletta *et al.*, 2008] and at a suburban site (Xinken) close to WQS in Guangzhou [Liu *et al.*, 2008a]. As shown in Figure 3a, while average total mixing ratio of NMHCs was only about 7% lower in 2007 than that in 2008, their compositions exhibited great changes. Consistent with results by Liu *et al.* [2008a] in the upwind Dongguan in 2004, observed AHs at WQS in 2007 ranked the first among NMHCs with a share of 44.2% in average, followed by alkanes (34.8%), alkenes/alkynes (20.9%). In 2008, however, alkanes (50.8%) shared the largest fraction and aromatics (22.1%) ranked the third after alkenes/alkynes (27.2%). Average total mixing ratio of AHs dropped about 53% in 2008 compared to that in 2007,

while total alkanes and alkenes/alkynes increased 36.1% and 20.6%, respectively.

[18] To compare and recognize the contribution of individual hydrocarbons to photochemical ozone formation, a maximum incremental reactivity (MIR) method proposed by Carter [1994] was applied to indicate their ozone formation potentials (OFPs). While in average total mixing ratios of NMHCs were quite similar in both years, their calculated total OFPs, however, dropped from 135.5 ppbv in 2007 to 95.7 ppbv in 2008 (Figure 3b), a decrease of about 30%. This decrease, as illustrated in Figure 3b, was attributed to the decreased contribution of aromatics against the increased contribution of other NMHC fractions. Figure 4 showed the

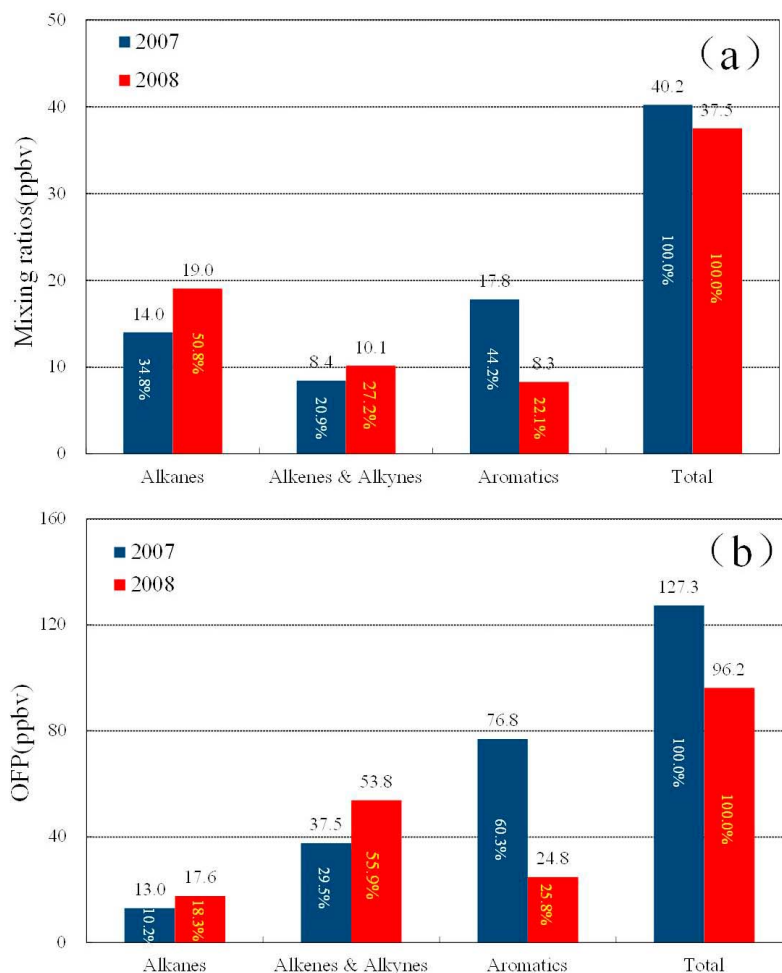


Figure 3. (a) Mixing ratios (ppbv) and (b) Ozone formation potentials OFP (ppbv) by total and grouped NMHCs in 2007 and 2008.

top 30 anthropogenic non-methane hydrocarbons ranked by their OFPs based on our measurements in both years. Similar to previous observations in Guangzhou in 2005 by *Tang et al.* [2007] in Dongguan and in 2005 by *Barletta et al.* [2008], AHs topped in the contribution to total OFP in 2007, but in 2008 alkenes, mainly C_2 - C_4 alkenes, replaced AHs as top OFP contributors.

3.2. Diagnostic Analysis of Changing Sources

[19] The great changes in NMHCs compositions in 2008 implied the changing pattern of emission sources. What were the reasons for the unusual drop of observed aromatic hydrocarbons in 2008? During the sampling periods in both 2007 and 2008, prevailing winds were all NNE and back trajectories showed that air masses mostly passed Dongguan before arriving at the sampling site WQS. Since average wind speed during the sampling period in 2008 (1.3 m/s) was lower than that in 2007 (1.6 m/s), if meteorological condition was the sole factor leading to the changed mixing ratios, observed AHs, just like other NMHCs, would have elevated levels in 2008 due to less favorite dispersion conditions. Therefore, the decrease of AHs implied their reduced emission, especially in the upwind Dongguan.

[20] As ambient levels of an individual VOC species are determined not only by its emission, but also by its atmospheric reactions and meteorological conditions, levels of a VOC species would give no indication of its emission sources. However, the ratios of levels for VOC pairs, which are not influenced by dilution, can be used to trace sources if they remain relatively stable during atmospheric reactions, or to indicate aging of air masses if they are changed with atmospheric reactions. As the rate constants of aromatics with OH radical are about five magnitudes larger than with NO_3 radical or with O_3 [Finlayson-Pitts and Pitts, 1999; Atkinson and Arey, 2003], reaction with OH was the major pathway for their removal. Since our samples were collected in wintertime when OH radical should be much lower than in summertime, even using a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3} in wintertime [Kanaya et al., 2007], with the rate constants by Atkinson and Arey (2003) we can calculate the life times for benzene and toluene as 114 and 25 h, respectively. As average transport time from major source regions in the daytime was about 3 h during sampling periods, loss due to photochemistry for benzene and toluene should be less than 10% and thus were negligible, and T/B ratios could be used

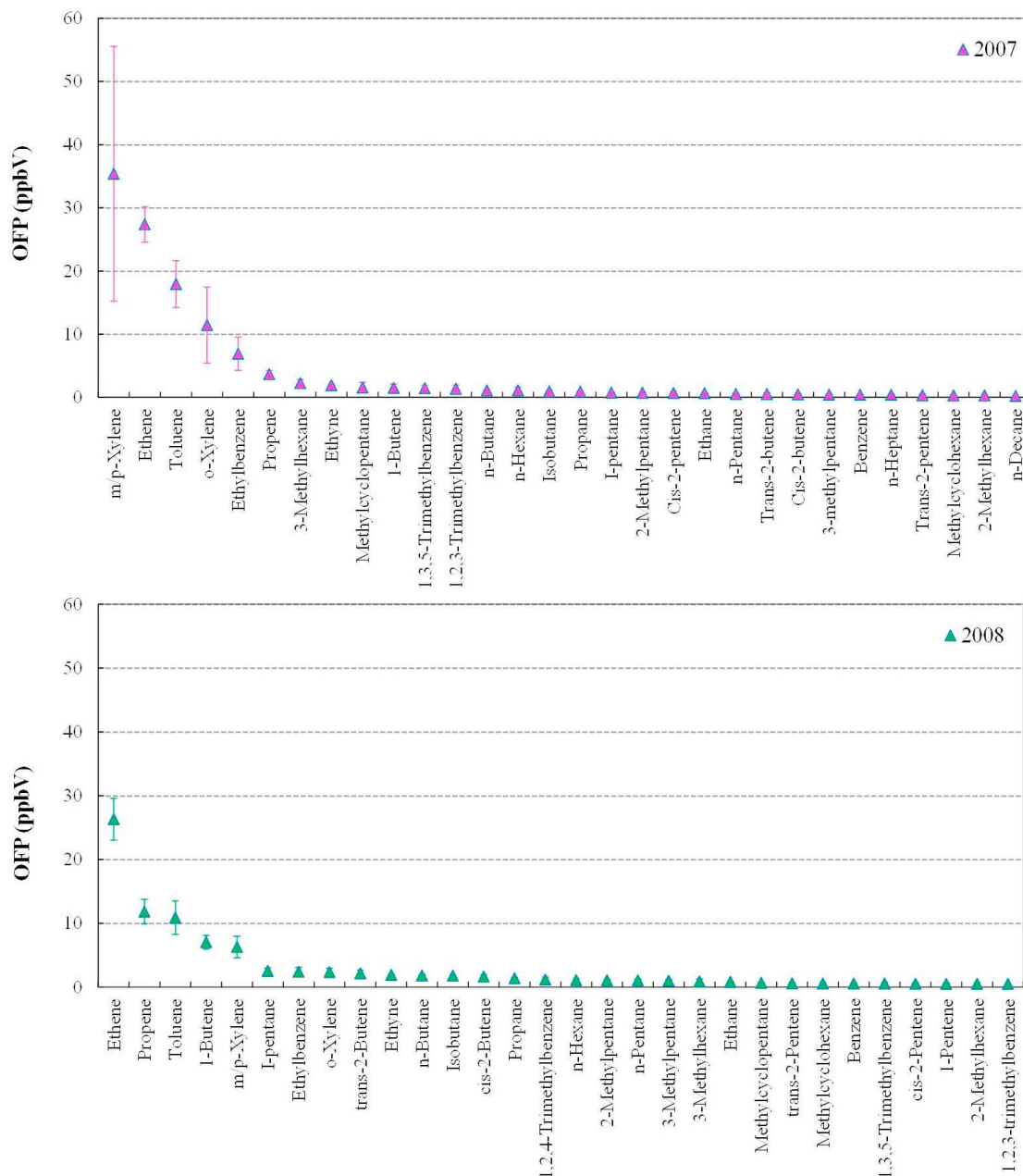


Figure 4. The top thirty anthropogenic hydrocarbons ranked by their ozone formation potentials in 2007 and 2008.

for diagnosing sources in the present study. Benzene, as a carcinogenic compound forbidden to be used in industry solvents or consumer products, is usually associated with combustion processes and in urban areas automobile exhaust is its major source [Barletta *et al.*, 2002; X. M. Wang *et al.*, 2002; Zhao *et al.*, 2004]. For toluene, ethylbenzene and xylenes, however, they also have emission sources from industrial solvent use in the painting, coating, printing, cleaning processes in addition to vehicle exhaust, especially in the highly industrialized regions like the PRD region [X. M. Wang *et al.*, 2002; Guo *et al.*, 2007]. Therefore, in urban areas higher toluene to benzene (T/B) ratios typically suggest more source input from industry, and/or transported pollutants from additional sources of toluene from upwind

industrial activities [Chan *et al.*, 2006]. As showed in Table 1 and Figure 5, although total aromatics showed a significant drop in 2008, benzene levels still rose at similar percentages as other NMHCs like alkanes and alkenes. High T/B ratios observed in Dongguan in 2005 by Barletta *et al.* [2008] and at our sampling site downwind Dongguan in 2007 from this present study all indicated industry emissions as important sources of AHs in Dongguan. Mean T/B ratio in 2008 was 2.78, near 2.0 typical of vehicle exhaust [X. M. Wang *et al.*, 2002] but much lower than that of 7.42 in 2007, implying much less contribution from industry emissions to the aromatics in 2008 in the upwind regions. These results were consistent with the higher T/B ratio of 4.25 reported in urban Shanghai in the highly industrialized Yangtze River

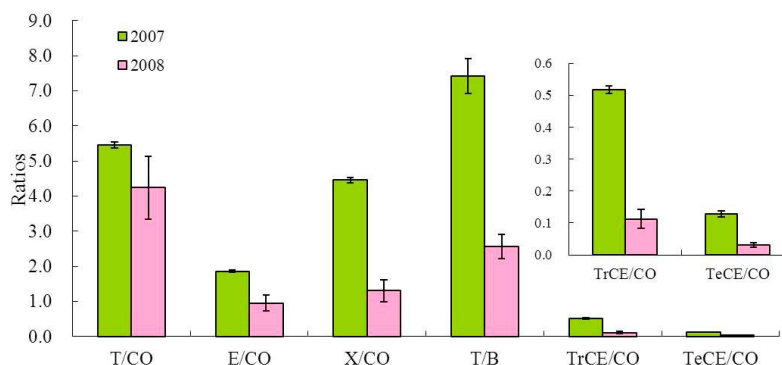


Figure 5. Ratios of typical VOCs to CO and T/B in 2007 and 2008. B: Benzene; T: Toluene; E: Ethylbenzene; X: Xylenes; TrCE: Trichloroethylene; TeCE: Tetrochloroethylene.

Delta [Barletta *et al.*, 2005] and much lower T/B ratios (~ 2.0) in urban areas of Changchun, Beijing and Changsha with traffic emission as dominant sources of AHs [Liu *et al.*, 2000; Barletta *et al.*, 2005].

[21] CO is generally emitted from incomplete combustion of fossil fuel in urban areas and of biomass and crop residues in non-urban areas [T. Wang *et al.*, 2002], whereas trichloroethylene (TrCE) and tetrochloroethylene (TeCE) widely used as industrial solvents and degreasers are excellent urban/industrial tracer [Wang *et al.*, 1995]. The ratios of aromatics, TrCE and TeCE to CO are therefore indicators of solvent use relative to combustion sources. Slopes from scatterplots between VOCs and CO are much better to indicate the emission ratios [Borbon *et al.*, 2003; Warneke *et al.*, 2007]. In the present study, no significant correlations were found between toluene/xylenes and CO or between TrCE/TeCE and CO due largely to their different sources; and CO background levels, all less than 200 ppbv if the lowest observed CO were taken as the background ones, were much lower than the observed average CO mixing ratios (~ 900 ppbv) in both years, therefore here we just calculated the ratios by dividing the mixing ratios of VOCs to that of CO for indicating the changes in emission sources. Much lower aromatics/CO, TrCE/CO and TeCE/CO ratios in 2008 than in 2007 (Figure 5) also suggest less industry emission in 2008. The ratio of xylenes to CO (X/CO) dropped from 4.5 in 2007 to 1.2 in 2008 (Figure 5). p-Xylene is the principal precursor to terephthalic acid and dimethyl terephthalate, both of which are used in the production of polyethylene terephthalate (PET) plastics and polyester fiber. Xylene mixture is a common solvent in ink, rubber, adhesive and leather industries, in thinning paints and varnishes as a substitute for toluene to slow the drying, and in cleaning agent for steel, silicon wafers and chips. As computer accessories, automobiles, textiles and apparels, printing and dyeing, metal and plastic products, and furniture are among the major products in the PRD region, xylenes are in fact widely used as chemical feedstock and industrial solvents in the region. The drop of X/CO ratios in 2008 probably also reflected the decreased emission of xylenes from industries due to the influence of financial crisis.

3.3. Source Apportionment by PMF

[22] VOC emission inventories are difficult to assemble because significant emissions come from natural sources

(biogenic emission) and fugitive (evaporative) sources, which are even harder to estimate [Kourtidis *et al.*, 1999]. A quantitative assessment of the contributions from various sources to ambient VOCs can be obtained by applying receptor models, which are supposed to provide an independent check on the quality of the VOC emission inventories [Jorquera and Rappengluck, 2004]. As biogenic VOC species like isoprene and monoterpenes are highly reactive gases and typically has mixing ratios less than 1 ppbv due to their very short lifetimes [Atkinson and Arey, 2003], it is not proper to include these species in receptor models otherwise their emission would be underestimated [Atkinson and Arey, 1998]. Here we just put our focus on the anthropogenic NMHCs, 30 dominated NMHC species excluding biogenic VOCs were subsequently analyzed using the PMF. To better understand the contribution of biomass burning and coal burning, the combustion marker CO and the biomass burning marker CH_3Cl were also included in the PMF model. As illustrated in Figure 6, six major sources were resolved in 2007 and 2008, respectively. Source 1 is diesel exhaust which is characterized by a significant amount of n-decane [Yuan *et al.*, 2009; Song *et al.*, 2008] and light hydrocarbons like ethyne and $\text{C}_3\text{-C}_4$ alkanes [Watson *et al.*, 2001; Na *et al.*, 2004]. Source 2 shows a dominance of i-pentane, 2-methylpentane, and 2,3-dimethylbutane in the source profile, and the least amount of combustion produced CO, therefore this source is believed to be evaporative emissions [Na *et al.*, 2004]. Source 3 is LPG/LNG, which is characterized by a high mass percentage of propane, isobutane, n-butane and ethane, typically tracers of emission from LPG/LNG [Barletta *et al.*, 2002, 2008]. Source 4 is rich in aromatic species and $\text{C}_6\text{-C}_7$ alkanes which are major components in various solvents commonly used in many manufacturing industries [He *et al.*, 2002; Chan *et al.*, 2006], such as electronics industry in particularly the PRD region. Also much higher T/B ratio occurred in this source. So this source is considered to be a composite of emissions from industrial solvent use [Seila *et al.*, 2001]. Substantial contribution to CH_3Cl and CO in the source 5 indicated this source is related to biomass burning and/or coal burning [Blake *et al.*, 1996; McCulloch *et al.*, 1999]. Source 6 is identified by gasoline exhaust on the basis of a significant presence of ethyne, aromatics, n-pentane and CO [Watson *et al.*, 2001; Guo *et al.*, 2007] and by its higher contribution in rush hours.

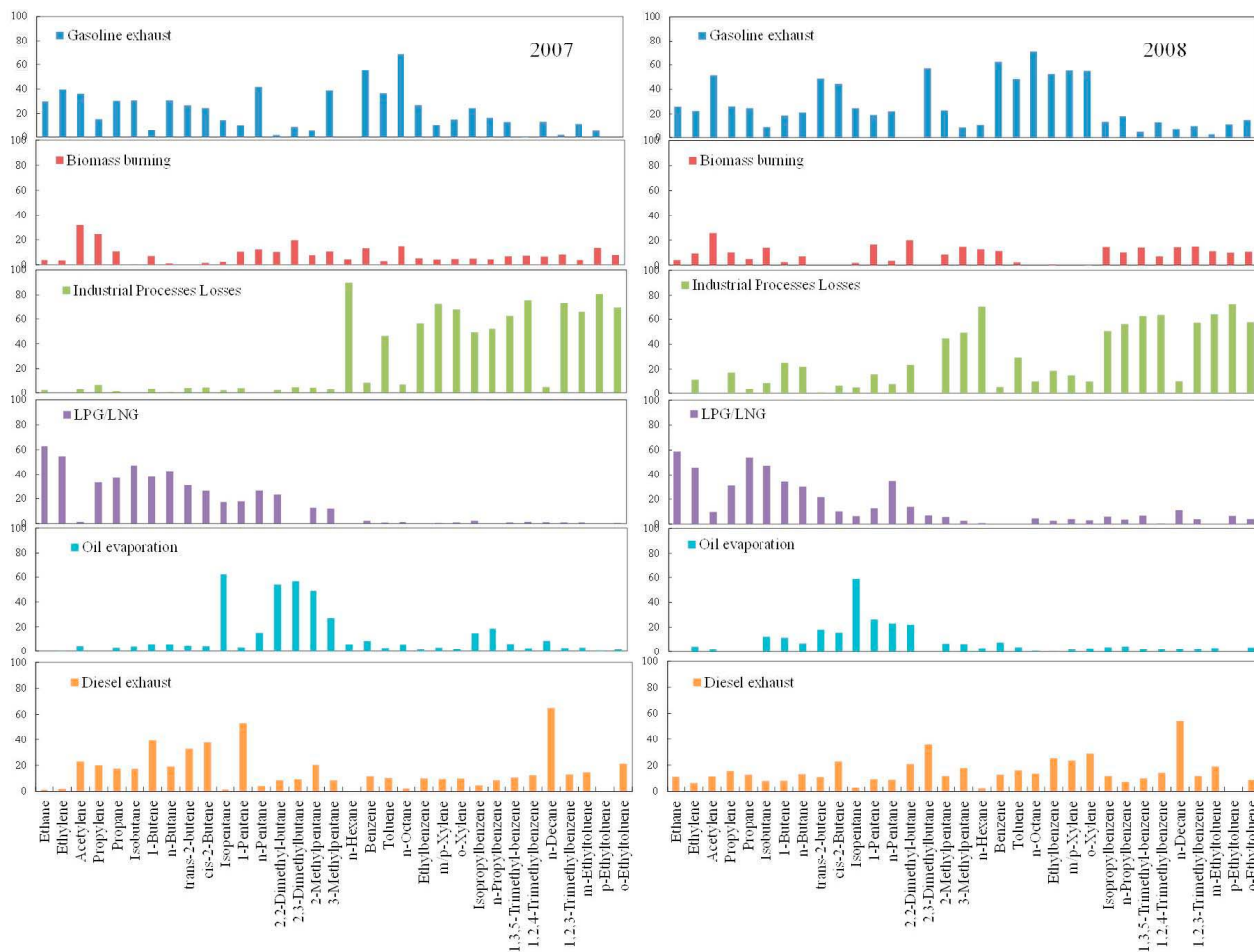


Figure 6. Factor profiles (% of species) for NMHCs in 2007 and 2008.

[23] The PMF reconstructed mass matched the measured mass very well, with slopes (reconstructed to measured) of 0.95 and 0.97 and r^2 of 0.91 and 0.93 for the data set of 2007 and 2008, respectively. The average contributions of each source to NMHCs in the PRD region are illustrated in Figure 7. Quite similar contributions were observed between the two years for diesel exhaust, 11.5% in 2007 and 11.9% in 2008, and for biomass burning, 8.4% in 2007 and 8.7% in 2008. The most significant change was that of industrial emission, from 29.2% in 2007 to 14.2% in 2008. This huge drop of contribution from industry was consistent with diagnostic ratios discussed above. As showed in Figure 7, contributions from gasoline exhaust and oil evaporation increased in 2008, which, as discussed below, matched the increased numbers of vehicles, especially gasoline-powered private cars, in the whole PRD region and in cities around the sampling site. The shares of gasoline-powered vehicle exhaust in this study (28.0% in 2007 and 32.8% in 2008) were similar to share of $\sim 31\%$ in Xinken quite near WQS in 2004 by a CMB approach [Liu *et al.*, 2008b], and much lower than those in urban Guangzhou in 2004 [Liu *et al.*, 2008b] and in cities like Milan and Los Angeles [Latella *et al.*, 2005; Brown *et al.*, 2007] where traffic-related sources dominated in VOC emissions. Elevated contribution

from LPG in 2008 can be well explained by increased consumption of LPG in the region, as the daily consumption of LPG in Guangdong Province increased from 16,595 tons standard coal equivalent (SCE) in 2007 to 17,458 tons SCE in 2008 [GPBS, 2009], an annual increase of 5.2%; and the LPG consumption in the much more developed PRD region was supposed to have an even higher annual increase rate than the whole province, although no statistical data are available. The only available bottom-up VOC emission inventory in the region was compiled by Zheng *et al.* [2009b]. Our results about contribution from industry emission and gasoline exhaust in 2007 (“normal year”) were similar to that by Zheng *et al.* [2009b] in upwind Dongguan, but contributions of diesel exhaust, oil evaporation, biomass burning and LPG from our results were much higher than those by Zheng *et al.* [2009b].

[24] As mentioned above, benzene is a carcinogenic compound forbidden to use in industrial processes, so it should come predominantly from combustion of fuels and biomass, as can also be reflected from our PMF results. As showed in Figure 8, PMF results revealed that in both years vehicle exhaust was the major source of benzene, accounting for about 70% of benzene in both years; and oil evaporation, LPG and industrial processes only had minor contributions.

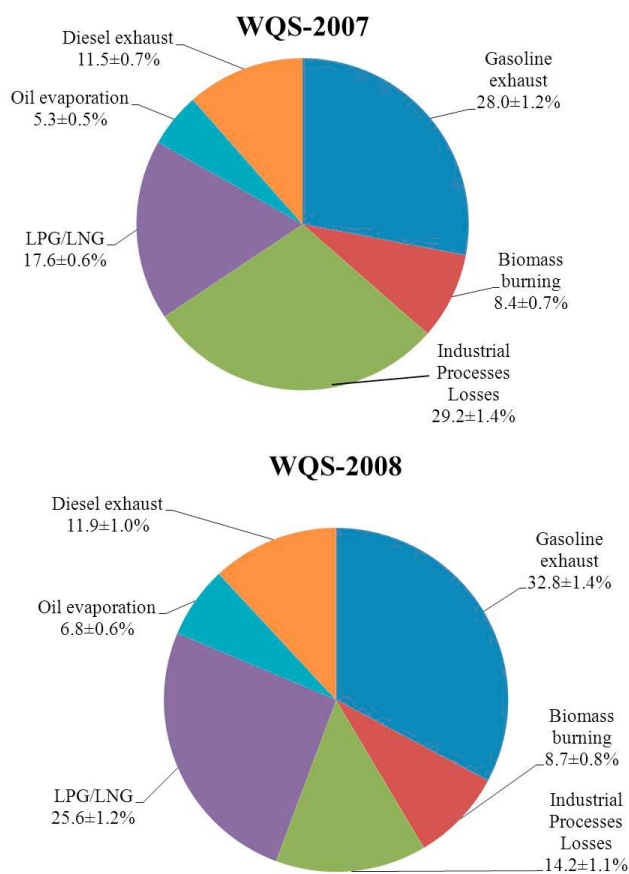


Figure 7. Source contribution in percentages to the total NMHCs in 2007 and 2008 (mean ± standard error).

While contribution from diesel exhaust was only a little higher in 2008 (12.8%) than in 2007 (11.6%), contribution from gasoline exhaust enlarged from 55.4% in 2007 to 62.5% in 2008. Increased share of vehicle exhaust in 2008 in fact matched very well with the increase of vehicle number in the PRD region. In the whole PRD region, total vehicle number rose from ~4.2 million in 2007 to ~4.7 million in 2008; and in Guangzhou and Dongguan, total vehicle numbers rose from 1,041,917 and 608,933 in 2007 to 1,171,731 and 701,600, respectively [GPBS, 2008, 2009]. In particular, the most striking increase of vehicle numbers was that of gasoline-powered sedan cars. Numbers of sedan cars in Guangzhou and Dongguan were 408,139 and 262,218 in 2007, and were 575,676 and 357,676 in 2008, with annual increase of 41% and 36%, respectively. This rapid increase of vehicle numbers in the PRD region would certainly lead to larger amount of VOCs emitted from vehicles to the ambient. As shown in Table 1 and Figure 3a, the ~30% increase of benzene and light alkanes was largely explained by the elevated vehicle emission and less favorable dispersion conditions in 2008.

[25] For other AHs like toluene and xylenes, there are two major sources: vehicle (diesel + gasoline) exhausts and industrial emissions. Toluene and xylenes, as widely used solvents and chemical feedstock, would have less emission from industrial processes if the industry was hard-hit by the

financial crisis. As showed in Figure 8, PMF results indicated that vehicle exhausts and industrial emission together covered over 90% of toluene and C8-aromatics (ethylbenzene and xylenes) in both years. For toluene the contribution from industrial processes (46.3%) was comparable with that from vehicle emissions (46.9%) in 2007; while in 2008 64.5% and 29.3% of toluene were from vehicle exhausts and industrial emission, respectively (Figure 8). Contribution from industrial emission dropped even more for C8-aromatics (ethylbenzene and xylenes). As showed in Figure 8, industrial emission accounted for 65.9% of C8-aromatics in 2007 in contrast of only 15.7% in 2008. Contributions to C8-aromatics by diesel exhaust and gasoline exhaust, however, changed drastically from 9.7% and 16.9% in 2007 to 25.1% and 54.2% in 2008, respectively. The PMF results also confirmed the significant drops in emission of toluene and xylenes from industrial processes due to the influence of the financial crisis.

3.4. Contribution of OFPs by VOCs From Different Emission Sources

[26] For each VOC species, PMF can get an estimate of its contributions from different sources. Therefore, OFP from source i , OFP_i , can be calculated as the sum of OFP due to amount of VOC species from source i :

$$OFP_i = \sum_j OFP_{ij} = \sum_j C_{ij} \times MIR_j \quad (3)$$

where OFP_{ij} is the OFP of VOC species j from source i , C_{ij} is the reconstructed mixing ratios by PMF for species j from source i and MIR_j is the MIR coefficient for VOC species j [Carter, 1994].

[27] Apart from the total OFP decrease and OFP changes for each group of NMHCs (Figure 3b), Contributions to OFP by different sources based on results from above equation (3) are illustrated in Figure 9. In 2007 OFP by industrial emission (40.8%) topped, followed by gasoline exhaust (23.5%), LPG (17.2%) and diesel exhaust (9.5%). Therefore in the “normal” years like 2007 industrial emission, vehicle exhaust and LPG are responsible for about 90% of the OFP from anthropogenic sources. With industrial emission significantly reduced as the case in 2008, although this reduction was due to financial crisis instead of positive emission control, significant drop of OFP by industrial emission (Figure 9) was the main reason for the decreased total OFP in 2008 (Figure 3b). As discussed above, increased OFP percentages from vehicle exhaust (particularly gasoline-powered vehicle exhaust) and LPG were related to the rising vehicle numbers and LPG consumption. Therefore, to lower OFPs from anthropogenic VOCs in the PRD region, the effective approach should be the reduction of reactive organic gases from industrial processes, vehicle exhausts, and LPG-related emission. The latter can be achieved by further replacing LPG with cleaner LNG as done very recently in the urban Guangzhou.

3.5. Implication of AHs From Industrial Emission: Role of Small Enterprises/Fugitive Sources?

[28] As discussed above, diagnostic ratios and PMF results all indicate much less contribution from industrial emission in 2008 for AHs. One question is whether this

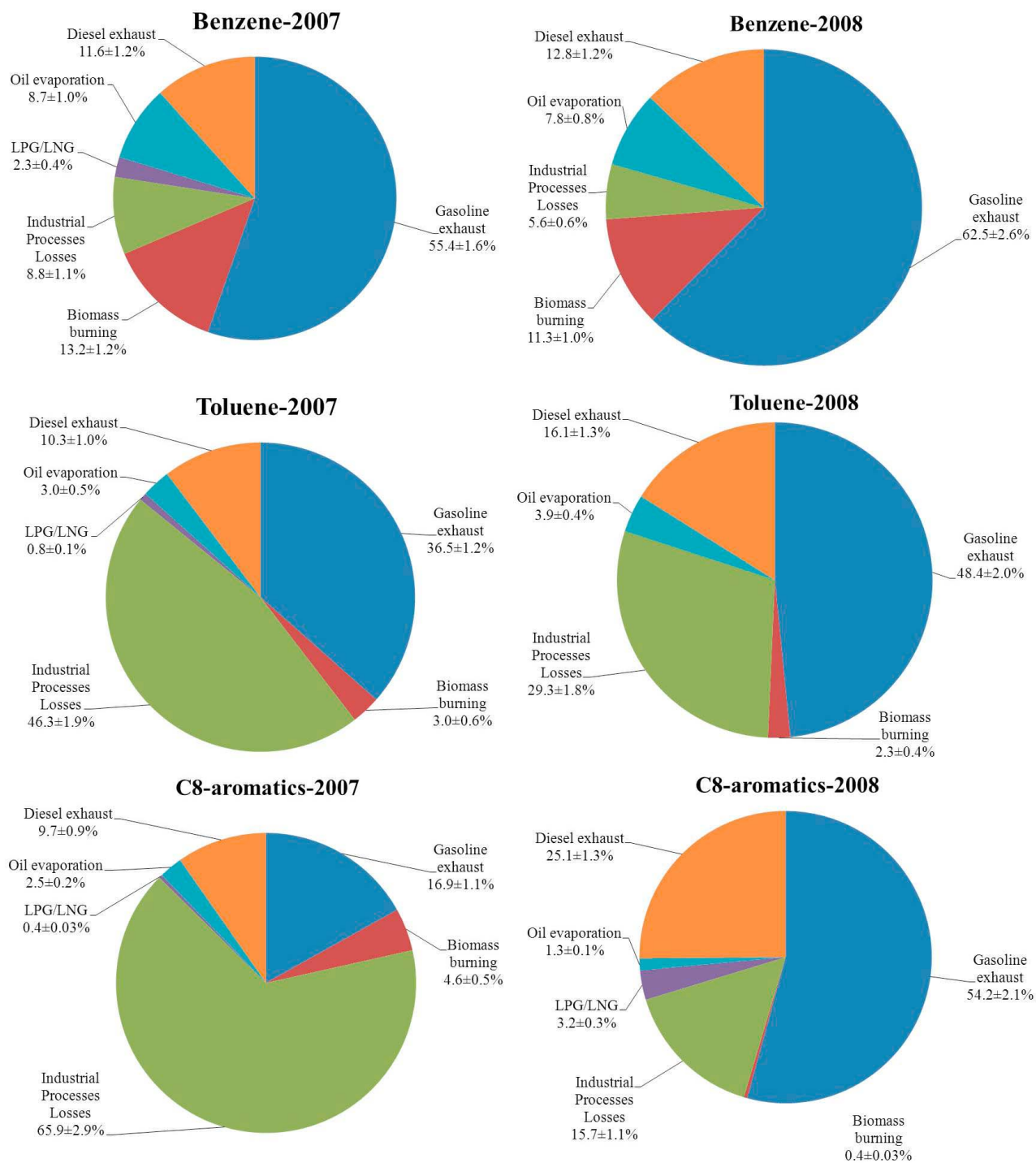


Figure 8. Contribution (Percentage \pm 95% Confidence Interval) of different sources to benzene, toluene and C8-aromatics (ethylbenzene and xylenes).

abrupt decrease was consistent with changes of real-world industrial activities. Vehicle exhausts and industrial emissions are two major sources for AHs, and emission of AHs from vehicle exhaust was expected to increase in 2008 due to rapid increase of motor vehicles. If there were no financial crisis, elevated mixing ratios of toluene and xylenes, just like that of benzene, would also be expected even the industrial emission remained the same in 2008 as that in 2007. So the

over 50% drop of ambient total AHs and largely decreased industrial contribution to AHs based on PMF results all suggested that reduction of AHs from industry emission would be at least 50% in 2008. However, a great puzzle is that according to official statistical survey, gross industry output of enterprises above the designated size (20 million RMB annual gross output) still exhibited very fast annual increase rates for most industry sectors in 2008 (Table 2),

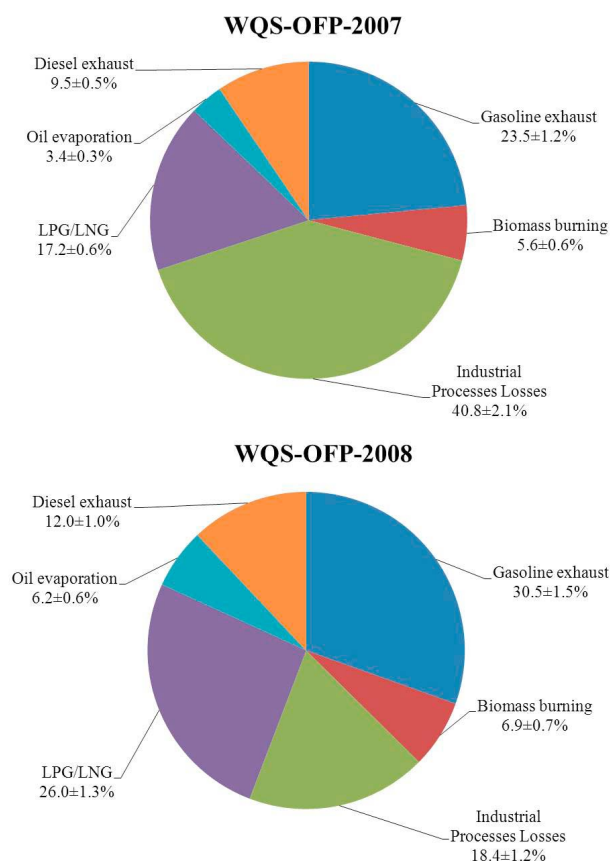


Figure 9. Contributions to OFPs from different emission sources based on PMF results.

although the annual increase rate of gross industry output slowed down, e.g., from 18.2% in 2007 to 13.4% in 2008 in Dongguan. As showed in Table 2, in Dongguan only petroleum refining and coking, as well as manufacturing of chemical fibers, had significantly dropped production. However, the outputs of petroleum refining and coking in Dongguan were minor or negligible compared to their counterparts in Guangdong province and in Guangzhou. In the whole province only manufacturing of chemical fibers had an output about 8% lower in 2008 than in 2007, and this industry sector recorded a 76% decrease in 2008 in Dongguan. As mentioned above, manufacturing of chemical fibers might have emissions typical of p-xylene; and if this industry sector was responsible for the decreased AHs we observed at WQS in 2008, much lower m,p-xylene to o-xylene ratios (m,p/o-X) would be expected in 2008. In fact, average m,p/o-X in 2008 (2.7) was about 10% higher than that in 2007 (2.4). Therefore, reduced production in manufacturing chemical fibers or in petroleum refining and coking in Dongguan was not the right reason for largely decreased AHs, and the increasing trends of gross industry outputs were obviously not in line with the largely decreased AHs in the ambient air as well as their contribution in total anthropogenic ozone precursors.

[29] One reason for this inconsistency is that the annual average would mask the bad situation in the 4th quarter of 2008. Although statistical data are not available for each quarter of 2008, the macro economic climate situations of enterprises did indicate the influence of financial crisis in the PRD region in the second half of 2008 [GPBS, 2009]. In Guangdong province the 3rd quarter of 2008 was the first quarter since 2004 that percentage of enterprises optimistic

Table 2. Gross Industry Output ($\times 100$ Million) From Enterprises Above the Designated Size in Guangdong Province and in Cities of Guangzhou and Dongguan in 2007 and 2008, and the Increase Rate (IR) Between 2007 to 2008^a

Item	Provincial			Guangzhou			Dongguan		
	2007	2008	IR (%)	2007	2008	IR (%)	2007	2008	IR (%)
Total	55253	65425	18.4	8903	10515	18.1	5852	6633	13.4
<i>Grouped by Sector</i>									
Textile Industry	1485	1747	17.6	197	221	12.5	231	227	-1.8
Manufacture of Textile Garments, Footwear and Headgear	1391	1725	24.1	190	276	45.4	177	232	31.4
Leather, Fur, Feather, Down and Related Products	979	1174	20.0	156	184	17.5	166	191	15.3
Manufacture of Furniture	671	831	23.9	45	77	69.3	165	181	9.6
Papermaking and Paper Products	999	1324	32.6	109	139	27.4	295	401	36.2
Printing and Record Medium Reproduction	519	653	25.7	47	63	33.9	65	79	22.4
Manufacture of Cultural, Educational and Sports Articles	737	873	18.6	68	76	12.4	150	173	15.4
Petroleum Refining, Coking and Nuclear Fuel Processing	1621	1898	17.1	472	594	25.7	11	6	-41.6
Manufacture of Raw Chemical Materials and Chemical Products	2578	3124	21.2	930	1113	19.7	127	161	26.4
Manufacture of Chemical Fibers	168	154	-8.1	13	16	21.9	17	4	-75.7
Rubber Products	275	324	17.5	85	84	-1.8	33	58	75.0
Plastic Products	2024	2423	19.7	223	261	17.4	280	345	23.4
Nonmetal Mineral Products	1790	2221	24.1	123	137	11.5	87	102	18.4
Smelting and Pressing of Ferrous Metals	1247	1493	19.8	445	467	4.9	39	34	-14.4
Smelting and Pressing of Nonferrous Metals	1520	1817	19.6	173	183	5.8	64	82	27.7
Metal Products	2621	3095	18.1	250	298	19.0	238	231	-2.8
Manufacture of General-purpose Machinery	1101	1530	39.0	261	322	23.6	95	150	58.3
Manufacture of Special-purpose Machinery	923	1151	24.7	92	128	40.2	130	152	17.1
Manufacture of Electrical Machinery and Equipment	6243	7145	14.4	549	645	17.5	737	731	-0.7
Manufacture of Communication Equipment, Computers and Other Electronic Equipment	13377	15374	14.9	767	953	24.3	1609	1774	10.3
Manufacture of Instruments, Meters and Machinery for Cultural and Office Use	1336	1352	1.2	82	96	17.4	216	232	7.8
Handicraft and Other Manufactures	842	1067	26.7	85	104	21.4	91	124	36.6

^aGPBS [2008, 2009].

about economic climate situations fell below 40%, and this percentage further plummeted to 23.6% in the 4th quarter of 2008, the lowest since 2000. It worth noting that the above mentioned economy and industry data only referred to enterprises above the designated size, that is, only enterprises with annual gross output over 20 million RMB were included in the official statistical data, and small enterprises were excluded from the official statistical survey. However, small enterprises were the hard-hit by the financial crisis. Therefore the most probable reason for the inconsistency between the decreased industry-emitted AHs and increased official gross industry output was related to small enterprises.

[30] Small factories are excluded not only from the official survey by the provincial and national bureau of statistics, they are also mostly excluded from the air pollutants survey of local environmental protection agencies due to lack of enough manpower and test facilities. Since emission of air pollutants from large enterprises is surveyed regularly by local environmental monitoring centers, their emissions are controlled with a considerable portion of air pollutants removed by treatment facilities before discharge. Small factories, however, often have no treatment for the evaporated solvents, which will therefore enter the atmosphere by natural and/or forced ventilation as fugitive emissions. According to *GONEC* [2010], in 2008 there were 54,366 registered enterprises above the designated size and 454,812 registered enterprises below the designated size in Guangdong province; the numbers of registered enterprises above and below the designated size were 11, 002 and 127,169 in Guangzhou, and 5,960 and 42,389 in Dongguan, respectively. Moreover, a considerable portion (~40%) of small business, especially self-employed ones, was even not registered [*GONEC*, 2010]. Due to the huge numbers and almost zero-treatment of solvent emission, small factories in the PRD region in fact contributed largely to ambient AHs in economic-booming years like 2007, yet they are not included in official economic and environmental survey. Therefore the significant drop of AHs' emission in 2008 could be explained by this kind of "black-hole" emission from small factories, which would be greatly reduced since small enterprises were much more influenced by the financial crisis than the larger ones, as could be reflected by that a large number of small- and medium-sized enterprises reduced production, suspended business, or even went bankruptcy, and ~52% enterprises were running under deficit in Dongguan in 2008 due to the influence of the financial crisis. If ambient levels of VOCs were proportional to their emissions during the two sampling periods, combined measured levels with PMF results, we could estimate, though very roughly, those small industries contributed at least 55% of NMHCs from industry emission. The unexpected reduction of air pollutants as a side-effect of financial crisis in 2008 revealed that small enterprises might be big emitters of some reactive organic gases like AHs, and it would be a great challenge for local air quality control in China's industrialized zones like the PRD region. In fact, as the economy began to recover, our monitoring at the same site WQS during the same period in 2009 revealed that total mixing ratios of NMHCs reached an average of 45.4 ppbv, higher than those in both 2007 and 2008; and that the contribution of industry emission based on PMF results rebounded from $14.2\% \pm 1.1\%$ in 2008 back to

$24.4\% \pm 1.3\%$, only a little bit lower than that of $29.2\% \pm 1.4\%$ in 2007.

4. Conclusions

[31] At a regional station in the central PRD region, ambient NMHCs measured during identical time intervals in 2008 after the outbreak of the financial crisis and in 2007 before the outbreak of the financial crisis revealed that their compositions and OFPs changed drastically although they had quite similar average total mixing ratios in both years. Aromatic hydrocarbons were most important ozone precursors among NMHCs before the financial crisis, but in 2008 their mixing ratios and OFPs dropped significantly due to reduced emission from industries hard-hit by the financial crisis; on the contrary mixing ratios and OFPs of alkanes and alkenes increased in 2008 due largely to fast rising vehicle numbers and LPG consumption in the region. Both diagnostic ratios and PMF results confirmed that decreased mixing ratios and OFPs for AHs in 2008 were attributed to the reduced industrial emission. Further analysis of economic and industrial survey data suggested that the hard-hit small enterprises were probably responsible for the AHs' drop in 2008. Our study revealed the important role of AHs as ozone precursors in the highly industrialized PRD region, the dominant contribution of toluene and xylenes from industrial emission due to their widely use as solvents, and the need of emission control for small factories in the PRD region in reducing aromatic hydrocarbons for the reduction of secondary pollutants like ozone and secondary organic aerosols in ambient air.

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