



Which emission sources are responsible for the volatile organic compounds in the atmosphere of Pearl River Delta?

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ABSTRACT

A field measurement study of volatile organic compounds (VOCs) was simultaneously carried out in October–December 2007 at an inland Pearl River Delta (PRD) site and a Hong Kong urban site. A receptor model i.e. positive matrix factorization (PMF) was applied to the data for the apportionment of pollution sources in the region. Five and six sources were identified in Hong Kong and the inland PRD region, respectively. The major sources identified in the region were vehicular emissions, solvent use and biomass burning, whereas extra sources found in inland PRD included liquefied petroleum gas and gasoline evaporation. In Hong Kong, the vehicular emissions made the most significant contribution to ambient VOCs ($48 \pm 4\%$), followed by solvent use ($43 \pm 2\%$) and biomass burning ($9 \pm 2\%$). In inland PRD, the largest contributor to ambient VOCs was solvent use ($46 \pm 1\%$), and vehicular emissions contributed $26 \pm 1\%$ to ambient VOCs. The percentage contribution of vehicular emission in Hong Kong in 2007 is close to that obtained in 2001–2003, whereas in inland PRD the contribution of solvent use to ambient VOCs in 2007 was at the upper range of the results obtained in previous studies and twice the 2006 PRD emission inventory. The findings advance our knowledge of ozone precursors in the PRD region.

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1. Introduction

Identification of emission sources and quantification of source contributions to ambient air pollutants are prerequisite for the formulation and implementation of air pollution control measures and strategies. Volatile organic compounds (VOCs), precursors of photochemical smog and toxic substances, have attracted widespread attention of environmental communities for decades [1–12]. Previous research suggests that high ozone production rates in many locations are strongly associated with high anthropogenic VOC emissions [13–19]. Hence, effort has been made to identify and quantify source emissions of VOCs in different cities and regions so that photochemical air pollution could be controlled [20–25].

Receptor-oriented source apportionment models are the main tools for the source identification of pollutants and the estimation of source contributions to pollutant concentrations. The most widely used models are the chemical mass balance (CMB) [22,26], principal component analysis (PCA)/absolute principal component scores (APCS) [27–29], positive matrix factorization (PMF) [24,30], and graphical ratio analysis for composition estimates (GRACE)/source

apportionment by factors with explicit restriction (SAFER), incorporated in the UNMIX model [31]. Watson et al. [21] reviewed VOC source apportionment by CMB in more than 20 urban areas. Gasoline vehicle exhaust, liquid gasoline, and gasoline evaporation contributed over 50% of the ambient VOCs in many of these studies. Vega et al. [20] estimated VOC source apportionment in Mexico City in 1996–1997 and reported that vehicle exhaust made contribution of 54.9–63.8% and handling and distribution of liquefied petroleum gas (LPG) 20.0–28.5%. Sosa et al. [32] re-conducted source apportionment in Mexico City using VOC data collected in 2000–2001 and found that handling and distribution of LPG was the major source (42–52%), followed by vehicle exhaust (25–28%), asphalt works (12–14%) and cooking (5–10%). In Houston, refinery (26–35%), petrochemical and evaporative emissions (20–22%) and natural gas (13–17%) were the dominant sources of VOCs in 2003 [23], while the major VOC sources in 2006 became natural gas/crude oil (32–39%), LPG (26%), fuel evaporation (20–23%) and vehicular exhausts (11–13%) [33]. All these studies have provided robust results for VOCs in the study areas.

The Pearl River Delta (PRD) (Fig. 1) is a dynamic region on the southern coast of China that has become distinguished for its astonishing industrial development and thriving economy. The PRD region comprises nine cities within Guangdong Province, i.e. Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Fos-

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Fig. 1. Location of the two sampling sites (Tung Chung (TC), Hong Kong and Wan Qing Sha (WQS), Guangzhou).

han, Jiangmen, Huizhou and Zhaoqing (these cities comprise the inland PRD region), plus Hong Kong and Macau Special Administrative Regions. The manufacturers produce a wide variety of goods from electronics and air conditioners to refrigerators and automobiles. Previous studies [10,27,28] have shown complex VOC sources and their contributions in this region. Guo et al. [27,28] revealed that vehicular emissions (39–48%), solvent use (32–36%) and LPG/natural gas usage (11–19%) were the dominant sources in 2000–2002 in Hong Kong, whereas the major VOC sources in inland PRD were industrial emissions (43%), vehicular emissions (32%) and biomass burning (25%). However, in 2004, vehicular emissions (>50%) became the most important source of VOCs in inland PRD due to the significant increase in vehicles, and solvent use accounted for 33% of the total VOCs [10].

In recent years, due to industrial restructure and recognition of adverse impact of VOCs on visibility reduction and human health by local governments, VOC sources and their contributions to ambient VOCs in this region may have been significantly revised. Indeed, to reduce VOC emissions, the Hong Kong government has implemented, and the Guangdong government has proposed control measures to recover petrol vapor released during petrol unloading and refueling at petrol stations, and to tighten emissions standards of motor vehicles in line with the European Union standards [34,35]. The VOC Regulation, effective from 1 April 2007 under the Air Pollution Control Ordinance in Hong Kong, controls the VOC content in 51 types of architectural paints/coatings, 7 types of printing inks and 6 broad categories of consumer products; and requires emission reduction devices to be installed on certain printing machines. The regulation was amended in October 2009 to extend the control to other products with high VOC content, including adhesives, sealants, vehicle refinishing paints/coatings, and marine vessel and pleasure craft paints/coatings, starting from 1 January 2010 in phases [36]. On the other hand, inland PRD has shifted its emphasis from light industry in early 1990s to heavy industry featuring hi-tech electronic equipment and machinery, chemical products and autos in recent years [37]. Hence, in order to efficiently mitigate photochemical air pollution in the study region, it is crucial to obtain updated VOC inventory on emission sources and their contributions.

In this study, a field measurement study of VOCs was simultaneously carried out in October–December 2007 at an inland PRD site and a Hong Kong urban site. The major VOC sources in the

region will be identified and their contributions to ambient VOCs will be quantified. The profiles of the VOC sources in Hong Kong and inland PRD will be updated. The spatial variations of source apportionments and the directional dependence of sources will be analyzed. The findings obtained in this study are expected to better formulate and implement VOC control strategies in the PRD region.

2. Methodology

2.1. Sampling sites

The sampling sites—Wan Qing Sha (WQS) and Tung Chung (TC)—are shown in Fig. 1. The distance between the two sites is about 62 km. WQS (22.711°N, 113.549°E) is a small town located near the center of the PRD. This town is surrounded by farmlands and has no major local sources, except some activities of burning agricultural residues by local farmers. The major air pollutants are mainly from the surrounding cities. This site is 50 km to the southeast of the Guangzhou urban center, 40 km southwest of Dongguan, 50 km northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good location to characterize the air pollution in the inland PRD. The measurements were carried out on the rooftop of a 15 m high building.

TC (22.30°N, 113.93°E) is located on northern Lantau Island, about 3 km south of the Hong Kong International airport. It is a newly-developed residential town, but adjacent to the highway and railway lines. It is about 20 km to the southwest of Hong Kong urban center, and 38 km northeast of Macau. Our previous study indicated that the impact from the airport on VOCs levels at TC was insignificant [25]. The main local sources are vehicular emissions and domestic activities. The samples were collected on the rooftop of a 15 m high building.

2.2. Sampling and analyses of VOCs

Ambient non-methane hydrocarbon (NMHC) samples were collected using cleaned and evacuated 2 L electro-polished stainless steel canisters. Details of the preparation and pre-conditioning of the canisters are described in [38]. The original purpose of this study was to understand the role of VOCs in the photochemical processes. Hence, 12–13 h integrated canister samples were collected between 6:00 and 18:00 on the selected days within the

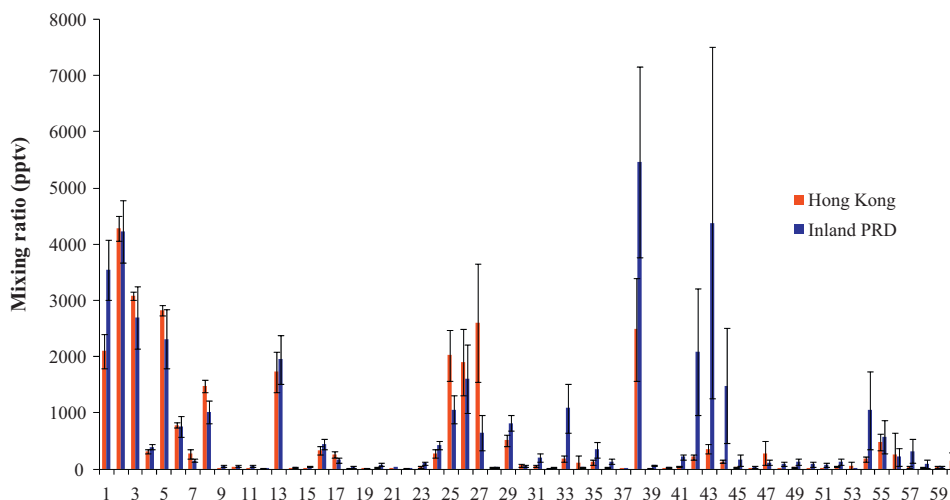


Fig. 2. VOC composition in the atmosphere of Hong Kong ($n = 88$) and inland PRD ($n = 63$). 1. Ethene; 2. Ethyne; 3. Ethane; 4. Propene; 5. Propane; 6. *i*-Butene; 7. 1-Butene; 8. *n*-Butane; 9. *trans*-2-Butene; 10. 1,3-Butadiene; 11. *cis*-2-Butene; 12. 3-Methyl-1-butene; 13. *i*-Pentane; 14. 1-Pentene; 15. 2-Methyl-1-butene; 16. *n*-Pentane; 17. Isoprene; 18. *trans*-2-Pentene; 19. 2-Methyl-2-butene; 20. *cis*-2-Pentene; 21. 2,2-Dimethylbutane; 22. Cyclopentane; 23. 2,3-Dimethylbutane; 24. 2-Methylpentane; 25. 3-Methylpentane; 26. *n*-Hexane; 27. Methylcyclopentane; 28. 2,4-Dimethylpentane; 29. Benzene; 30. Cyclohexane; 31. 2-Methylhexane; 32. 2,3-Dimethylpentane; 33. 3-Methylhexane; 34. 2,2,4-Trimethylpentane; 35. *n*-Heptane; 36. Methylcyclohexane; 37. 2,3,4-Trimethylpentane; 38. Toluene; 39. 2-Methylheptane; 40. 3-Methylheptane; 41. *n*-Octane; 42. Ethylbenzene; 43. *m/p*-Xylene; 44. *o*-Xylene; 45. *n*-Nonane; 46. *i*-Propylbenzene; 47. α -Pinene; 48. Propylbenzene; 49. *m*-Ethyltoluene; 50. *p*-Ethyltoluene; 51. *o*-Ethyltoluene; 52. 1,3,5-Trimethylbenzene; 53. β -Pinene; 54. 1,2,4-Trimethylbenzene; 55. *n*-Decane; 56. 1,2,3-Trimethylbenzene; 57. 1,3-Diethylbenzene; 58. 1,4-Dimethylbenzene; 59. 1,2-Diethylbenzene; 60. *n*-Undecane.

sampling period. During the sampling, a flow-controlling device was used to collect 1 h integrated canister samples at both sites. In total, 104 and 96 whole air samples were collected at WQS and TC, respectively. The samples were analyzed by an Entech Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled with a gas chromatography-mass selective detector (GC-MSD, Agilent 5973N). A HP-1 capillary column (60 m \times 0.32 μ m \times 1.0 μ m, Agilent Technologies, USA) was used with helium as carrier gas. The detection limit of aromatics is 3 pptv and of other NMHCs is 5 pptv. In total, 60 C₂–C₁₁ NMHC species were quantified.

Not all NMHC species were used for source apportionment analysis. Species that are highly reactive or with high uncertainty were excluded, since they react away quickly in the atmosphere and including them may bias the modeling results [24]. An exception was ethene because it is a marker of incomplete combustion. Eventually, 16 VOC species were selected for the source apportionment analysis since they are the most abundant species and/or are typical tracers of various emission sources (Table 1).

On days with strong solar radiation, VOCs significantly participated in photochemical reactions at daytime hours. Consequently, the signature and original composition of source sectors would be lost, leading to the misidentification of emission sources. Hence, to minimize the impact of photochemical degradation on the measured VOCs, only VOC samples collected in early morning i.e. before 8:00 and late afternoon i.e. after 17:00 were selected for source apportionment study as at these specific hours of the day the radiation impact is minimum. In addition, VOC samples collected between 8:00 and 17:00 were also selected on some days when the solar radiation was weak, determined by the fact that the maximum hourly O₃ level on these days (<50 ppb) was much lower than the Hong Kong Air Quality Objectives (hourly O₃ level \leq 122 ppb). Eventually, 63 and 88 samples were applied to the receptor model for WQS and TC sites, respectively.

2.3. PMF receptor model

The PMF was used to resolve the NMHC data obtained at WQS and TC. Briefly, a mass balance equation can be written to account for all m chemical species in the n samples as concentrations from

p independent sources:

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

where x_{ij} is the j th species concentration measured in the i th sample, g_{ik} is the species contribution of the k th source to the i th sample, f_{kj} is the j th species fraction from the k th source, e_{ij} is residual associated with the j th species concentration measured in the i th sample, and p is the total number of independent sources [39]. PMF provides a matrix of the source profiles and a matrix of the time series of source contributions without prior knowledge of VOC sources. In PMF, sources are constrained to have non-negative species values, and no sample can have a negative source contribution.

To solve the PMF problem, an object function to be minimized is introduced:

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left[\frac{e_{ij}}{s_{ij}} \right]^2, \quad (2)$$

where s_{ij} is an uncertainty estimate in a data point with the j th species measured in the i th sample. PMF uses a unique algorithm in which both source profile and contribution matrices are varied simultaneously in each least squares step [39].

The application of PMF depends on the estimated uncertainties for each measured data. Polissar et al. [40] provided guidelines for estimating the input uncertainties. In this study, the USEPA equation approach was used to estimate the uncertainty associated with each data point and missing concentration values were replaced by the geometric mean of the species [41,42]. However, species that had >20% of missing values or values below detection limit were removed from the analysis.

To find the number of sources, it is necessary to test different numbers of sources and find the optimal value with the most reasonable results. If the number of sources is estimated properly, the theoretical Q value should be approximately the number of degree of freedom, or approximately the total number of data points. How-

Table 1
Source profiles resolved from PMF in (a) Hong Kong and (b) inland PRD.

(a)												
	F1		F2		F3		F4		F5			
	Conc. ^a	% ^b	Conc.	%	Conc.	%	Conc.	%	Conc.	%		
Ethane	0.17	9	0.57	29	0.13	7	0.02	1	1.04	54		
Propane	0.15	3	0.80	16	0.35	7	0.37	7	3.43	67		
<i>i</i> -Butane	0.07	4	0.12	6	0.12	7	0.17	9	1.39	74		
<i>n</i> -Butane	0.00	0	0.36	11	0.03	1	0.73	23	2.07	65		
<i>i</i> -Pentane	0.23	5	0.00	0	0.29	6	3.90	76	0.68	13		
<i>n</i> -Pentane	0.10	11	0.07	8	0.00	0	0.40	48	0.27	32		
2-Methylpentane	0.37	42	0.04	4	0.29	33	0.00	0	0.19	22		
<i>n</i> -Hexane	0.00	0	0.29	4	5.55	83	0.87	13	0.00	0		
<i>n</i> -Heptane	0.36	70	0.00	0	0.02	4	0.07	13	0.06	12		
Ethene	0.12	8	0.69	45	0.12	8	0.04	2	0.57	37		
Ethyne	0.03	2	0.41	22	0.11	6	0.20	11	1.09	59		
Benzene	0.13	9	0.05	3	0.24	16	0.53	35	0.55	37		
Toluene	7.76	74	0.19	2	0.58	5	2.01	19	0.00	0		
Ethylbenzene	0.63	48	0.11	8	0.15	12	0.05	3	0.39	29		
<i>m,p</i> -Xylene	0.81	54	0.10	7	0.19	12	0.04	3	0.37	25		
<i>o</i> -Xylene	0.32	50	0.09	13	0.08	13	0.02	3	0.14	22		
Total concentration	11.25		3.89		8.25		9.42		12.24			
Source	Paint and varnish		Biomass burning		Household solvent use		Gasoline vehicular emissions		Diesel vehicular emissions			
(b)												
	F1		F2		F3		F4		F5		F6	
	Conc. ^a	% ^b	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
Ethane	0.45	17	1.64	61	0.03	1	0.00	0	0.22	8	0.36	13
Propane	0.00	0	0.31	7	0.18	4	0.30	7	3.17	76	0.22	5
<i>i</i> -Butane	0.58	33	0.10	6	0.08	4	0.28	16	0.73	41	0.00	0
<i>n</i> -Butane	0.79	34	0.29	12	0.09	4	0.16	7	0.84	36	0.15	7
<i>i</i> -Pentane	0.00	0	0.84	15	0.21	4	3.83	66	0.83	14	0.06	1
<i>n</i> -Pentane	0.52	41	0.23	19	0.00	0	0.17	14	0.26	21	0.07	6
2-Methylpentane	0.61	43	0.33	23	0.06	4	0.11	8	0.13	10	0.16	11
<i>n</i> -Hexane	0.00	0	0.18	3	0.06	1	0.25	4	0.00	0	5.09	91
<i>n</i> -Heptane	1.12	82	0.00	0	0.00	0	0.12	9	0.02	1	0.10	7
Ethene	0.32	9	2.69	71	0.10	3	0.15	4	0.15	4	0.40	11
Ethyne	0.63	18	1.13	33	0.12	4	0.22	6	1.02	29	0.34	10
Benzene	1.05	42	0.49	20	0.07	3	0.16	6	0.37	15	0.36	15
Toluene	15.23	73	0.00	0	3.83	18	0.00	0	0.00	0	1.87	9
Ethylbenzene	1.75	20	0.60	7	5.67	66	0.30	3	0.10	1	0.17	2
<i>m,p</i> -Xylene	0.41	2	0.90	5	16.60	88	0.83	4	0.16	1	0.00	0
<i>o</i> -Xylene	0.00	0	0.48	8	5.28	85	0.32	5	0.07	1	0.03	1
Total concentration	23.46		10.21		32.38		7.20		8.07		9.38	
Source	Vehicular emissions		Biomass burning		Paint and varnish		Gasoline evaporation		LPG usage		Household solvent use	

^a concentration, unit: $\mu\text{g}/\text{m}^3$.^b percentage of factor total.

ever, if the number of sources is not well determined, the Q value may deviate from the theoretical value.

2.4. Conditional probability functions

The conditional probability function (CPF) analysis was undertaken in order to identify the most probable location of the sources resolved by PMF. Thus the source contribution results obtained from the PMF analysis were combined with the wind speed and wind direction data measured at the receptor sites [33]. The CPF is the fraction of total samples in wind sector $\Delta\theta$ that have a higher source contribution than a threshold criterion value. The equation used for the analysis is shown below:

$$\text{CPF} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}}$$

where $m_{\Delta\theta}$ is the number of samples in a specific wind sector ($\Delta\theta = 30^\circ$) that are greater than the 75% percentile of the fractional contribution from each source, and $n_{\Delta\theta}$ the total number of observations in the same wind sector. This is to ensure that only 'high'

contributions are used for the determination of source directionality. If insufficient samples were contained within a sector or the wind speed was less than 1m/s, the sector was discarded.

3. Results and discussion

3.1. General characteristics

The spatiotemporal characteristics of NMHCs were overviewed in [43]. Briefly, the mean mixing ratio of total VOCs was 34 ± 5 ppbv at TC for the 88 samples and 42 ± 9 ppbv at WQS for the 63 samples. Fig. 2 shows the mean ambient VOC compositions in Hong Kong and inland PRD derived from the selected samples. The bars in the figure represent standard errors. In general, the mean VOC profile at both sites was similar, and key abundant VOCs i.e. ethene, ethyne (acetylene), C_2 – C_6 alkanes, toluene, ethylbenzene and xylene isomers (TEX) suggest that vehicular emissions and solvent use were important sources at both sites. However, significant differences in VOC mixing ratios between the two sites were identified. The mixing ratios of ethene, 3-methylhexane, benzene and TEX at WQS

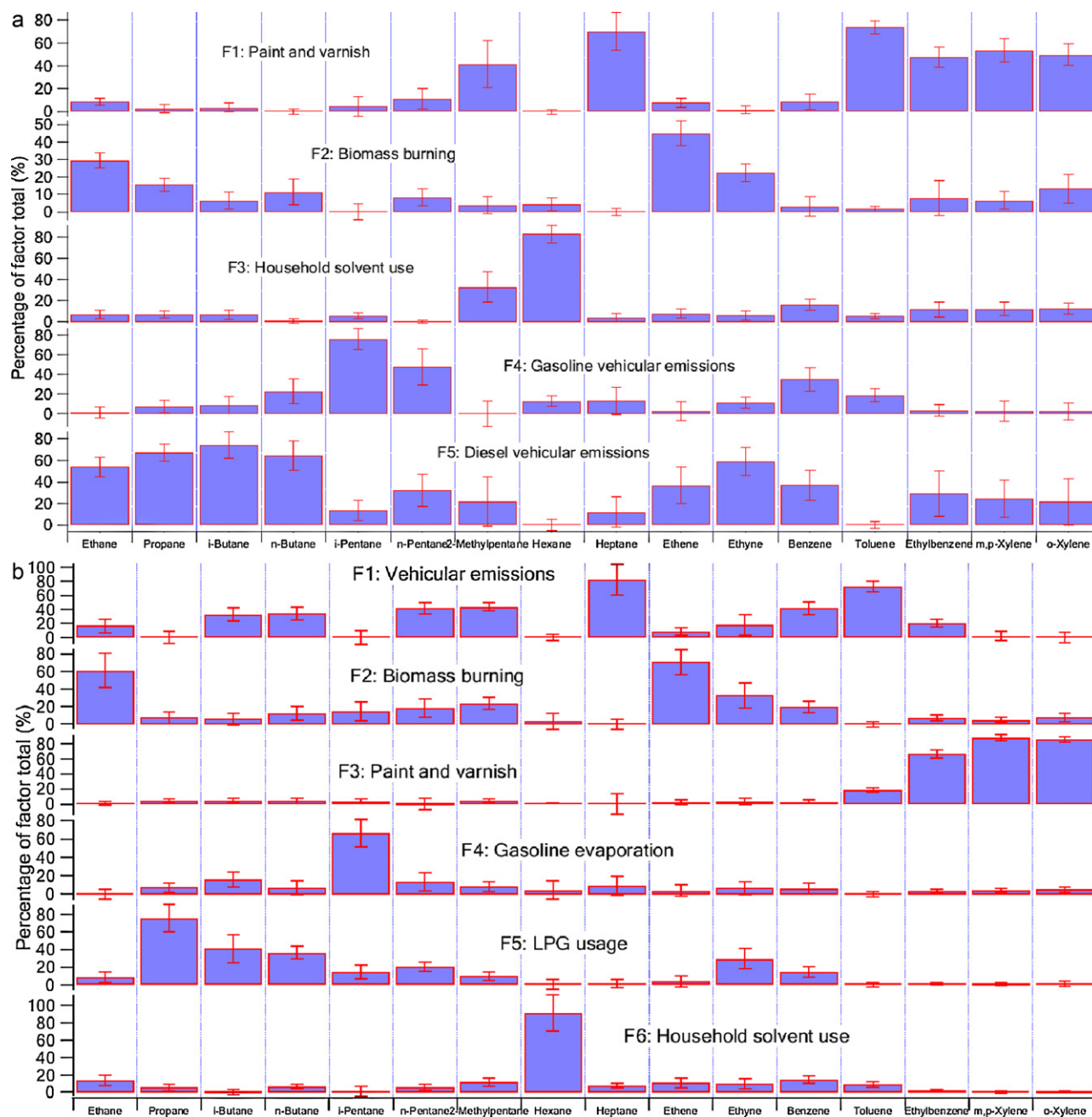


Fig. 3. Source profiles (percentage of factor total) resolved from PMF in (a) Hong Kong and (b) the inland PRD. The error bars in the figure represent standard deviation.

were significantly higher than that at TC ($p < 0.05$), indicating more fossil fuel use and biomass burning, and use of paint and varnish in inland PRD. In contrast, *n*-butane and hexanes showed higher mixing ratios at TC than at WQS ($p < 0.05$), suggesting important contribution of domestic solvent use to ambient VOCs in Hong Kong.

3.2. PMF results

Before data input to the PMF model, the mixing ratios (in pptv) of all selected VOCs were converted into concentrations (in $\mu\text{g}/\text{m}^3$). After running the model, five and six sources were identified at the Hong Kong site and the inland PRD site, respectively (Table 1 and Fig. 3).

In Hong Kong, high percentage was found for 2-methylpentane, *n*-heptane, and TEX in factor 1 (Fig. 3a). *n*-Heptane and 2-

methylpentane are widely applied as a non-polar solvent [44], whereas TEX is often used as a solvent in paints, coatings, synthetic fragrances, adhesives, inks, and cleaning agents in addition to its use in fossil fuel [45–46], (<http://www.arb.ca.gov/consprod/regact/2003surv/datasum2003.htm>). This factor 1 is therefore assigned to paint/varnish-related solvent use. The profile of this source is somewhat similar to that of factor 3 in inland PRD, which had high percentage of TEX (Fig. 3b). However, based on the PMF results, more *n*-heptane, 2-methylpentane and toluene were used in the paint and varnish of Hong Kong.

Factor 2 was distinguished by high percentage of ethene (45%), ethyne (22%) and ethane (29%) in Hong Kong (Fig. 3a). These species are typically tracers of incomplete combustion such as vehicular exhaust and biomass burning [38,47–49]. Since vehicular exhaust also emits relatively high percentage of other species such as pentane and BTEX, the factor 2 is therefore assigned to biomass burning.

Table 2
Comparison of results with previous studies and emission inventories.

Factor	Hong Kong					Inland PRD			
	Fall, 2007 This study	2001 ^a	2001–2002 ^b	2002–2003 ^c	2007 ^d	Fall 2007 This study	2001–2002 ^b	Fall 2004 ^e	2006 ^f
Vehicle exhaust:	48 ± 4%	39–48%	39%	48–65%	20%	26 ± 1%	32%	31–53%	40%
Gasoline	21 ± 2%							31–51%	
Diesel	27 ± 3%							0.1–1.5%	
Gasoline evaporation			14%	21–26%		8 ± 1%		5.6–6.5%	
LPG/natural gas usage		11–19%	12%	15%		9 ± 1% ^{ss}		5–16%	
Paint/varnish/solvents	43 ± 2%	32–36%	35%	14–24%	75%	46 ± 1%	43%	16–44%	~25%
Industrial		5–9%		8–15%				2–7.5%	~8%
Biomass	9 ± 2%					11 ± 1% ^{ss}	25%	14%	~2%
Biogenic	Not included			0.2–2%		Not included			25%
Remark	PMF	PCA/APCS			EI ^g	PMF	PCA/APCS	CMB	EI

^a Guo et al., 2004b.

^b Guo et al., 2006.

^c Guo et al., 2007.

^d HKEPD, http://www.epd.gov.hk/epd/english/environmentinhk/air/data/emission_inve.html.

^e Liu et al., 2008a.

^f Zheng et al., 2009.

^g EI – Emission Inventory.

This can be further confirmed by the ratio of ethyne to ethane (0.49–1.02) in this factor, which was consistent with that in fresh biomass burning (0.57) [38]. Similarly, the factor 2 in inland PRD was also dominated by ethane, ethene and ethyne, suggesting its source of biomass burning (Fig. 3b). It is noteworthy that the percentage of ethene, ethane and ethyne in the factor 2 of inland PRD was almost double that in factor 2 of Hong Kong, implying that the biomass burning source in Hong Kong was much weaker than that in inland PRD. Indeed, the MODIS fire map showed that there were fewer fire events in Hong Kong than that in inland PRD during the sampling period (Fig. 4). Furthermore, the analysis on the directional dependence of sources indicated that the biomass burning in Hong Kong was mainly from local source (see Section 3.5 below).

n-Hexane and its isomer 2-methylpentane had high percentage contributions in factor 3 in Hong Kong (Fig. 3a). *n*-Hexane is a common constituent of glues used for shoes, leather products and roofing. Additionally, it is used in solvents to extract oils for cooking and as a cleansing agent for shoe, furniture and textile [50]. As such, this source is identified as household solvent use. The source profile is similar to that of factor 6 in inland PRD, which had high percentage of *n*-hexane (Fig. 3b). However, based on the PMF results, much less 2-methylpentane was used in the household solvent in inland PRD region.

Factor 4 in Hong Kong was characterized by high percentages of *i/n*-pentanes and benzene, and to a lesser extent, *n*-butane and toluene, suggesting it is related to vehicular emissions (Fig. 3a),

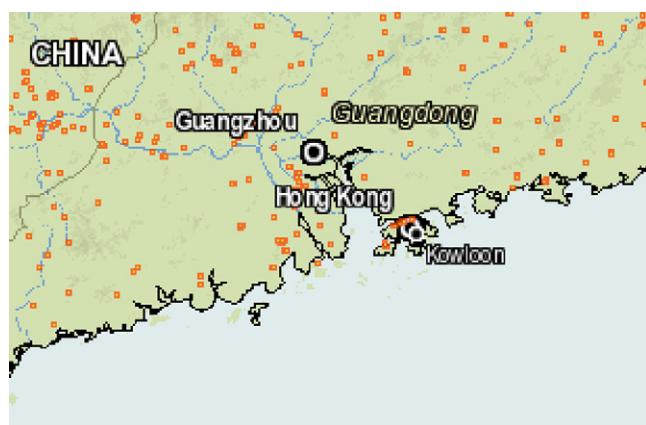


Fig. 4. MODIS fire map in autumn 2007 in the PRD region. The red spots in the map represent the fire events.

likely from gasoline-fuelled vehicles as the contributions of ethene and ethyne were usually low while *i/n*-pentanes, benzene and toluene levels were relatively high [51–53]. Previous studies have demonstrated that vehicular emissions not only contain C₁₀–C₁₅ VOCs, but also C₂–C₉ VOCs, especially ethene and ethyne, typical markers of vehicular emissions [51–54]. As such, it is sufficient to use C₂–C₈ VOCs to identify vehicular emissions in this study. The source profile extracted from this study is generally consistent with the results of previous studies [51,52].

Factor 5 in Hong Kong possessed high percentage of C₂–C₄ alkanes, ethene, ethyne, benzene, ethylbenzene and xylenes. These species are all associated with vehicular emissions, especially diesel vehicular emissions as diesel engine combustion generated much higher percentages of ethene and ethyne than gasoline vehicles [51,53,54]. Indeed, the source profile extracted here is similar to that of diesel-fuelled vehicles in Hong Kong [52].

In inland PRD, high percentage of *i/n*-butanes, *i/n*-pentanes, *n*-heptane, benzene, toluene and ethylbenzene was found in factor 1, suggesting the dominance of vehicular emissions [51–54]. In contrast to the PMF result in Hong Kong where two vehicular sources

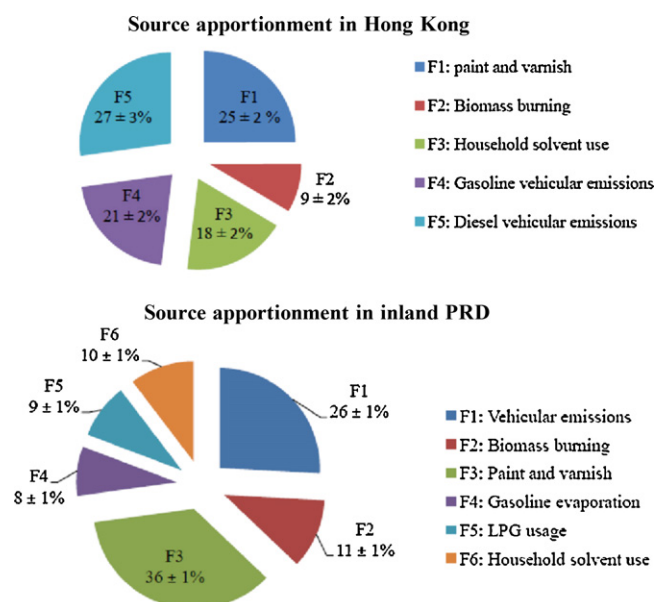


Fig. 5. Source apportionments of VOCs at (a) TC, Hong Kong; and (b) WQS, inland PRD.

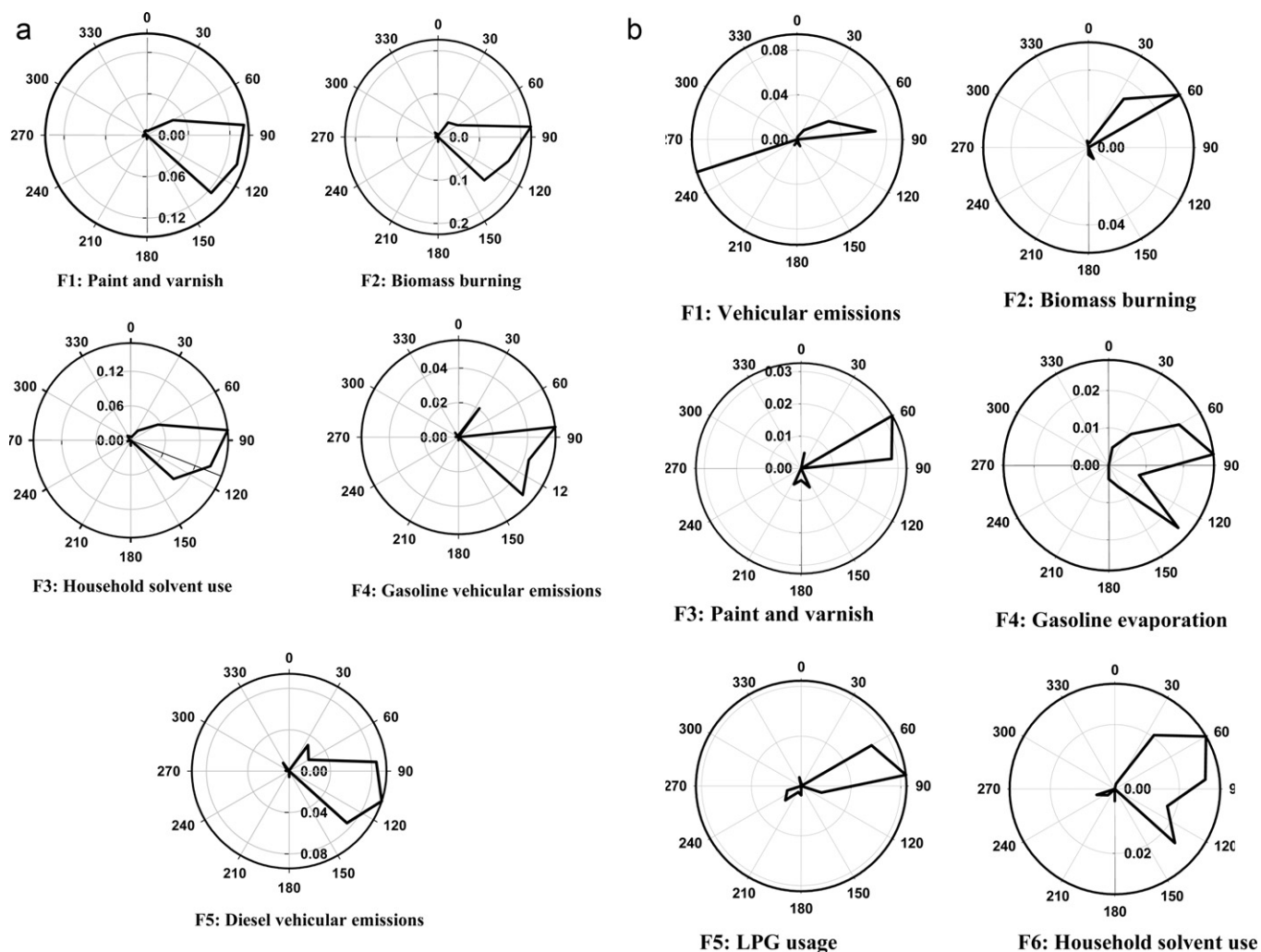


Fig. 6. Directional dependence of sources at (a) TC, Hong Kong and (b) WQS, inland PRD.

were extracted, only one vehicular source was identified in inland PRD. It is noteworthy that ambient toluene in inland PRD was mainly from vehicular emissions (~73%), whereas about 74% of toluene in the atmosphere of Hong Kong was attributed to the use of paint and varnish.

i-Pentane had the highest percentage (>53%) in factor 4 in inland PRD, while other individual VOC species contributed a very small proportion to the total VOCs (from 0 to <10%) (Fig. 3b). Pentanes are main constituents of gasoline [55]. Thus, this factor is related to gasoline evaporation. It is noteworthy that the difference in source profile between gasoline vehicular emissions (factor 4, Hong Kong site) and gasoline evaporation (factor 4, inland PRD site) was obvious. Apart from high percentage of *i*-pentane emission in the gasoline vehicular emission source, other species such as benzene, toluene, *n*-butane and *n*-pentane also had high percentage of the factor total. Interestingly, this source was not identified in Hong Kong, perhaps due to the effectiveness of control measures during petrol unloading and refueling at petrol stations.

High percentage of propane and *i/n*-butanes was distinguished in factor 5 in inland PRD (Fig. 3b). The squared correlation coefficients (R^2) among these species were over 0.87. These species are the main composition of LPG [56]. Therefore, this factor can be identified as LPG usage. It is noteworthy that LPG source was not found in Hong Kong, although taxis were using LPG as fuel. This is probably owing to the small proportion (<4%) of LPG-fuelled taxis in the total regis-

tered vehicles in Hong Kong (Hong Kong Transport Department, http://www.td.gov.hk/filemanager/en/content_281/table41a.pdf).

3.3. Spatial patterns of source apportionments

By summing up the concentration of each species in a source, we were able to obtain the total concentration of VOCs in each source (Table 1). Hence, the contributions of each individual source to ambient VOC concentrations are computed and presented in Fig. 5. The standard errors in the figure were obtained from bootstrap analyses extracted from PMF results.

It is evident that vehicular emissions (totally $48 \pm 4\%$) made the most significant contribution to ambient VOCs in Hong Kong ($27 \pm 3\%$ and $21 \pm 2\%$ for diesel and gasoline vehicular emissions, respectively), followed by the use of solvent ($43 \pm 2\%$, in which, $25 \pm 2\%$ for paint/varnish, and $18 \pm 2\%$ for household solvent use), and biomass burning emissions ($9 \pm 2\%$) (Fig. 5a). In inland PRD, the use of solvent was the largest contributor ($46 \pm 1\%$) ($36 \pm 1\%$ and $10 \pm 1\%$ for paint/varnish and household solvent use, respectively), while the vehicular emissions made the second highest contribution ($26 \pm 1\%$). About $11 \pm 1\%$ of the total ambient VOCs was attributed to biomass burning whereas LPG usage and gasoline evaporation accounted for $9 \pm 1\%$ and $8 \pm 1\%$, respectively (Fig. 5b).

The sources of vehicular emissions, paint/varnish, biomass burning and household solvent use were identified at both sites. Gasoline evaporation and LPG usage were only found at the

inland PRD site. Though vehicular emission was the source of VOCs at both sites, gasoline and diesel vehicular emissions were distinguished from each other in Hong Kong. Significant differences in source contributions were observed between the two locations. The contribution of paint/varnish in Hong Kong ($11.25 \pm 0.96 \mu\text{g}/\text{m}^3$) was about 1/3 that from the same source in inland PRD ($32.38 \pm 1.04 \mu\text{g}/\text{m}^3$), whereas the contribution from household solvent use was similar at both sites ($8.25 \pm 1.11 \mu\text{g}/\text{m}^3$ in Hong Kong and $9.38 \pm 0.98 \mu\text{g}/\text{m}^3$ in inland PRD) (Table 1). We also found that the VOC concentration from vehicular emission in Hong Kong ($21.66 \pm 1.41 \mu\text{g}/\text{m}^3$) was similar to that in inland PRD ($23.46 \pm 1.03 \mu\text{g}/\text{m}^3$), though the percentage contribution of vehicular emissions in Hong Kong ($48 \pm 4\%$) was much higher than that in inland PRD ($26 \pm 1\%$) (Fig. 5). In addition, although the percentage contribution of biomass burning was similar at both sites ($9 \pm 2\%$ in Hong Kong versus $11 \pm 1\%$ in inland PRD), the VOC concentration from biomass burning in inland PRD ($10.21 \pm 1.22 \mu\text{g}/\text{m}^3$) was more than twice that in Hong Kong ($3.89 \pm 0.71 \mu\text{g}/\text{m}^3$). The comparison indicated that there were more industrial activities associated with furniture production and/or utilization of solvent in housing development, and more biomass burning in inland PRD.

3.4. Comparison with other studies

It is of interest to compare the results of this study with existing emission inventories and previous source apportionment studies. It should be emphasized that the top-down source apportionment is based on ambient measurement data, while the emission inventory depends on bottom-up survey which can estimate the emission amounts of individual sources. The top-down approach does not provide information about absolute emission whereas the bottom-up method could miss important sources. If we consider the atmosphere as a confined space and ignore the effect of wind, atmospheric stability and deposition, the concentration of an air pollutant is proportional to its emission amount. Therefore, it would be valuable to perform inter-comparison between the results of these two approaches, based on the percentage contributions. Table 2 shows the comparison to previous results in the PRD region.

In Hong Kong, the contribution of vehicular emissions in 2007 ($48 \pm 4\%$, top-down approach) is close to that obtained in 2001–2003, about twice that estimated in the Hong Kong Environmental Protection Department (HKEPD) emission inventory (EI) (20% , bottom-up approach) [25,27,28], suggesting that vehicular emission in Hong Kong is still the major contributor to ambient VOCs and that effectively controlling vehicular emissions is important. As stated earlier, the Hong Kong government has taken a series of measures to reduce vehicular emissions such as replacing diesel-fuelled taxis by LPG and utilizing cleaner diesel for buses since 1999 (http://www.epd.gov.hk/epd/english/environmentinhk/air/air_maincontent.html). The remaining high vehicular contribution might owe to the increase of the vehicular fleet and/or miss-counting of emissions from marine vessels. Although the contribution of solvent use in this study ($43 \pm 2\%$) is consistent with that found in 2001 ($32\text{--}36\%$), it is 2–3 times that in 2002–2003 ($14\text{--}24\%$), perhaps due to much fewer household, commercial and industrial activities caused by the SARS event in 2002–2003 in Hong Kong. Furthermore, the proportion of solvent use in the HKEPD EI (75%) is almost twice that in this study. It is noteworthy that our study conducted in 2001–2003 identified ignorable contribution from biomass burning in Hong Kong [25,27,28], while its contribution in this study was neglectable ($9 \pm 2\%$), suggesting some biomass burning activities in Hong Kong and/or the transport of biomass burning plume from inland PRD region in 2007. Indeed, MODIS fire map showed some fire spots within Hong Kong

territory during the sampling period (Fig. 4). Interestingly, the sources of gasoline evaporation and LPG usage were not identified in Hong Kong, reflecting the insignificant impact of these two sources on ambient VOCs at TC during the sampling period. It may also suggest the effective control of these two sources in recent years, compared to the source apportionment results obtained in previous years [25,27,28].

In inland PRD, the contribution of vehicular emissions obtained in 2001–2002 [28], in fall 2004 [10] and in the PRD EI for 2006 [57] was 1–2 times that found in this study ($26 \pm 1\%$). On the other hand, the contribution of solvent use in 2007 ($46 \pm 1\%$) was at the upper range of the results in previous studies ($16\text{--}44\%$), but almost twice the 2006 PRD EI ($\sim 25\%$). Additionally, the contribution of biomass burning in this study was similar to that in autumn 2004 [10], lower than that estimated in 2001–2002 [28], and much higher than the PRD EI [57] (Table 2). It should be noted that biomass burning is a transient activity, which could be a reason for the large variations in biomass burning apportionment in various years. Moreover, the percentage contributions of gasoline evaporation and LPG usage in this study are well in line with those obtained by CMB in fall 2004 [10].

3.5. Directional dependence of sources

In this section, the relationship between wind direction and emission sources was examined to better understand the source regions. Fig. 6 shows the directional dependence of sources at the TC and WQS sites.

At TC, all the five sources displayed significantly higher contributions from easterly and southeasterly directions, pointing towards the residential area and the major expressway. High values from easterly and southeasterly directions for the biomass burning source (factor 2) were confirmed by the fire spots shown in Fig. 4. However, the CPF values for the gasoline and diesel vehicular emissions were low, compared to that for other three sources.

At WQS, high contributions of all the six sources were more correlated to northeasterly directions, pointing towards upwind Guangzhou and Dongguan cities (Figs. 1 and 6b). The sources of gasoline evaporation and household solvent use also showed a peak of high contribution from southeastern direction.

4. Conclusions

VOC measurement data at two sites in the PRD region were analyzed to better understand their emission characteristics and relative contributions from major source sectors. Based on the PMF results, the dominant sources of VOCs were solvent use, vehicular emissions, biomass burning, LPG usage and gasoline evaporation in the region. The main contributors in Hong Kong were vehicular emissions ($48 \pm 4\%$), solvent use ($43 \pm 2\%$), and biomass burning ($9 \pm 2\%$). In contrast, in inland PRD, solvent use accounted for $46 \pm 1\%$ of ambient VOCs, whereas vehicular emissions and biomass burning contributed $26 \pm 1\%$ and $11 \pm 1\%$, respectively. Compared to previous years, the contribution of vehicular emissions in Hong Kong remained high, implying the importance of effectively controlling vehicular emissions. In contrast, the contribution of vehicular emissions in previous years in inland PRD was 1–2 times that in this study, while the solvent use in 2007 was at the upper range of the results in previous studies and nearly doubled the 2006 PRD emission inventory. Analysis on the directional dependence of sources indicated that the VOC sources at TC were mainly associated with easterly and southeasterly winds whereas the contributors to ambient VOCs at WQS originated from northeasterly directions.

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