Atmospheric Pollution Research

Non–methane hydrocarbon emission profiles from printing and electronic industrial processes and its implications on the ambient atmosphere in the Pearl River Delta, South China

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ABSTRACT

Thirty–seven non–methane hydrocarbons (NMHCs) were quantified for seven industrial work processes, covering the electronic industry and the printing industry, in the Pearl River Delta (PRD). NMHC source profiles (% by wt.) for the respective work processes and their associated industrial solvents were obtained. In order to examine the contribution of the individual work processes to the neighborhood atmospheres, ambient samples on the rooftop of the printing and electronic factories were collected. Total NMHC concentrations of 3 700±740 ppbv and 169±64 ppbv were detected, respectively. Air samples from roadside of a main roundabout, from rooftop of a residential building in the town center and from a background site were also collected to examine the impact of industrial and vehicular emissions on local NMHC levels. NMHC emissions from the printing factory were significantly higher than that from the electronic factory. The two work processes, plastic molding and soldering in the electronics factory, emitted mainly C_3–C_7 alkanes, while paint solvents used in the printing factory released C_7–C_8 aromatics. Toluene was the most abundant NMHCs measured for all work processes in the printing factory. It was due to the heavy usage of various solvent–based inks and paint solvents. In general, high toluene levels were found in the ambient and industrial–related atmosphere and this led to low benzene–to–toluene ratios (B/T, ppbv/ppbv) in this study. The B/T ratios for urban, suburban and roadside ambient atmospheres were smaller than 0.2. Much lower ratios (<0.04) were measured for industrial work processes associated with usage of ink and paint solvents. Our study suggests that toluene–rich emission from the printing industry contributes to the gradual increase in the atmospheric toluene background in the PRD.

Keywords: *NMHCs, industrial emission, toluene, solvent, printing*
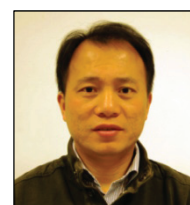
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1. Introduction

The Pearl River Delta (PRD), located in South China, is among the top urbanized and industrialized regions and is also a world renowned manufacturing base in China. With the rapidly growing economy and industrial activities, it experiences deteriorating air quality, such as extremely high surface ozone levels (Jiang et al., 2010), frequent haze episodes as well as remarkable visibility reduction (Wu et al., 2005). Non–methane hydrocarbons (NMHCs) are important precursors of tropospheric ozone and secondary organic aerosol (SOA). Under favorable meteorological conditions and in the presence of nitrogen oxides, NMHCs can produce a series of intermediate organic species, ozone and SOA (Odum et al., 1997; Poisson et al., 2000). Hydrocarbons, such as benzene and toluene, are toxic. Under high exposure, they can pose adverse effects to the health of local residents (Caprino and Togna, 1998).

Several studies have shown that industrial emissions are an important contributors to the high levels of NMHCs in the PRD region (Chan et al., 2006; Tang et al., 2007; Barletta et al., 2008; Ling et al., 2011; Yuan et al., 2013). However, there is very limited data on the NMHC emission profiles from specific industrial processes in the PRD, although chemical composition of major VOC emission sources have been reported in other countries (Scheff and Wadden, 1993; Chen et al., 2001; Na et al., 2004). An investigation of VOC profiles in a printing factory of Beijing showed

that *n*–nonane, *n*–decane, *n*–undecane, toluene, and *m/p*–xylene were the dominant species (Yuan et al., 2010). In source samples collected from stack emissions and fugitive emissions of printing industry in the PRD, benzene and toluene were found to be the major species associated with letterpress printing, while ethyl acetate and isopropyl alcohol were the most abundant compounds of offset and gravure printing processes (Zheng et al., 2013). However, VOC source profiles are regional–specific and vary largely. We hence carried out this field measurement to characterize the NMHC industrial emissions for two prominent PRD industries: electronics and printing.

According to an annual projected emission inventory study (CH2M HILL, 2002), the largest VOC contributor in the industrial sector in the PRD was the printing industry. It was estimated that about 15 400 tons in 1997 (CH2M HILL, 2002) and about 318 000 tons in 2006 in the PRD (Yu et al., 2011) and about 895 000 tons for the whole China in 2009 (Yang et al., 2012) were emitted from the printing industry. Wadden et al. (1995) reported that there were strong fugitive emissions from an offset printing shop in US. The average VOC emission rate was 470 g/hr with a range of 160–1 100 g/hr (Wadden et al., 1995). Thus, the printing industry is the first choice in our study. The electronic industry (4 tons/yr) was also selected for the study, because the work processes are also employed in a variety of other manufacturing industries. Processes

such as plastic casing molding and paint spraying can be found in the toy, shoe and car manufacturing industries.

In this paper, the NMHC source signatures of individual industrial work processes of the electronics and printing industries were reported. The source signatures were used to examine the impact of emissions from these two industries on local atmospheric NMHC levels. Also, we compare benzene–to–toluene (B/T) ratios measured in this study with previous PRD studies to illustrate the recent changes in the NMHC composition in the PRD atmosphere. The industrial source signatures obtained will also help in the improvement of uncertainties in modeling results for this region.

2. Experiment

2.1. Sampling design

The field experiment was carried out in Qingxi town within a highly industrialized PRD city, Dongguan, in January of 2005. Dongguan is bounded by Guangzhou, Huizhou and Shenzhen (Figure 1). Its good geographical position and infrastructural logistics support led to tremendous industrial development. Dongguan is among China's largest exporting domains in recent years. Using a regional chemical transport model – Sulfur Transport Eulerian Model (STEM–2Kl), the values of VOCs in wide areas of Dongguan in 2001 were found to be 14–16 ppbv, and were just lower than those in areas of Hong Kong and Guangzhou (Streets et al., 2006). The diversity of industries in Dongguan provides an almost self–supported industrial development environment. For example, 70–90% of electronic accessories and parts are available locally. Qingxi, situated in the southeast comprehensive manufacturing base in Dongguan, was an ideal location for the study of VOC emissions from the electronics and printing industries, because they are the prevalent industries there. Medium–sized enterprises of two target industries, with 200–300 staff, were selected in this study.

In this study, three categories of VOC samples were collected, including ambient, source of industrial work processes, and utilized industrial solvents. Five types of ambient air examined include suburban background, urban roadside, urban rooftop, electronics factory (EF) rooftop, and printing factory (PF) rooftop. The electronics factory mainly manufactures computer accessories such as, keyboards, speakers and power supply units. Electronics work processes examined included plastic casing molding, logotype printing, circuit board assemblies soldering and paint spraying. The printing factory mainly produces printed products and decorating cartons. Printing work processes examined include printing, glossing and carton gluing. Source samples were collected inside the two factories in the proximity of the seven industrial work processes. Also, evaporative VOC compositions of nine industrial solvents were obtained. The site description, daily sampling schedule and sample size are briefly listed in Table 1. Two background ambient samples were also collected in the early morning (06:00–07:00) of the last two sampling days. The other ambient samples were taken during working hours (08:30–16:30) with ambient temperatures ranging between 18.1–26.5 °C. The sampling height was 1–1.5 m above the ground or rooftop.

2.2. Sample collection and chemical analysis

From 6th January to 8th January, 2005, 42 VOC samples (14 ambient, 19 industrial source and 9 solvent) were collected using evacuated 2–L electropolished stainless steel canisters, prepared by the Rowland–Blake Laboratory of University of California–Irvine (UCI). Fifteen–minute "integrated" samples were collected for ambient and source categories. A calibrated critical orifice flow controller and a vacuum gauge were used. Initial sampling flow rates (100±5 mL/min) were calibrated using a digital flow meter (DC–Lite, BIOS, US). Approximately 1.5 L air sample was collected for each canister. The solvent category was obtained by another method. A drop of solvent was introduced into a canister, and let to be evaporated inside the canister. This method would underestimate the abundance of heavy molecular weight hydrocarbons (HC), because they have a lower tendency to evaporate. For example, components with carbon number greater than six constitute lesser fractions of gasoline vapor compared with gasoline (Na et al., 2004). Solvent evaporative compositions rather than actual compositions are given in this study.
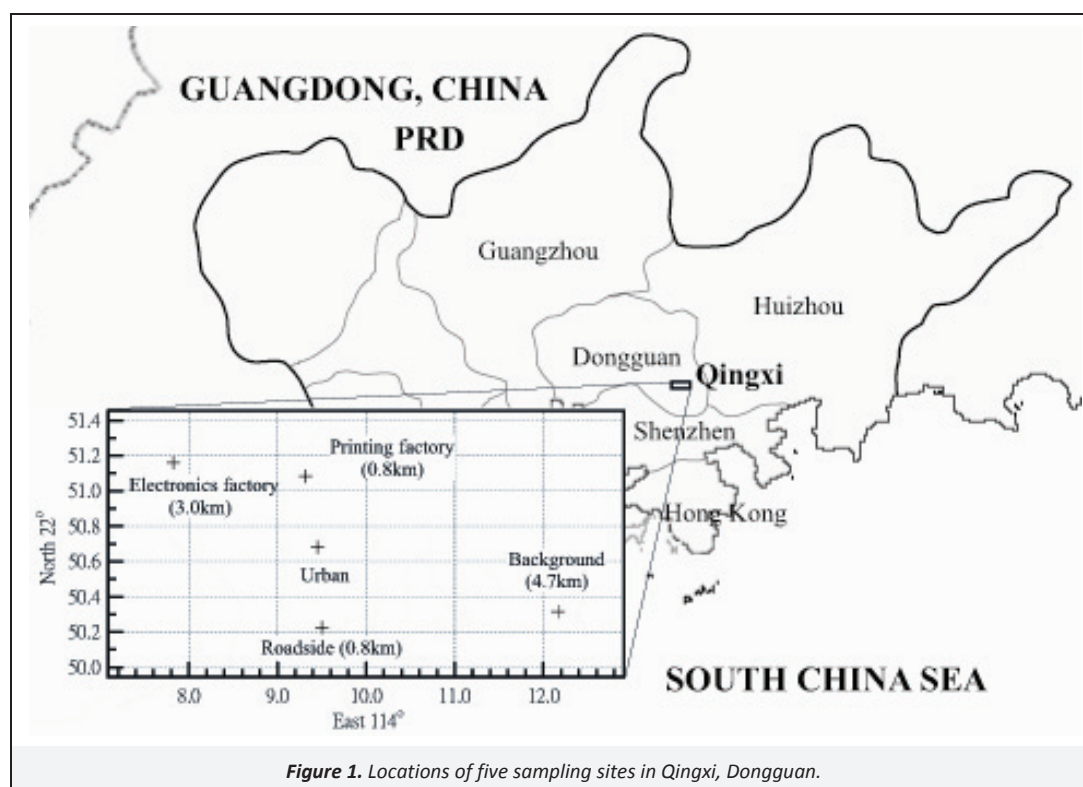

Figure 1. Locations of five sampling sites in Qingxi, Dongguan.

Table 1. Schedule of 3–day intensive sampling in Qingxi, Dongguan. Number of samples are shown in brackets

Site	Period	Category	Site Description
Background	06:00–07:00	Background [a] (2)	Near a reservoir in a suburban area
Electronics Factory (EF)	08:30–10:30	Plastic molding [b] (4)	10 m apart in the same large workshop (G/F[c])
		Logo printing [b] (2)	
		Spray painting [b] (2)	A separated small workshop (G/F)
		Soldering [b] (2)	A large workshop (1/F[d])
	09:30–10:30	EF Rooftop [a] (3)	Rooftop (2/F[e]), near a road and three factories of metalwork
Roadside	11:30–12:30	Roadside [a] (3)	In a roundabout with smooth traffic of Qingxi town
Printing Factory (PF)	13:30–15:30	Paper printing [b] (3)	A small workshop (G/F[c])
		Glossing [b] (3)	Partly separated from the small workshop by plastic curtain (G/F[c])
		Gluing [b] (3)	
	14:30–15:30	PF Rooftop [a] (3)	Rooftop (2/F[e]); very close to dense traffic roads, houses and other factories
Urban	15:30–16:30	Urban [a] (3)	Rooftop of a 9/F[f] building within commercial/residential area

[a] Ambient samples; [b] Source samples; [c]G/F: ground floor; [d]1/F: first floor; [e]2/F: second floor; [f]9/F: ninth floor

The canisters were shipped to UCI's laboratory after sampling. Chemical analysis for carbon monoxide (CO), methane (CH_4), NMHCs, halocarbons and alkyl nitrate was performed. Details of the analytical system, data analysis, and the measurement precision and accuracy for each species were described in detail elsewhere (Colman et al., 2001). Briefly, an aliquot of samples is cryogenically pre–concentrated at −196 °C in liquid nitrogen, and then vaporized and split to five different column/detector combinations: two flame ionization detectors (for detection of hydrocarbons), two electron capture detectors and a mass spectrometer. NMHCs in all ambient and source samples were present at mixing ratios above their detection limits. The limit of detection for all NMHCs is 10 pptv for ambient samples and 50 pptv for source samples. The precision of measurement is 3% for NMHCs. The measurement accuracy ranged between 2–20% for NMHCs.

In this paper, 37 C_2–C_9 NMHCs were used to explore the characteristics of PRD printing and electronic industrial emissions. Source signatures of respective industrial work processes were extracted to obtain the full profile. Other important NMHCs, especially C_2–C_4 unsaturated HCs, which were present at low levels in the industrial source samples, were also examined. These species are major components of automobile exhaust and existed in elevated levels in the urban roadside atmosphere. It should be pointed out that values in figures are presented in mole percentage (mole %) for illustration purpose, while those in tables are presented in weight percentage (wt. %), to facilitate input into receptor models.

3. Result and Discussion

3.1. General NMHC characteristics in ambient air

Figure 2 presents the composition of three HC groups (by mole %), covering 16 saturated, 9 unsaturated and 12 aromatic HCs, for ambient and industrial source categories. Although the total NMHC levels were different in the atmospheres of background (41.0 ppbv) and urban (105 ppbv), we observed similar mole fractions, approximately 50% for the aromatic HCs, 30% for saturated HCs, and 20% for unsaturated HCs, for both types of ambient air. In contrast, we noted that each HC group contained approximately a third of the total NMHCs in the roadside atmosphere. It was probably due to the freshly emitted ethene, ethyne and propene from automobiles (Barletta et al., 2002), which shifted the composition to the highest percentage of unsaturated HCs.

Inside the electronic factory, plastic molding and soldering produced mainly saturated HCs (>80%), while logo printing and spray painting emitted aromatic HCs (>50%). Subsequently, these emissions caused high percentages of saturated HCs (53%) and aromatic HCs (34%) measured in the EF rooftop atmosphere. The three work processes of the printing factory and the PF rooftop atmosphere contained mainly aromatic HCs (63–88%), with toluene being the most abundant aromatic HC (>85% of total aromatics). The total NMHCs in the PF rooftop (3 700 ppbv) was substantially higher than those in the other four ambient environments (41–169 ppbv) (see the Supporting Material, SM, Table S1). The large difference between the PF and EF rooftop ambient atmosphere implies that the industrial work processes inside the printing factory contributed higher VOC loadings to the local atmosphere than those inside the electronics factory.

3.2. NMHC characteristics in solvents associated with printing and electronic industries

Nine different types of solvents were collected from the industrial workshops, which covered most of solvents commonly used in different industrial processes or during instrument maintenance. The evaporative NMHC compositions of these solvents are shown in Table 2. Among the 37 NMHCs, 25 of them are used for compiling the evaporative compositions of various industrial solvents. These 25 compounds include only saturated and aromatic HCs, but they comprised 82–100 % by wt. of the total identified VOCs (halocarbons and NMHCs) in all solvents, except the glue. In general, hexane, heptane, toluene, ethylbenzene and xylenes were the common components in solvents, but their percentages varied largely among solvents. *n*–hexane and *n*–heptane were the dominant species in mold releasing agent, and C_6–C_7 alkanes contributed nearly 92% (by wt.) of the total NMHCs in this solvent. For the solvents involved in the printing processes, silk–screen cleaning solvent mainly constituted of toluene, ethylbenzene and xylenes (TEXs, 74% in total), and paint thinning and cleaning solvents contained high percents of *n*–hexane, *n*–heptane, and TEXs. While one spray paint thinning solvent was predominated by toluene (99.5%), the other one dominated by toluene (24.1%), *n*–heptane (20.9%) and *n*–hexane (10.4%). Fountain solution is a common solvent used in printing industry, and it has various types. In this study, the major hydrocarbons found in this solvent were *n*–hexane (21.3%), *m*–xylene (21.8), *p*–xylene (13.7%), and *n*–heptane (12.0%). For a UV vanishing solvent, toluene (80.7%) was the predominant species, followed by xylenes (14.8%) and ethylbenzene (3.34%).
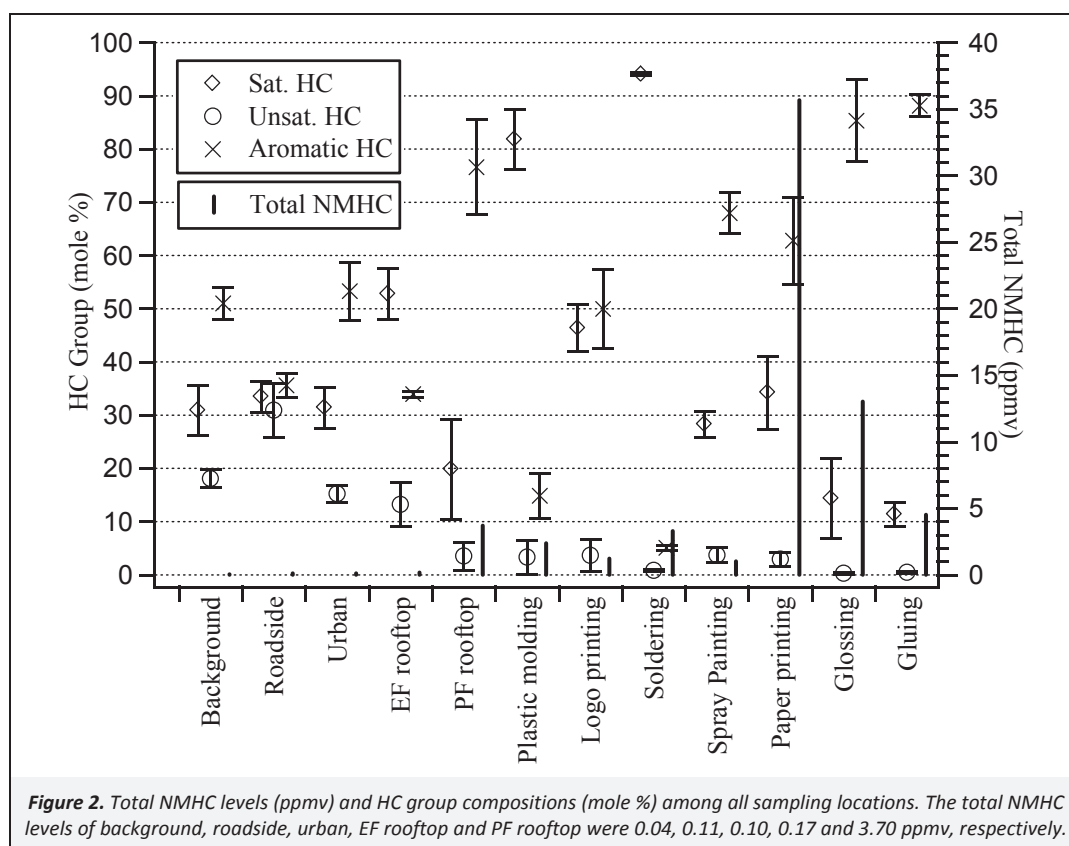
Figure 2. *Total NMHC levels (ppmv) and HC group compositions (mole %) among all sampling locations. The total NMHC levels of background, roadside, urban, EF rooftop and PF rooftop were 0.04, 0.11, 0.10, 0.17 and 3.70 ppmv, respectively.*

Table 2. *NMHC evaporative compositions (% by wt.) of solvents used in electronics and printing factories*

NMHCs	Mold Releasing Agent	Paint Thinning Solvent	Paint Cleaning Solvent	Silk–screen Cleaning Solvent	Spray Paint Thinning Solvent 1	Spray Paint Thinning Solvent 2	UV Varnish	Fountain Solution	Glue
propane	0.40	0.12	0.39	0.01	nd [b]	nd [b]	0.01	1.45	4.50
i–butane	1.37	0.10	0.39	nd [b]	nd [b]	nd [b]	0.01	1.24	3.88
n–butane	5.69	0.16	0.54	0.01	0.02	0.01	0.01	1.93	6.14
2,3–dimethylbutane	1.26	0.20	0.35	nd [b]	0.28	0.01	nd [b]	0.53	1.71
n–hexane	37.2 [a]	9.42 [a]	9.49 [a]	0.05	10.4 [a]	0.10	0.06	21.3 [a]	36.7 [a]
2–methylpentane	9.94	1.02	2.03	0.03	2.02	0.05	0.01	2.04	7.68
3–methylpentane	5.74	0.80	1.61	0.02	1.54	0.04	nd [b]	1.04	3.26
n–heptane	30.6 [a]	5.17 [a]	11.9 [a]	0.07	20.9 [a]	0.07	0.03	12.0 [a]	20.3 [a]
2–methylhexane	3.10	3.66	5.18	0.07	7.69	nd [b]	nd [b]	0.51	nd [b]
3–methylhexane	4.39	5.15	7.38	0.10	8.40	0.04	nd [b]	0.47	nd [b]
2,2,4–trimethylpentane	0.14	0.17	0.50	0.01	4.39	nd [b]	nd [b]	0.33	1.26
n–octane	nd [b]	0.23	0.86	1.77	9.46	0.01	0.01	0.07	0.43
n–nonane	nd [b]	1.14	1.47	4.52	0.14	nd [b]	0.03	0.25	0.94
benzene	0.03	0.18	0.50	1.49	4.07	0.01	0.02	0.81	1.87
toluene	0.01	4.42 [a]	5.49 [a]	11.4 [a]	24.1 [a]	99.5 [a]	80.7 [a]	1.36	2.30
ethylbenzene	0.01	14.9 [a]	6.28 [a]	25.7 [a]	1.53	0.08	3.34	8.21	0.29
o–xylene	0.01	15.9 [a]	3.50 [a]	14.0 [a]	0.43	0.01	5.15	9.34	0.35
m–xylene	0.01	18.4 [a]	10.3 [a]	13.3 [a]	2.87	0.02	6.05	21.8 [a]	0.36
p–xylene	0.01	12.8 [a]	6.47 [a]	9.92 [a]	1.78	0.01	3.60	13.7 [a]	0.26
i–propylbenzene	nd [b]	1.54	2.88	3.63	nd [b]	nd [b]	0.20	0.23	0.26
n–propylbenzene	nd [b]	1.51	6.22	5.04	nd [b]	nd [b]	0.15	0.26	0.46
o–ethyltoluene	0.01	0.54	3.42	1.64	nd [b]	nd [b]	0.17	0.16	nd [b]
m–ethyltoluene	0.01	1.59	7.57	4.66	0.01	nd [b]	0.23	0.41	1.65
p–ethyltoluene	0.01	0.68	3.36	2.09	nd [b]	nd [b]	0.06	0.15	0.87
1,2,4–trimethylbenzene	0.02	0.22	1.94	0.42	nd [b]	0.01	0.11	0.46	4.52

[a] *Values are the suggested primary evaporative components in the respective solvents,* [b] *nd: not detected.*

3.3. NMHC characteristics in emissions from electronics industry

In general, the four work processes inside the electronic factory emitted primarily either saturated HCs or aromatic HCs (Figure 2). Plastic molding emitted mainly alkanes. Propane (n–C_3; 23.9%), i–butane (i–C_4; 8.3%), n–butane (n–C_4; 18.6%) and n–hexane (n–C_6; 6.6%) comprised 57% by wt. in the source signature (Table 3). Plastic polymers, such as polyester, polypropylene and acrylonitrile butadiene styrene, were melted to form a plastic casing under high temperature. It is believed that these four saturated HCs are emitted from molding machines. Their mixing ratios were found to be one order of magnitude higher than those in an additional sample (PM4), which was collected during the maintenance and testing operations of a molding machine. Ratios of i–C_4/n–C_3, n–C_4/n–C_3 and n–C_6/n–C_3 showed small deviations among the four samples collected near the plastic molding process (see the SM, Table S2). Their mean ratios (ppbv/ppbv) were 0.26±0.02, 0.60±0.04, and 0.14±0.01, respectively. The minor usage of a mold releasing agent contributed partially to n–hexane in the source signature of plastic molding, as n–hexane comprised more than one–third of this agent (Table 2).

Soldering also emitted large quantities of alkanes. 2,3–dimethylbutane (5.9%), 2–methylpentane (25.8%), 3–methyl-pentane (30.3%), 2–methylhexane (14.9%) and 3–methylhexane (10.2%) were the most abundant species in the source signature (Table 3). The high abundance of these five C_6–C_7 alkanes suggests that there was rapid evaporation of deflux agents on hot surface of semi–products to the workshop atmosphere. In addition, some halocarbons, such as trichloroethylene (C_2HCl_3), tetrachloro-ethylene (C_2Cl_4), methyl chloroform (CH_3CCl_3) and methylene chloride (CH_2Cl_2), simultaneously elevated in the samples (data not shown). They were also found in other studies (McCulloch and Midgley, 1996; Chang et al., 2001) inside metal degreasing agent, cleaning solvent and deflux agent. However, there were no deflux agents, which were used to remove excess flux residues, collected for chemical analysis to verify the source signature of soldering.

Table 3. *NMHC source signatures (% by wt.) of work processes in electronics and printing factories*

NMHCs	Plastic Molding	Logo Printing	Soldering	Spray Painting	Paper Printing	Glossing	Gluing
ethane	0.45±0.19	0.28±0.16	0.07±0.00	0.22±0.13	0.01±0.01	0.02±0.01	0.04±0.02
propane	23.9±2.97 [a]	8.55±0.27	1.82±0.41	1.61±1.65	0.03±0.02	0.04±0.00	0.08±0.06
i–butane	8.30±0.67 [a]	3.37±0.47	0.65±0.07	0.58±0.46	0.22±0.13	0.02±0.01	0.05±0.02
n–butane	18.6±1.15 [a]	7.90±0.99	1.37±0.00	1.38±0.89	0.51±0.30	0.05±0.03	0.10±0.05
i–pentane	0.81±0.55	0.65±0.68	0.94±0.44	1.05±0.13	7.31±3.84 [a]	0.34±0.43	0.43±0.14
n–pentane	0.62±0.65	0.61±0.59	0.61±0.25	1.13±0.04	2.33±1.17	0.13±0.16	0.16±0.05
2,3–dimethylbutane	1.29±0.20	0.68±0.14	5.91±0.68 [a]	0.36±0.07	1.64±0.43	0.12±0.15	0.14±0.05
n–hexane	6.63±0.66 [a]	4.41±0.33 [a]	0.75±0.81	3.13±0.65 [a]	1.26±0.07	0.38±0.47	0.31±0.25
2–methylpentane	4.99±0.82	2.72±0.53	25.8±1.90 [a]	1.51±0.24	2.74±0.58	0.28±0.34	0.30±0.13
3–methylpentane	4.33±0.64	2.63±0.40	30.3±0.34 [a]	1.16±0.13	1.90±0.46	0.21±0.25	0.22±0.10
n–heptane	0.63±0.36	0.42±0.33	0.32±0.01	5.62±1.18 [a]	3.57±0.65	3.98±2.07	2.98±0.85
2–methylhexane	1.99±0.30	1.16±0.18	14.9±1.79 [a]	2.50±0.17	3.52±0.81	3.60±1.55	2.47±0.68
3–methylhexane	1.88±0.37	1.05±0.35	10.2±0.73 [a]	2.66±0.08	4.46±0.73	5.08±1.98	3.52±1.02
2,2,4–trimethylpentane	0.09±0.06	0.07±0.04	0.21±0.03	0.71±0.09	2.57±0.75	0.25±0.28	0.21±0.05
n–octane	0.11±0.05	0.26±0.18	0.02±0.00	2.97±2.85	0.78±0.17	0.14±0.09	0.09±0.04
n–nonane	0.12±0.07	0.15±0.10	0.03±0.00	0.28±0.17	0.22±0.12	0.03±0.02	0.04±0.01
ethene	0.61±0.61	0.53±0.47	0.11±0.03	0.39±0.25	0.01±0.00	0.03±0.01	0.04±0.03
ethyne	0.59±0.59	0.51±0.42	0.11±0.02	0.43±0.34	0.01±0.01	0.03±0.01	0.04±0.03
propene	0.14±0.15	0.12±0.11	0.03±0.00	0.14±0.02	nd [b]	0.01±0.00	0.01±0.00
trans–2–butene	0.03±0.03	0.03±0.03	0.01±0.00	0.07±0.03	0.50±0.24	0.02±0.03	0.03±0.01
cis–2–butene	0.03±0.03	0.03±0.03	0.01±0.00	0.08±0.04	0.50±0.23	0.02±0.03	0.03±0.01
1–butene	0.06±0.05	0.05±0.04	0.01±0.00	0.23±0.23	0.16±0.10	0.01±0.01	0.01±0.00
i–butene	0.08±0.07	0.06±0.04	0.01±0.00	0.06±0.05	0.12±0.07	0.01±0.01	0.02±0.01
1,3–butadiene	0.04±0.04	0.03±0.03	0.01±0.00	0.03±0.01	0.38±0.16	nd [b]	nd [b]
isoprene	0.02±0.02	0.03±0.03	0.01±0.00	0.02±0.02	0.04±0.01	nd [b]	0.01±0.01
benzene	0.82±0.61	0.79±0.49	0.33±0.07	1.90±0.28	0.88±0.36	0.16±0.11	0.18±0.03
toluene	6.45±3.81	5.09±1.73 [a]	2.39±0.13	62.4±1.07 [a]	56.8±9.73 [a]	71.2±18.5 [a]	69.2±27.1 [a]
ethylbenzene	3.52±1.31	13.6±0.18 [a]	0.67±0.19	1.70±0.29	0.61±0.16	0.31±0.15	0.37±0.09
o–xylene	2.39±0.90	7.28±2.40 [a]	0.37±0.02	0.75±0.22	0.85±0.27	0.44±0.36	0.49±0.37
m–xylene	6.81±2.49	23.2±4.54 [a]	1.06±0.09	2.74±1.42	2.02±0.63	0.89±0.45	0.98±0.34
p–xylene	1.81±0.85	10.5±2.98 [a]	0.62±0.33	0.64±0.32	0.61±0.19	0.45±0.38	0.32±0.18
i–propylbenzene	0.11±0.05	0.21±0.18	0.02±0.00	0.06±0.01	0.08±0.04	0.26±0.40	0.26±0.38
n–propylbenzene	0.23±0.05	0.70±0.15	0.03±0.01	0.15±0.01	0.26±0.16	0.89±1.35	1.29±2.02
o–ethyltoluene	0.17±0.08	0.36±0.07	0.03±0.01	0.12±0.04	0.27±0.23	1.22±1.85	1.91±2.97
m–ethyltoluene	0.44±0.14	0.91±0.12	0.08±0.03	0.31±0.11	1.21±0.76	3.19±4.81	4.13±6.25
p–ethyltoluene	0.20±0.06	0.42±0.06	0.04±0.01	0.14±0.06	0.38±0.22	1.38±2.08	2.21±3.42
1,2,4–trimethylbenzene	0.69±0.50	0.62±0.01	0.14±0.09	0.78±0.05	1.23±0.85	4.82±6.99	7.29±10.6 [a]

[a] *Values are the suggested primary components in the respective source signatures,* [b] *nd: not detected.*

In contrast, logo printing produced mainly aromatics. Toluene (5.1%), ethylbenzene (13.6%), *o*–xylene (7.3%), *m*–xylene (23.2%) and *p*–xylene (10.5%) were the primary components in the source signature (Table 3). These five aromatics were the major components of paint thinning solvent (66%), paint cleaning solvent (32%) and silk–screen cleaning solvent (74%), which were used in the process (Table 2). The total NMHCs of logo printing was the lowest among the four work processes (Figure 2), and the air sampled could be strongly affected by other work processes nearby. Hence, the signature posed by these five aromatic HCs could be underestimated, due to induced quantities of propane, *i*–butane, *n*–butane and *n*–hexane (24%) emitted from molding machines in the same workshop. The mean ratios of i–C_4/n–C_3 (0.30±0.03) and n–C_4/n–C_3 (0.70±0.07) were similar to those of plastic molding. A two–fold increase in the n–C_6/n–C_3 ratio (0.26±0.01) compared with plastic molding may be attributed to additional contribution of *n*–hexane emitted from the paint thinning and cleaning solvents (see the SM, Table S3).

Toluene constituted 62% in the signature of spray painting, followed by *n*–heptane (5.6%) and *n*–hexane (3.1%) (Table 3). High toluene content (54% in ppbC) was also measured in emissions from an automobile paint shop in Mexico (Seila et al., 2001). The source signature was consistent with the evaporative composition of the two spray paint thinning solvents. One solvent was nearly pure toluene, and the other one contained toluene (24%), *n*–heptane (21%) and *n*–hexane (10%) (Table 2). Similar to a Korean study (Na et al., 2004), paint solvents were mainly composed of HCs greater than C_5, especially aromatic HCs.

In order to further investigate the contribution of the respective processes, their individual source signatures (by mole %) were sorted and compared with the EF rooftop ambient NMHC mixing ratio (Figure 3). It should be noted that differences in exhaust condition and transport distance from the respective work processes to the rooftop, as well as irregular operation frequencies for the respective work processes can lead to variations in the ambient rooftop NMHC levels. Propane, *i*–butane, *n*–butane, 2,3–dimethylbutane, *n*–hexane, 2–methylpentane, 3–methylpentane, *n*–heptane, toluene, ethylbenzene, *o*–xylene, *m*–xylene and *p*–xylene were found to be substantial in the atmosphere of EF rooftop. With the help of the industrial source signature obtained, these NMHCs were traced back to the corresponding work processes. Nevertheless, ethane, ethyne, ethene, propene, *i*–pentane and *n*–pentane, with low abundance in the four source signatures, were found to have high mixing ratios on the EF rooftop (Figure 3). The ambient rooftop ethane level (5.5 ppbv) was similar to those measured in the background, urban and roadside atmospheres (4.2–5.4 ppbv), while ethyne, ethene, propene, *i*–pentane and *n*–pentane were mainly contributed by nearby on–road sources.

3.4. NMHC characteristics in emissions from printing industry

Paper printing had the highest total NMHC value (Figure 2). It was the largest contributor among the three target work processes, which included printing, glossing and gluing. Toluene (57%) and *i*–pentane (7.3%) were the two most abundant NMHCs in weight percentage composition (Table 3). Our results are significantly different from those by Yuan et al. (2013), of which *n*–decane (16.9%), *n*–octane (14.8%) and *n*–undecane (13.0%) were the major compounds and toluene (4.1%) and *i*–pentane (1.4%) only accounted for minor percentages, but similar to the work by Zheng et al. (2013), of which toluene was the predominant species in the fugitive emission samples of gravure printing (9.6%) and letterpress printing (12.9%). This may due to the use of different solvents in the investigated printing factories. The high toluene abundance was attributed to uses of thinning solvents and solvent–based inks. High toluene contents were reported for graphite art (93% by wt.) in U.S. (Scheff and Wadden, 1993), for solvent–based ink (69% by wt.) in Korea (Na et al., 2003), and for vehicle coating (45% by wt.) in Taiwan (Lai et al., 2005). Toluene was also the major component in the thinning solvents of paint spraying used in the electronic factory.
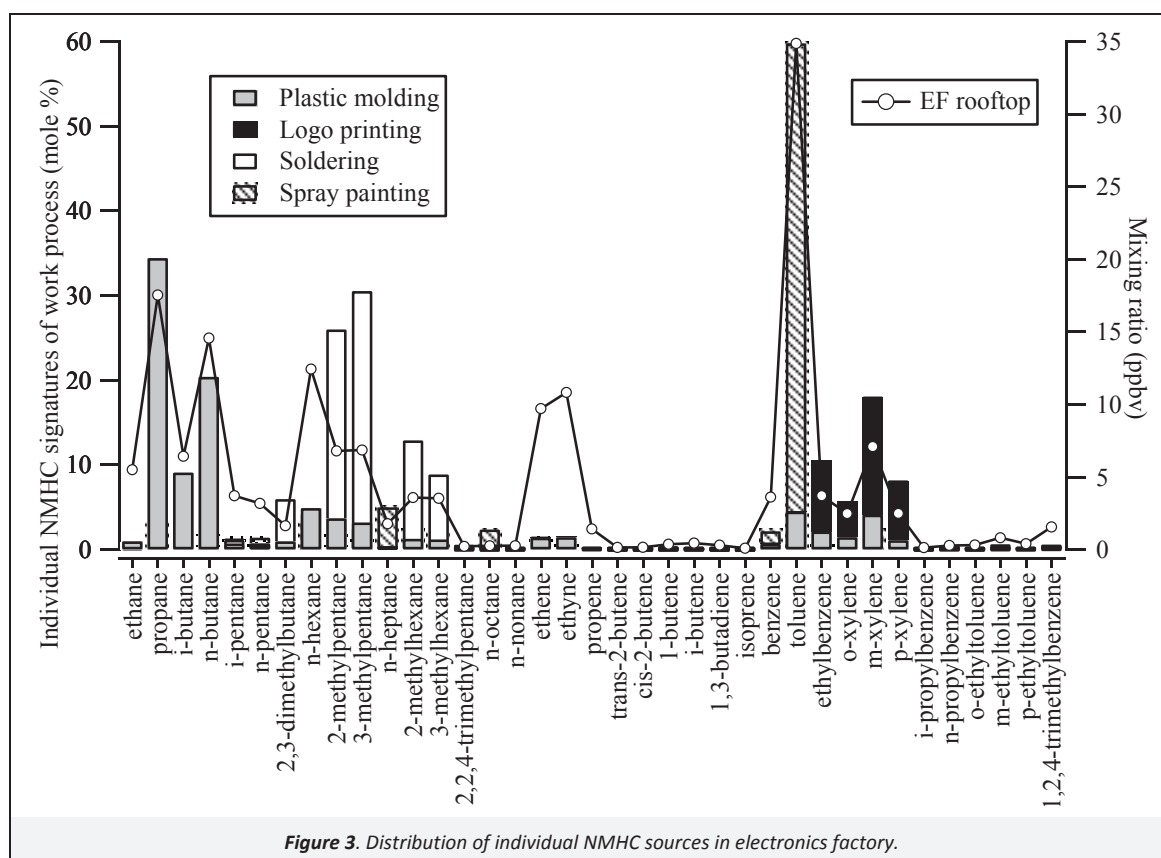

Figure 3. Distribution of individual NMHC sources in electronics factory.

i–pentane is a known marker for gasoline evaporation. Gasoline solvent was traditionally used in press cleaning (Wadden et al., 1995). Considering that gasoline solvent is flammable, its uses for press cleaning have been banned in many developed countries, but not in the PRD. Thus, gasoline solvent cleaning contributed to *i*–pentane and a variety of C_4–C_9 HCs in the source signature. The fountain solution was also used in printing. It mainly constituted *n*–hexane, *n*–heptane, *m*–xylene and *p*–xylene (69%) (Table 2). However, only a small percentage (7%) of these four constituents was observed in the source signature of paper printing. This difference demonstrates the influence of the large quantities of NMHCs, in particular toluene, emitted from the use of solvent–based inks, thinning solvents and cleaning solvents, that were not collected for chemical analysis.

Because the three work processes are located in the same large workshop, there existed strong inter–contamination in the three respective source signatures (Table 3). As a result, the three "interfered" source signatures may contained higher values of some species and hence could not completely characterize the "real" signatures for each work process. The solvent evaporative compositions of ultra–violet (UV) varnish and glue is an alternative to characterize major emissions from glossing and gluing, and the UV varnish and glue were the main solvents used in glossing and gluing, respectively.

The glue contained high percent of *n*–hexane and *n*–heptane (57%), but trivial amount of toluene (Table 2). The phenomenon of strong inter–contamination was confirmed by the very high toluene content (69%) shown in the source signature of gluing (Table 3). In addition to paper printing, glossing emitted mainly toluene and could contaminate the other source signatures as well, though it was similarly affected by the ultra–strong emission from paper printing. The high percentage of toluene (71%) shown in the source signature of glossing (Table 3) was consistent with the high toluene content (81%) quantified in the UV varnish (Table 2). The varnish was smeared onto the surface of print product to give a glossy coating when dry. We also observed that extremely high toluene emission was caused by a follow–up work, baking. Among the three glossing samples, one sampled during baking showed a five–fold increase in toluene level (22.6 ppmv) compared to those without baking. This elevated toluene level was comparable with those emitted from paper printing (11.6–32.9 ppmv).

The printing factory is located in a dense area, in the proximity of other factories which manufacture adhesive tape and household appliances. Unlike the last case, it was difficult to relate

corresponding contributions through signatures of individual industrial work process (by mole %) to the elevated NMHCs measured on the PF rooftop (Figure 4). An evaluation using the source signatures of the work process and industrial solvent showed that aromatic HCs was the major HC group in the emissions from the printing factory, with toluene being the dominant NMHCs. The heavy utilization of a variety of inks and complementary solvents led to the extremely high total NMHC levels. In general, their total NMHC levels, except gluing, were one order of magnitude higher than those inside the electronics factory. Paper printing consumes large quantities of ink and solvent. Thus, this process emitted almost all NMHCs, and in particular high toluene and *i*–pentane. Glossing plus baking also produced large quantities of toluene. Thus, it is difficult to separate the contribution to toluene from these two processes. We also noted that there were high mixing ratios of ethane, ethene, ethyne, propane and propene measured on the PF rooftop which were trivial in the emissions from the printing factory (Figure 4). We hence suggested that automobile, other industrial activities and LPG leakage outside the factory were the major sources of these five C_2 and C_3 HCs (Figure 4).

3.5. Impact of industrial emission on local VOCs

Two local background samples were collected in the early morning near a reservoir (Figure 1), as there were only few fresh emission sources. Almost all NMHC mixing ratios were the lowest of this study (Figure 5). Nevertheless, the levels of toluene (15.6±0.89 ppbv) in this inner PRD town were still significantly higher than those measured in the South China Sea background air (0.070±0.071 ppbv) and the outflow from the PRD (6.01±7.21 ppbv) in 2002 (Wang et al., 2005). It is worth noting that the level of toluene was substantially higher than the next three most abundant species, which were ethane (4.15 ppbv), ethyne (3.42 ppbv) and ethene (2.83 ppbv). This high toluene background would hence strongly affect local ambient and roadside atmospheres. Toluene mean mixing ratios reported were 0.07 ppbv and 6.01 ppbv for the South China Sea background and the PRD regional outflow air to Tai O (a rural site in Hong Kong), respectively, in 2002 (Wang et al., 2005), 11.5–14.5 ppbv for Kaohsiung urban atmosphere in 2003 (Lai et al., 2005), 10.0 ppbv for Guangzhou urban atmosphere in 2007 (Tang et al., 2007) and 4.6 ppbv in 2009 (Zhang et al., 2013), 8.46 ppbv for rural atmosphere (Xinken) of PRD in 2004 (Liu et al., 2008a), 5.9 ppbv for the atmosphere of small industrial related town (Wangqingsha) in the PRD in 2009 (Zhang et al., 2013), and 4.18 ppbv for the atmosphere of entire PRD region between 2008–2009 (Louie et al., 2013).
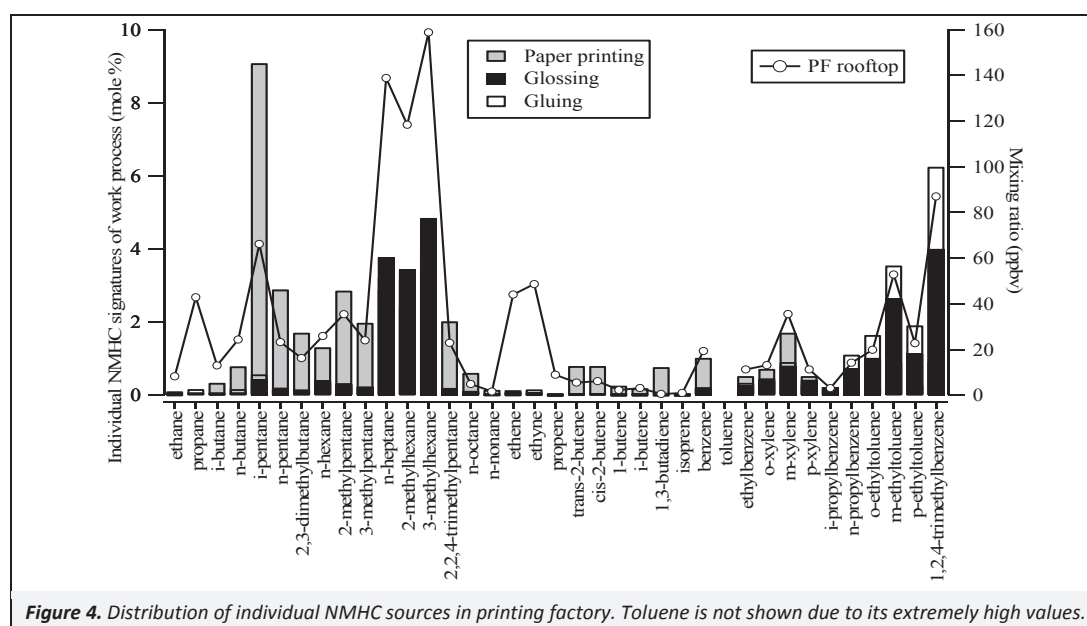

Figure 4. *Distribution of individual NMHC sources in printing factory. Toluene is not shown due to its extremely high values.*
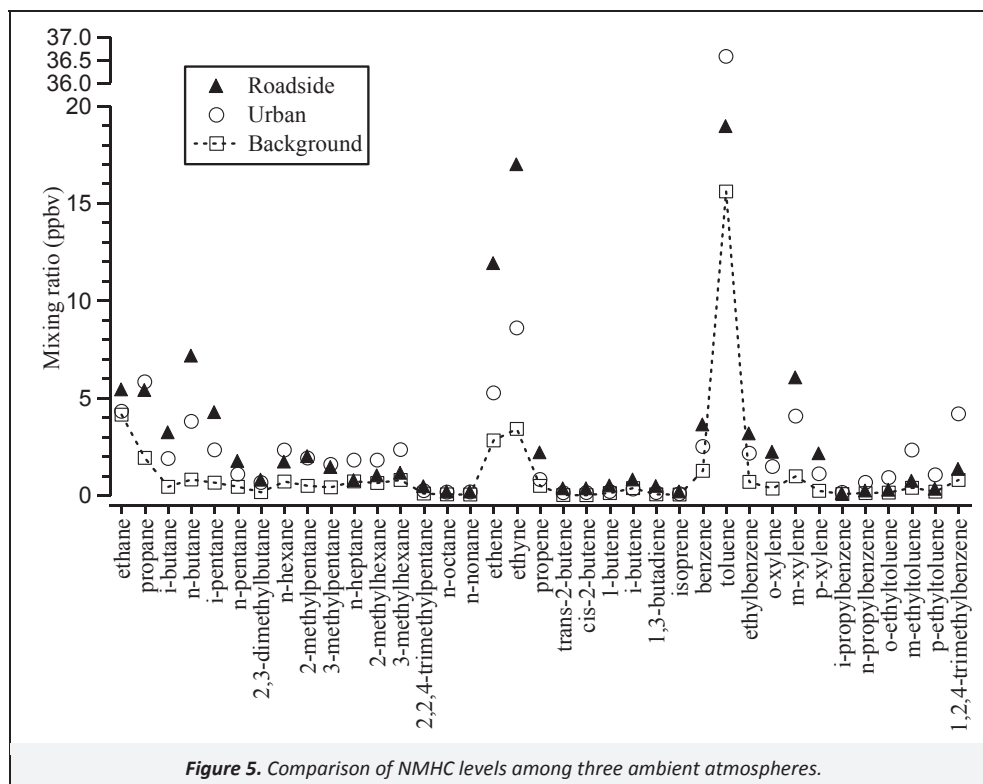
Figure 5. *Comparison of NMHC levels among three ambient atmospheres.*

Ethyne, ethene, propene, *i*–butane, *n*–butane, *i*–pentane, benzene, toluene and C_8 aromatic HCs increased in the roadside ambient air relative to the background (Figure 5). These NMHCs were highly weighted in the VOC profiles of vehicular exhaust and gasoline evaporation which were used to input into models in other studies (Buzcu and Fraser, 2006; Liu et al., 2008b). All unsaturated HCs were the highest in the roadside atmosphere due to the contribution of fresh automobile emissions. In contrast, their levels were relatively lower in the urban atmosphere, as these reactive unsaturated HCs with short lifetime are rapidly removed by photochemical reactions. However, the longer–lifetime species, namely toluene, C_6–C_7 alkanes and C_9 aromatics were found to have the highest levels in the urban atmosphere (Figure 5), despite the expanding of the boundary layer in the late afternoon. As a result of emissions from factories, the toluene level in the urban atmosphere was about twice those of the background and roadside atmospheres. The printing industry was the potential contributor to this high toluene level (36.6 ppbv), as 2 560 ppbv of toluene was measured on the PF rooftop. The use of solvent–based inks may also contribute C_9 aromatic HCs to the urban atmosphere (Figure 4). The electronic industry and other industries with similar work processes likely led to high C_6–C_7 alkane levels through solvent usage (Figure 3).

Benzene, ethylbenzene, and *m/o/p*–xylenes (BEX) showed good correlations (R^2=0.58–0.84) among the roadside, background, urban rooftop, and industrial rooftop samples. If one sample with high benzene level (40.36 ppbv, collected at the rooftop of printing factory) excluded, better correlations are obtained (R^2=0.81–0.94). However, poor correlations are found between toluene and benzene (also for ethylbenzene and xylenes), even if the three samples collected in the rooftop of printing factory are excluded (R^2=0.25). These indicate that BEX have similar or common sources in this small industrial town, while toluene has additional sources other than BEX, most likely the industrial emissions.

Benzene to toluene ratios (B/T) are widely used to indicate their source signatures (Barletta et al., 2002; Barletta et al., 2008). Mean B/T ratios (ppbv/ppbv) measured in the background and urban atmospheres (0.08 and 0.07) were similar, and they were

lower than the roadside B/T ratio (0.20) (see the SM, Table S3). Although the roadside B/T ratio was the highest in this study, it was lower than those measured in other PRD cities, such as Guangzhou roadside (0.7) (Chan et al., 2006). A specific B/T ratio (<0.20) was used as an indicator of samples strongly affected by industrial emissions (Barletta et al., 2008). For the grid air samples collected in the entire PRD region, a B/T ratio of 0.4±0.04 was reported (Louie et al., 2013). At a rural site downwind of the industrial zones of PRD, a B/T ratio of 0.4 was also found to reflect substantial contribution of solvent use (Zhang et al., 2013). In this study, the mean B/T ratios (<0.2) measured in all ambient air samples were due to the high toluene background as well as the daily industrial toluene emissions. Much lower ratios (<0.04) were measured for industrial work processes associated with the usage of ink and print solvents, such as spray painting, paper printing and glossing (see the SM, Table S3).

Among the five ambient sites, we selected the background, roadside and urban samples to calculate the mean B/T characteristic ratio of the urban atmosphere for this inner PRD town. These ambient samples were collected in the daytime and were not directly affected by industrial sources. The B/T ratio of the local urban atmosphere was 0.12±0.07. If the three roadside samples were not included in calculation, the B/T ratio would decrease to 0.08±0.01. This result suggests that local industries, in our illustrated Qingxi study, substantially contributed to the toluene loading in the inner PRD atmosphere. The atmospheric toluene levels in the region have been increasing in the past few years. In addition to the usage of toluene–rich fuels in Hong Kong (Tsai et al., 2006), our data suggests an increasing trend in the regional toluene level and it was associated with increased PRD industrial emission.

4. Conclusions

This NMHC measurement in the PRD gave source signatures of seven industrial work processes in the electronic and printing industries. Nine NMHC profiles of industrial solvents were also obtained. Emissions from the electronic factory mainly contained C_3–C_4 alkanes, C_6–C_7 alkanes and C_7–C_8 aromatic HCs. They were

contributed by evaporative losses from molten plastic, deflux agent, thinning solvent, and cleaning solvent. For the three work processes of the printing factory, almost all NMHCs were heavily emitted, except for C_2 and C_3 HCs. Toluene was the most abundant NMHCs in these three work processes, while *i*–pentane was the next abundant NMHCs in emissions from paper printing. Our data showed that printing industry was a very strong NMHC contributor in the industrial sector in PRD. Thus, in addition to the recent introduction of toluene–rich fuel in this region, toluene–rich emission from the printing industry significantly contributed to the toluene loading in the PRD atmosphere and the toluene level is gradually increasing in the background atmosphere.

Acknowledgment

Supporting Material Available

Ambient NMHC levels (ppbv) of five ambient air sampling environments (Table S1), Concentrations of abundant NMHCs (ppbv) among four source samples of plastic molding and its ratios (ppbv/ppbv) (Table S2), Mean ratios of benzene to toluene (B/T, ppbv/ppbv) (Table S3). This information is available free of charge via the internet at: http://www.atmospolres.com.

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