

C₁–C₈ volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment

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Abstract

We present measurements of C₁–C₈ volatile organic compounds (VOCs) at four sites ranging from urban to rural areas in Hong Kong from September 2002 to August 2003. A total of 248 ambient VOC samples were collected. As expected, the urban and sub-urban sites generally gave relatively high VOC levels. In contrast, the average VOC levels were the lowest in the rural area. In general, higher mixing ratios were observed during winter/spring and lower levels during summer/fall because of seasonal variations of meteorological conditions. A variation of the air mass composition from urban to rural sites was observed. High ratios of ethyne/CO (5.6 pptv/ppbv) and propane/ethane (0.50 pptv/pptv) at the rural site suggested that the air masses over the territory were relatively fresh as compared to other remote regions. The principal component analysis (PCA) with absolute principal component scores (APCS) technique was applied to the VOC data in order to identify and quantify pollution sources at different sites. These results indicated that vehicular emissions made a significant contribution to ambient non-methane VOCs (NMVOCs) levels in urban areas (65 ± 36%) and in sub-urban areas (50 ± 28% and 53 ± 41%). Other sources such as petrol evaporation, industrial emissions and solvent usage also played important roles in the VOC emissions. At the rural site, almost half of the measured total NMVOCs were due to combustion sources (vehicular and/or biomass/biofuel burning). Petrol evaporation, solvent usage, industrial and biogenic emissions also contributed to the atmospheric NMVOCs. The source apportionment results revealed a strong impact of anthropogenic VOCs to the atmosphere of Hong Kong in both urban/sub-urban and rural areas.

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1. Introduction

High concentrations of ozone (O₃) (over 120 ppbv) have been observed in Hong Kong and the frequency of O₃ episodes has increased in recent years (e.g., So and Wang, 2003; EPD, 2003). Because volatile organic compounds (VOCs) play an important role in the formation of photochemical O₃ and other oxidants in the troposphere

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(NRC, 1991), it is crucial to characterize the sources and distribution of VOCs in the atmosphere of Hong Kong.

Hong Kong is a densely populated city situated in the rapidly developing Pearl River Delta (PRD) region of southern China. It is influenced by VOC emissions particularly from local vehicles and regional industrial activities. In 2002, there were over 524,000 vehicles registered in Hong Kong (TD, 2003), from which 8360 tonnes of non-methane VOCs (NMVOCs) were emitted (EPD, 2006). In addition, activities from power generation, marine vessels and aircraft generated 1229 tonnes of NMVOCs. A number of studies have been conducted to understand the spatial-temporal distribution of VOCs in Hong Kong (Lee et al., 2002; Ho et al., 2004; Guo et al., 2004a). These studies mainly addressed aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes in industrial and roadside areas. Recently, So and Wang (2004) presented the characterization of C₃–C₁₂ VOCs in Hong Kong with respect to their distribution, sources and reactivities. However, knowledge about the spatial-temporal variations and atmospheric processing of VOCs (especially C₁–C₂ VOCs) in this subtropical city is still limited. For effective control of photochemical O₃ pollution, there is an urgent need to better understand the atmospheric processing and source apportionment of VOCs in Hong Kong.

Therefore, the objectives of this study are to investigate the correlation of VOCs with trace gases such as CO and O₃ in order to assess the sources and photochemical processes in Hong Kong and its upwind regions, and to identify and quantify the relative contributions of emission sources to ambient VOCs using a receptor model.

2. Experimental

2.1. Environment of Hong Kong and the four monitoring sites

The general characteristics of topography and climate in Hong Kong have been reported elsewhere (Wang et al., 2001). Briefly, the territory has a complex terrain, with hilly areas making up about 70% of the total land. The climate of Hong Kong is governed by the Asian monsoons. Prevailing synoptic winds arriving in Hong Kong are from the north and northeast in winter, east in spring and autumn, and south and southwest during the

summer months. Field measurement was carried out at four sites, namely Tap Mun (TM), Central/Western (C/W), Tung Chung (TC) and Yuen Long (YL) from September 2002 to August 2003 (Fig. 1). These four sites cover different characteristic areas such as rural (TM), sub-urban (TC and YL) and urban (C/W). TM is in the northeastern rural area; CW is an urban residential area; TC is in the southwestern new town in proximity to the international airport; and YL is in the northwestern new town which is about 15 km southwest of Shenzhen, a large and developing industrial city in Guangdong Province in South China. There is also an industrial estate within 1 km to the northeast of the YL site. All four sampling sites are located on the rooftops of buildings with an elevation ranging from 11 to 25 m above the ground level.

2.2. Measurement of VOCs and other trace gases

In this study, continuous measurements of selected trace gases (O₃, SO₂ and NO₂/NO_x) were conducted, while whole air canisters samples were collected for the analysis of chemicals including CO and 22 VOCs. For the TM, C/W and TC sites, the analyzers for measuring O₃, NO₂/NO_x and SO₂ have been described by So and Wang (2003). Briefly, O₃ was monitored with commercial UV photometric analyzers (TECO 49/API 400); NO₂/NO_x was measured by commercial chemiluminescence instruments (ML 8840/API 200A); and SO₂ was monitored using UV fluorescence (ML 8850/TECO 43A). The detection limits are 2 ppbv for O₃, 0.5 ppbv for NO₂/NO_x and 1 ppbv for SO₂. At YL, continuous measurement of O₃, NO₂ and SO₂ was conducted using an open path differential optical absorption spectroscopy system (OPSIS AB) with detection limits less than 1 ppbv. All the instruments were regularly calibrated, tested, and audited using standards with known traceability (EPD, 2003).

For the VOC sampling, cleaned and evacuated 2-l electro-polished stainless steel canisters were used to collect whole air samples once every 6 days for a year. Therefore, a total of 62 samples were collected at each site, for a total of 248 samples. Each canister was filled to a pressure of 20 ± 2 psi using a sampling system equipped with a bellows pump (Model 910A; Xontech Inc., Van Nuys, California, USA). Each canister sample was collected over a 24-h integrated period. Every 2–3 weeks, the samples were shipped to the University of California at Irvine and analyzed within one to two months from sampling.

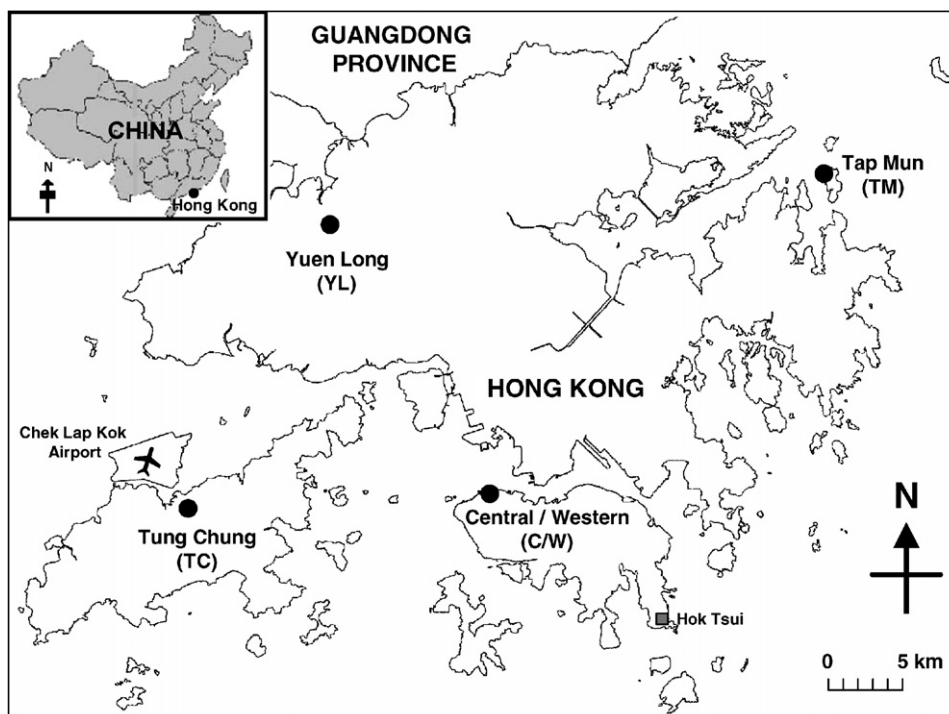


Fig. 1. Locations of the four sampling sites in Hong Kong: Tap Mun (TM, rural), Central/Western (C/W, urban), Tung Chung (TC, sub-urban), and Yuen Long (YL, sub-urban).

CO was quantified from the canister samples by first reducing CO to CH₄, then by analyzing using gas chromatography with a flame ionization detector. The mixing ratios of CH₄ and NMHCs were determined using a combination of gas chromatography with flame ionization detection and mass spectrometric detection. The detection limits are 5 ppbv for CO and 3 pptv for NMHCs (Blake et al., 1996; Colman et al., 2001; Barletta et al., 2002). The measurement accuracy and precision for each compound is listed in Colman et al. (2001).

2.3. The PCA/APCS receptor model

The principal component analysis (PCA)/absolute principal component scores (APCS) receptor model was used to identify and quantify the impact of relevant sources of NMVOCs at the four sites. This was achieved using the software package of SPSS. Details about the PCA/APCS receptor model are given elsewhere (Guo et al., 2004b,c, 2006). Briefly, the receptor model calculates the source profiles and source strengths in absolute concentration units using data measured at the receptor site. The multivariate method is performed by orthogo-

nal transformation with Varimax rotation and the retention of principal components whose eigenvalues are greater than one, followed by multi-linear regression analysis. While factor loadings indicate the correlations of each pollutant species with each factor and are related to the source emission composition, factor scores are related to the source contributions (Thurston and Spengler, 1985). The main limitations of multivariate techniques are that they can only identify 5–8 sources and that the dataset must contain a large number of samples, usually no less than 50 (Thurston and Spengler, 1985). Obtaining reliable results also requires the analysis of a variety of NMVOCs, including known source tracers for each major source. When the receptor model is used, the sampled air is assumed to be well mixed, with species from different sources, and the species are relatively stable during the transport from the emission sources to the receptor site. Instances where the receptor model did not appear to correctly attribute individual NMVOCs to specific sources are discussed where appropriate below. A detailed description of the PCA/APCS model is provided in Guo et al. (2006).

3. Results and discussion

3.1. Overall description: spatial/seasonal patterns in Hong Kong and inter-city comparison of VOCs

Table 1 shows the average values and 95% confidence intervals of O₃, SO₂, NO₂, CO, CH₄ and major NMHCs during the measurement campaign. The confidence intervals are used since it has statistical power to make multi-comparisons. As expected, the average levels of all VOCs at YL were the highest except isoprene, while the average levels of all VOCs at TM were the lowest except isoprene. The average isoprene level at TM was the highest due to the biogenic emissions. The average VOC levels at TC and C/W were similar except butanes, and in between the two extremes of TM and YL. The highest VOC average levels at YL are likely attributed to strong local urban activities and regional pollutants from the rapidly developing

PRD industrial region, especially under the prevailing northwesterly wind during the seasonally high pollution period (see Section 2.1). C/W and TC are typical urban and suburban areas, respectively, and their ambient VOC levels represent the general VOC patterns in Hong Kong. The comparable VOC levels at TC and C/W suggest an insignificant VOC contribution to TC from the nearby aircraft activities. TM is a rural area without major anthropogenic sources and appears to be less strongly influenced by PRD pollution. As a result, TM generally has the lowest VOC levels compared to the other sites.

Though TM is less strongly influenced by air pollution from the PRD and the levels of all anthropogenic VOCs were low, it had the highest O₃ level, which is attributed to regional chemical and transport processes (So and Wang, 2003). The formation of O₃ is a complicated process involving a series of photochemical reactions among VOCs and

Table 1
Statistics of trace gases and selected VOCs measured from September 2002 to August 2003 at the four sites in Hong Kong

	TM		C/W		TC		YL	
	Average	95% confidence interval	Average	95% confidence interval	Average	95% confidence interval	Average	95% confidence interval
Continuously measured trace gases								
O ₃ (ppbv)	31.6	3.6	20.0	3.0	20.1	2.9	15.3	2.2
SO ₂ (ppbv)	4.3	0.1	6.4	1.1	5.5	1.3	6.2	1.2
NO ₂ (ppbv)	6.7	0.5	24.8	2.9	21.1	3.3	29.1	3.0
Canisters samples of CO and VOC (pptv, unless otherwise stated)								
CO (ppbv)	310	40	376	43	351	53	511	59
CH ₄ (ppmv)	1.888	0.019	1.925	0.025	1.901	0.030	2.024	0.044
Ethane	1787	271	1829	263	1724	274	2116	300
Propane	861	142	1595	218	1196	266	2545	398
<i>i</i> -butane	341	57	899	98	502	102	1461	184
<i>n</i> -butane	592	96	1464	160	951	212	2625	356
<i>i</i> -pentane	369	51	519	62	450	91	1143	141
<i>n</i> -pentane	172	26	250	32	230	49	541	76
Ethene	859	143	1465	195	1297	259	2674	352
Propene	141	21	315	36	246	41	606	75
<i>i</i> -butene	114	22	173	26	140	28	344	35
1-butene	52	7	92	11	75	14	193	24
Isoprene	334	81	178	46	148	30	192	24
1,3-butadiene	19	3	48	6	38	7	106	13
Ethyne	1365	234	1950	279	1768	354	2872	460
Benzene	402	72	417	70	464	101	731	119
Toluene	1033	239	2765	421	2265	689	4340	871
<i>o</i> -xylene	57	15	222	39	163	50	306	61
<i>m</i> -xylene	95	26	445	87	311	108	590	130
<i>p</i> -xylene	62	18	258	46	178	54	340	70
Ethylbenzene	123	33	395	87	346	121	545	127

NO_x. In general, air masses in rural areas are more aged than that in urban areas, which leads to less titration of O₃ and more reaction time among VOCs and NO_x for the generation of O₃. Additionally, elevated levels of highly reactive biogenic species (i.e. isoprene) in rural areas make significant contributions to O₃ formation as compared to anthropogenic VOCs.

The seasonal variations of air pollutants in Hong Kong are greatly affected by the Asian monsoons, which bring in clean maritime air and unstable weather in summer and pollutant-laden continental air in winter (Chan et al., 1998). Fig. 2 shows the monthly mixing ratio of toluene at the four sites. Analysis of variance with post-hoc multiple comparisons showed that the winter levels of toluene at C/W, YL and TC were significantly higher than the summer levels at these sites, respectively ($p < 0.05$), indicating strong local/regional sources of toluene during winter months at urban and suburban sites. However, there was no significant difference among various seasons at TM ($p > 0.05$). Considering that there is more photochemical consumption of toluene in summer due to a higher abundance of the hydroxyl radical (OH), the constant toluene

concentrations at TM indicate higher toluene emissions in summer at this rural site. This is likely related to higher evaporation of fossil fuel in summertime. However, the exact reason for this needs more investigation. Other measured hydrocarbons such as ethane, ethyne and benzene had the same seasonal trends as toluene at urban and suburban sites (not shown here). The above seasonal patterns of toluene and other VOCs are consistent with those from other studies at urban sites in Hong Kong (e.g., So and Wang, 2003, 2004; Guo et al., 2004a, Wang et al., 2005). For example, So and Wang (2004) studied NMHCs collected from November 2000 to October 2001 at four sites in Hong Kong and found that all sites had the lowest NMHCs levels in summer and the highest NMHCs levels in winter/autumn.

Fig. 3 shows the monthly variations of isoprene at the four sites. In contrast to toluene and other VOCs, the average isoprene level was the highest at TM during the summertime. This is explained by the significant biogenic sources of isoprene in the rural area. The higher temperatures during summer also accelerated the biogenic emissions and gave higher isoprene levels. As noted above, OH

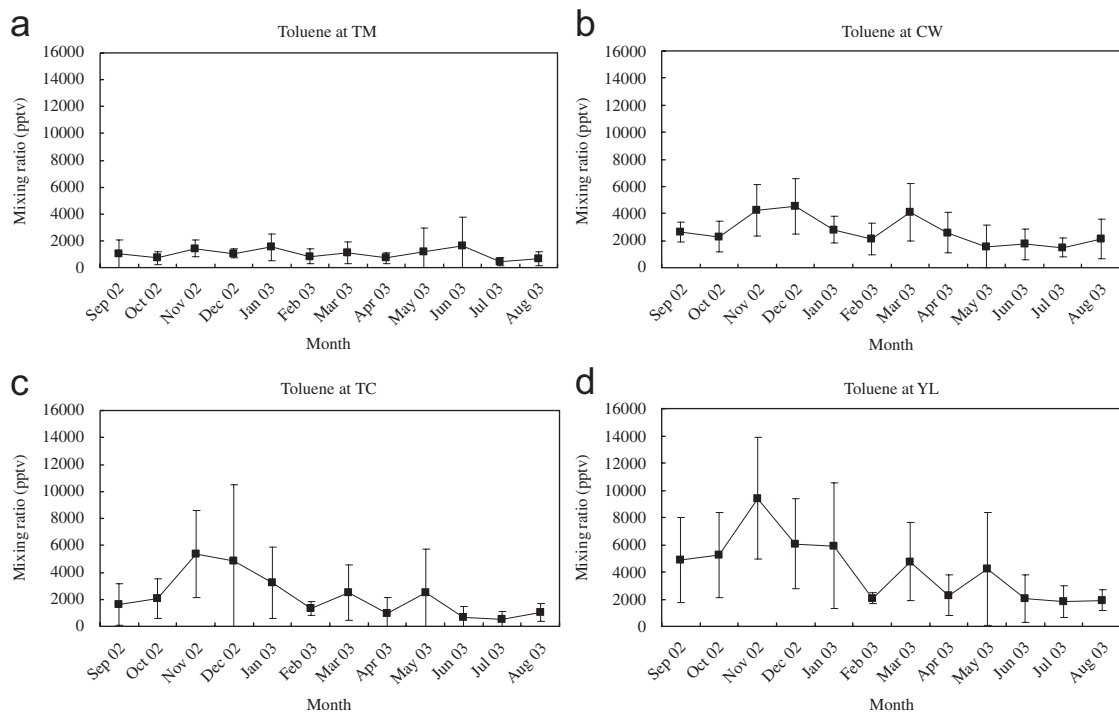


Fig. 2. Monthly average mixing ratios (with standard deviations) of toluene from September 2002 to August 2003 at the four sites in Hong Kong.

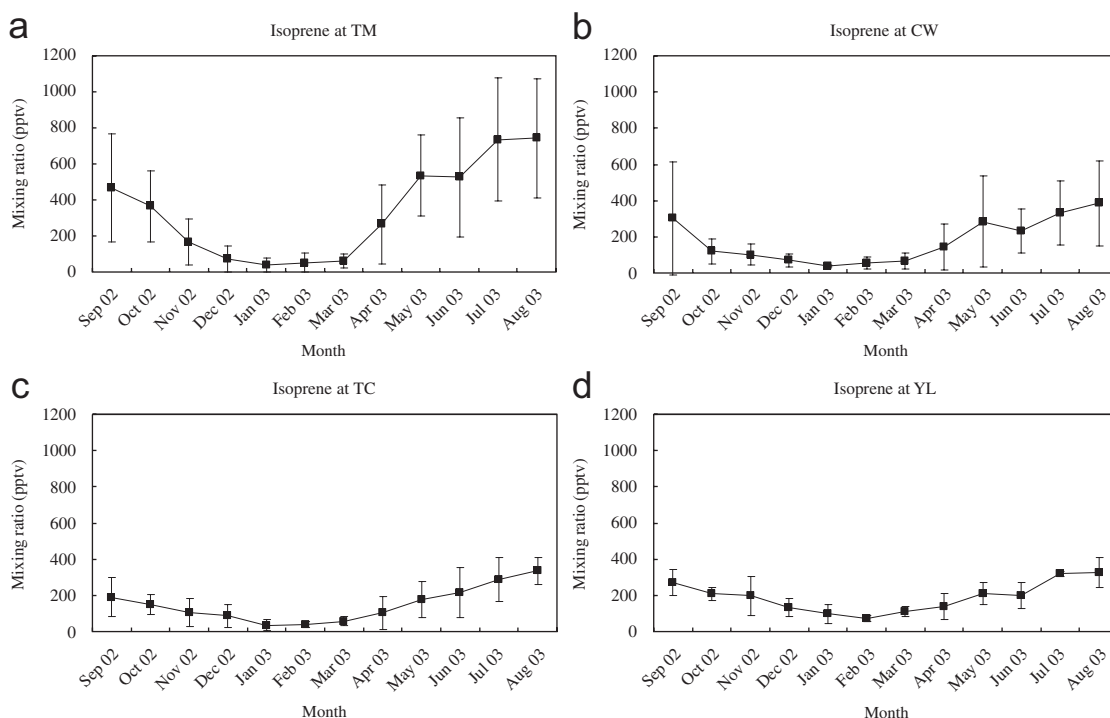


Fig. 3. Monthly average mixing ratios (with standard deviations) of isoprene from September 2002 to August 2003 at the four sites in Hong Kong.

concentrations are higher in summer than in winter, which would lead to more consumption of isoprene and toluene during summer months. Therefore, the seasonal variation of the sources is overwhelming this effect.

Table 2 shows the mixing ratios of 17 key VOCs measured in winter (December 2002–February 2003) and summer (June–August 2003) during this study (using the average levels of the three urban/sub-urban sites) and observed in other overseas cities. Sampling periods and standard deviations of the VOC data from different studies are also provided in Table 2, if available. It should be noted that the VOC levels in different cities are related to factors including sampling season, sampling duration, sampling location, meteorological conditions, site topography, and sampling methods. Bearing these factors in mind, both the winter and summer VOC levels in Hong Kong were on the lower side together with summertime values in cities like Athens and Lille, though the winter VOC levels were significantly higher than the summer values in Hong Kong. By comparison, Karachi, Kathmandu, Mexico City and Santiago had much higher levels for wintertime samples (because Santiago is in the

Southern Hemisphere, the June sampling corresponds to the local winter). For example, the winter average concentration of benzene (0.8 ± 0.2 ppbv) in Hong Kong was much less than the regulatory limit of $10 \mu\text{g m}^{-3}$ (3.1 ppbv) implemented in several countries, whereas the mean levels measured in Karachi, Mexico City and Santiago (4.6–6.0 ppbv) all exceeded the limit (Barletta et al., 2002).

It should be emphasized that the VOC levels measured in this study were listed as winter and summer data in Table 2 so that comparison between Hong Kong and other cities could be made, because in some cities (i.e., Karachi, Kathmandu, Mexico City and Santiago) the VOCs were measured only in winter. Since the meteorological conditions in Hong Kong are significantly affected by Asian monsoon circulation, the clean maritime inflow air in summer dilutes (reduces) the VOC levels in Hong Kong significantly, which is likely the reason for low annually averaged VOC levels in Hong Kong. However, in winter, the VOC levels in Hong Kong are significantly influenced by the polluted continental outflow from southern China and PRD (Wang et al., 2005). Thus, elevated VOC levels were usually observed in winter as shown in Table 2.

Table 2
Comparison of selected hydrocarbons measured in Hong Kong (average of three urban/sub-urban sites) and in other cities

Compound	Hong Kong, China (This study) (Dec. 2002–Feb. 2003, winter)	Hong Kong, China (This study) (June–Aug. 2003, summer)	Karachi ^a , Pakistan (Dec. 1998–Jan. 1999, winter)	Kathmandu ^b , Nepal (Nov. 1998, winter)	Ahmedabad ^c , India (Year 2002)	Taipei ^d , Taiwan (Jan. 1997, winter)	Seoul ^e , Korea (Aug. 1998–July 1999)	Mexico City ^f , Mexico (Feb. 1993, winter)	Santiago ^g , Chile (June 1996, winter)	Athens ^h , Greece (June 1993, May 1994 and Jul 1994, summer)	Copenhagen ⁱ , Denmark (Feb. 1994–Mar. 1995)	Lille ^j , France (July 99–June 2000)	London ^k , UK (Year 1996)
CH ₄ (ppmv)	2.0±0.1	2.0±0.1	6.3±4.7		1.9±±0.4			2.6	2.2				
Ethane	2.8±0.3	1.0±0.2	93±84	7.7	3.7±3.7	8.3	3.8	14	9.4		3.6	4.0	4.2
Propane	2.7±0.9	1.1±0.5	41±35	6.0	4.4±2.9	6.4	7.8	158	137.5	1.2	1.6	1.8	2.0
<i>n</i> -butane	2.2±1.0	1.3±0.7	19.8±16.9	42.2	2.8±2.4	5.2	3.4	70.4	27.0	2.1	6.5	1.6	3.2
<i>n</i> -pentane	0.5±0.2	0.2±0.1	13.4±13.9	24.8	0.6±0.6	4.3	1.3	14.4	6.6	4.2	2.4	0.5	0.6
Ethene	2.6±1.0	1.2±0.6	19.0±17.0	48.4	2.9±2.7	14.1	5.9	21.6	29.4		10.4	2.7	3.4
Propene	0.5±0.2	0.3±0.2	5.5±5.3	12.8	1.0±0.9	4.6	1.8	5	8.0	3.9	2.6	0.7	1.4
<i>i</i> -butene	0.3±0.1	0.20±0.09	1.2±1.1			2.7		1.8	2.8				
1-butene	0.10±0.07	0.10±0.06	1.1±1.2	2.5		0.9	0.5	2.1	2.4			0.2	0.2
Isoprene	0.09±0.04	0.30±0.03	0.8±1.1	0.3			0.3	0.1	0.5			0.05	0.1
1,3-butadiene	0.09±0.04	0.05±0.03	0.8±0.8						1.5			0.1	
Ethyne	3.3±0.9	1.3±0.4	18.0±16.2	36.0	2.1±1.9	15.1	3.4	31.6	25.9			1.5	4.6
Benzene	0.8±0.2	0.3±0.2	5.2±4.5				1.0	4.6	6.0	5.0	6.2	0.8	1.1
Toluene	4.3±1.3	2.2±0.9	7.1±7.6				6.4	21	21.8	14.3	13.5	2.3	2.2
<i>o</i> -xylene	0.3±0.1	0.20±0.06	1.1±1.0				0.8		3.8	3.7		0.3	0.4
<i>m</i> -xylene	0.6±0.2	0.3±0.1	2.1±2.0						7.0				
<i>p</i> -xylene	0.3±0.1	0.20±0.07	1.0±0.9						3.3				

Units are in ppbv unless otherwise specified.

^aBarletta et al. (2002).

^bSharma et al. (2000).

^cSahu and Lal (2006).

^dDing and Wang (1998).

^eNa and Kim (2001).

^fBlake and Rowland (1995).

^gChen et al. (2001).

^hMoschonas and Glavas (1996).

ⁱHansen and Palmgren (1996).

^jBorbon et al. (2002).

^kDerwent et al. (2000).

Table 3

Hydrocarbon reactivities: rate coefficients^{a,b} (at 298 K) with OH radicals (k_{OH}) and O_3 (k_{O_3}), and the corresponding lifetimes in the troposphere (Warneck, 2000)

Hydrocarbon	$k_{\text{OH}} \times 10^{12}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)	$k_{\text{O}_3} \times 10^{12}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)	Lifetime (days)
Ethane	0.26	a	56
Ethene	8.52	0.16	1.4
Propane	1.15	a	12
Benzene	1.23	a	12
Toluene	6.0	a	2.4
<i>m</i> -xylene	23.6	a	0.6
<i>p</i> -xylene	14.3	a	1.0
Ethylbenzene	7.1	a	2.0

^aRate coefficients for these reactions are less than $1 \times 10^{12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

^bRate coefficients from Atkinson (1994).

In addition to the wintertime sampling in Karachi and Kathmandu, when there is generally weaker sunlight, less vertical dilution and perhaps more source emissions, the high VOC levels in these cities were related to sampling location. For instance, the sampling sites in Karachi were close to the roadsides and one of the sites in Kathmandu was at the roadside. This would significantly enhance the levels of VOC species emitted from vehicular exhaust.

3.2. Atmospheric processing of air masses impacting Hong Kong

3.2.1. VOC ratios

To gain insight into the nature of VOCs impacting the different sites, we examine the ratios of VOCs with different photochemical lifetimes (or reactivities) against OH as a measure of the so-called “photochemical age” (Nelson and Quigley, 1983). Using the ratio of a more reactive hydrocarbon to a less reactive hydrocarbon, a higher ratio indicates relatively little photochemical processing of the air mass and major impact from local emissions. On the other hand, a lower ratio is reflective of more aged VOC mixes and thus presumably that the VOCs were emitted from more distant sources. Comparisons of the ratios among sites can be used to estimate the relative ages of air parcels and help provide evidence of transport histories. Moreover, this ratio analysis can further indicate whether the site is dominantly affected by pollutants from local or regional sources.

In this study, we compared the ratios of propane/ethane, ethene/ethane, *m,p*-xylene/ethylbenzene and toluene/benzene at the four sites as a measure of atmospheric processing in different air masses

(Nelson and Quigley, 1983; Smyth et al., 1999; So and Wang, 2004). The photochemical properties and atmospheric lifetimes for the eight hydrocarbons are listed in Table 3. As expected, TM had the lowest ratios among the four sites, characteristic of a rural site with more influence from photochemically aged air masses (Fig. 4a–d). The average value of propane/ethane at the rural TM site (0.50 ± 0.25 pptv/pptv) is close to the value of 0.47 pptv/pptv measured at the rural Linan site in eastern China (Wang et al., 2002), but is much higher than the ratio of 0.1 pptv/pptv for several day-old combustion emissions (Talbot et al., 1996). The YL site gives the highest average ratios of propane/ethane and ethene/ethane, suggesting the presence of a local source of C_2 – C_3 hydrocarbons (Fig. 4a,b). By comparison, the highest average aromatic ratios were observed at C/W (Fig. 4c,d), suggesting an important source of fuel and/or solvent usage in this urban site (see Section 3.3). These findings reveal the contributions of various sources and indicate different mixes of VOCs among the sites. In particular, toluene has previously been found to be the most abundant NMVOC in Hong Kong as a result of local use of toluene-rich fuels and solvents (Guo et al., 2006), which explains the relatively high toluene/benzene ratio at the urban C/W site.

3.2.2. Hydrocarbons versus CO

CO is generally emitted from incomplete combustion of fossil fuel in urban areas. Examining the relationship between CO and VOCs can provide useful information on their sources and emission signatures (Wang et al., 2002, 2003). For example, scatter plots of CO versus ethyne show very different

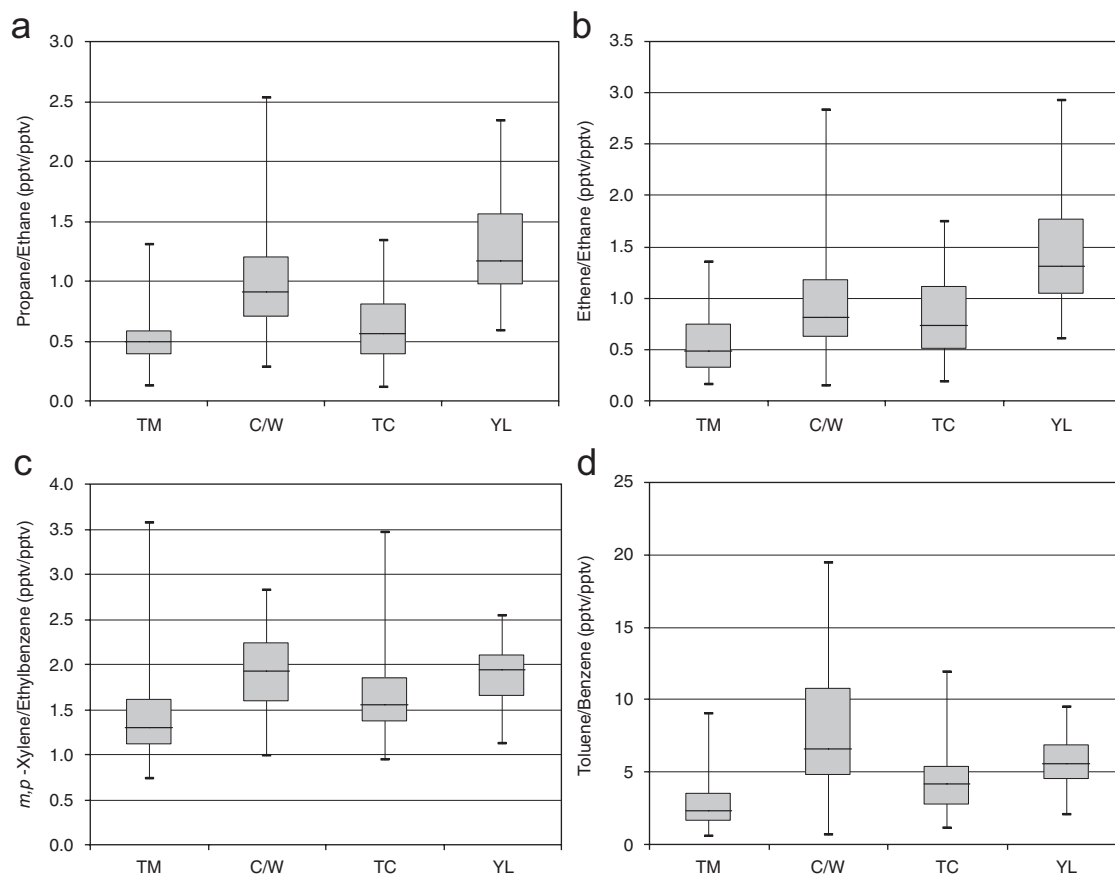


Fig. 4. Box plots of (a) propane/ethane; (b) ethene/ethane; (c) *m,p*-xylene/ethylbenzene; and (d) toluene/benzene ratios from September 2002 to August 2003 at the four sites. Whiskers indicate the minimum and maximum values and boxes indicate the 25th–75th percentile range, with a line to indicate the median.

emission patterns from plots of CO versus isoprene (Fig. 5). Among the hydrocarbons measured, ethyne was best correlated with CO (R^2 ranging from 0.91 to 0.93), confirming a common source origin in greater Hong Kong. The ethyne/CO ratios range from 5.6 pptv/ppbv in TM to 7.5 pptv/ppbv at YL (see Fig. 5a), indicating more fresh air masses at YL. The ratio at the rural TM site is close to that measured at a remote southeastern coastal site in Hong Kong (5.3 pptv/ppbv at Hok Tsui, see Fig. 1), suggesting a background ratio of 5.3–5.6 in Hong Kong (Wang et al., 2003). This relatively large background ratio shows the presence of fresh combustion emissions throughout the greater Hong Kong area. The ratio is significantly larger than the ratio of 2.1 pptv/ppbv based on airborne results during the SOS 1995 Nashville Study (Goldan et al., 2000).

Isoprene is known to be emitted from biogenic sources (e.g., Jobson et al., 1994) but there are also

studies of the contribution of isoprene from vehicular exhaust (e.g., Borbon et al., 2001; Barletta et al., 2002). Here, the poor correlation between isoprene and CO suggests that isoprene is emitted from sources other than mobile emissions at the four sites. From Section 3.1, the highest isoprene levels at the rural TM site reflect the influence of biogenic emissions.

3.3. Source apportionment of VOCs in Hong Kong

3.3.1. Source identification

We performed a PCA/APCS analysis on the measurement data to identify the sources of VOCs at different sites. Before applying PCA to the datasets, sensitivity tests were conducted (Guo et al., 2004b, c, 2006). In general, suspected outliers were taken out from the dataset one at a time until a stable PCA solution was achieved, in the sense that

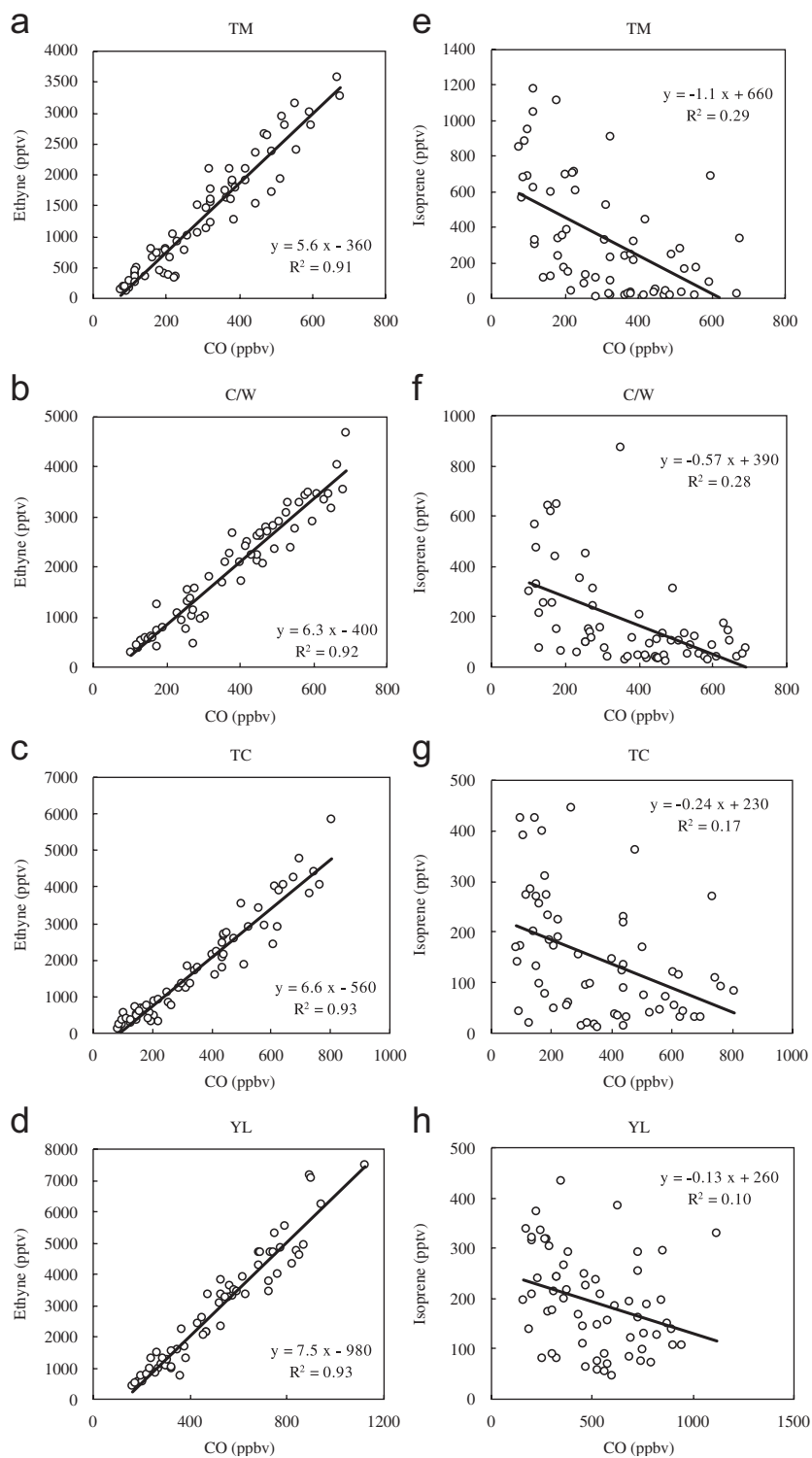


Fig. 5. Scatter plots of CO with ethyne (a–d) and isoprene (e–h) from September 2002 to August 2003 at the four sites in Hong Kong.

the random exclusion of further samples had very little effect on the solution and on the interpretation of the principal components as compared to actual physical/chemical sources. No outliers were found at YL, but 4, 9 and 13 samples at C/W, TC and TM, respectively, were removed prior to PCA/APCS analysis. In addition, CO and 21 VOCs were selected for the analysis since they are the most abundant parameters and are typical tracers of various emission sources.

Whereas only two factors were extracted at YL, four factors were extracted at each of the other three sites (see Table 4). From Table 4a, at TM the first factor (*F1*) is associated with solvent usage, as BTX and trimethylbenzenes are all main components of solvent usage (Borbon et al., 2002). *F1* is also associated with liquefied petroleum gas (LPG) usage, as indicated by the moderate butane loadings. It is interesting that propene rather than propane had a correlation with *F1* as well, possibly due to the fact that propene is a by-product of LPG burning. High factor loadings of CO, ethane, ethene, ethyne and benzene are found in the second factor (*F2*). These are all species emitted from combustion sources, i.e. vehicular exhaust in urban areas and biomass/biofuel burning in rural areas. This site is downwind of a rural area of the eastern China coast where biomass/biofuel burning is a common activity in autumn/winter seasons. Thus, impact from biomass/biofuel burning sources cannot be excluded. Propane is also associated with *F2*, and may indicate natural gas (consistent with the high loading of ethane on this factor) or possibly LPG influence. Propene and the butenes are highly correlated with the third factor (*F3*), indicating the contribution of industrial sources as these gases are widely used by industries for making organic chemicals (Tiscali, 2004). In the last factor (*F4*), moderate factor loadings of butanes and high loadings of pentanes represent gasoline evaporation.

At C/W, high factor loadings of TEX and trimethylbenzenes in *F1* indicate solvent usage (Table 4b). The pollutants associated with *F2* are predominantly of vehicular origins due to high factor loadings of vehicular tracers like CO, ethene, ethyne and propene (Nelson and Quigley, 1984; Wadden et al., 1986), and gasoline evaporation due to high loadings of butanes and pentanes. In *F3*, ethane, ethene, ethyne and benzene correlate well with the combustion tracer of CO. Apart from vehicular emissions, these species are also emitted

from oil/coal burning. High factor loadings of C_3 – C_4 alkenes in *F4* represent industrial sources.

At the TC site, high factor loadings of CO, ethene, ethyne and BTEX indicate vehicular emissions for *F1* (Table 4c). It should be noted that BTEX can be emitted from either vehicular exhaust or solvent use, and this can be evaluated using their correlation with the combustion tracer CO. In *F2*, propene, 1-butene and *i*-butene correlate well with *i*-pentane which is a known tracer of gasoline evaporation (Morikawa et al., 1998), indicating the co-location of industrial sources and gasoline evaporation. The high factor loadings of trimethylbenzenes in *F3* indicate solvent usage (Borbon et al., 2002) and the anti-correlation of isoprene with *F4* represents biogenic emissions.

Two factors were extracted at YL (Table 4d). *F1* has a poor correlation with the combustion tracers CO and ethyne, indicating its insignificant relation to vehicular emissions. In contrast, solvent usage is indicated by the high factor loadings of TEX and trimethylbenzenes in *F1*. *F1* is also correlated with VOCs from gasoline evaporation such as butanes and pentanes. Since propene and butenes are often used to make organic chemicals, *F1* is also associated with industrial sources. The VOCs associated with *F2* are predominantly of vehicular origin because vehicular tracers such as CO, ethene, ethyne and BTEX have high factor loadings in *F2*.

3.3.2. Source apportionment

Having identified the major sources of NMVOCs, we applied the receptor model to the extracted factors (from Table 4) to quantify the relative contributions of major sources to atmospheric NMVOCs at the four sites. Fig. 6 shows the mass contribution of each source (percentage in $\mu\text{g m}^{-3}$) to the total NMVOCs at the four sites. It is noteworthy that for factors containing more than one source, the tracers for a source were assumed to be exclusively emitted from this specific source and their contributions were assigned to this source. For the three urban/sub-urban sites, vehicular emissions were the dominant source, accounting for $50 \pm 28\%$ (average \pm standard deviation) at YL, $53 \pm 41\%$ at TC and $65 \pm 36\%$ at CW of the total NMVOCs. This is consistent with the fact that vehicular emission is the major source of VOCs in Hong Kong. In 2003, there were over 614,067 vehicles registered in Hong Kong, about 17% increase as compared to 2002 (TD, 2004). On the other hand, the road traffic density of Hong Kong is among the

Table 4
PCA results for CO and 21 NMVOCs measured from September 2002 to August 2003 at TM (4a), C/W (4b), TC (4c) and YL (4d)

	<i>F1</i>	<i>F2</i>	<i>F3</i>	<i>F4</i>
(a) TM				
CO		0.86		
Ethane		0.96		
Ethene		0.80		
Ethyne		0.93		
Propane		0.88		
Propene	0.57		0.70	
<i>i</i> -butane	0.53			0.55
<i>n</i> -butane	0.59			0.57
1-butene			0.84	
<i>i</i> -butene			0.80	
<i>i</i> -pentane				0.72
<i>n</i> -pentane				0.77
Isoprene		−0.65		
Benzene		0.86		
Toluene	0.76			
Ethylbenzene	0.88			
<i>m</i> -xylene	0.89			
<i>p</i> -xylene	0.88			
<i>o</i> -xylene	0.90			
1,3,5-trimethylbenzene	0.73			
1,2,4-trimethylbenzene	0.81			
1,2,3-trimethylbenzene	0.84			
Sources of VOC	Solvent usage/LPG usage	Combustion sources	Industrial sources	Gasoline evaporation
(b) C/W				
CO		0.46	0.76	
Ethane			0.88	
Ethene		0.69	0.56	
Ethyne		0.53	0.77	
Propane		0.75		
Propene		0.52		0.75
<i>i</i> -butane		0.84		
<i>n</i> -butane		0.89		
1-butene				0.84
<i>i</i> -butene				0.92
<i>i</i> -pentane		0.87		
<i>n</i> -pentane		0.83		
Isoprene			−0.70	
Benzene			0.81	
Toluene	0.64	0.57		
Ethylbenzene	0.84			
<i>m</i> -xylene	0.87			
<i>p</i> -xylene	0.85			
<i>o</i> -xylene	0.92			
1,3,5-trimethylbenzene	0.86			
1,2,4-trimethylbenzene	0.83			
1,2,3-trimethylbenzene	0.72			
Sources of VOC	Solvent usage	Vehicle emission and gasoline evaporation	Oil/coal burning	Industrial sources
(c) TC				
CO	0.83			
Ethane	0.62			
Ethene	0.76			
Ethyne	0.82			
Propane	0.72			

Table 4 (continued)

	F1	F2	F3	F4
Propene		0.76		
<i>i</i> -butane	0.70			
<i>n</i> -butane	0.78			
1-butene		0.90		
<i>i</i> -butene		0.91		
<i>i</i> -pentane	0.65	0.66		
<i>n</i> -pentane	0.80			
Isoprene				−0.89
Benzene	0.84			
Toluene	0.91			
Ethylbenzene	0.91			
<i>m</i> -xylene	0.84			
<i>p</i> -xylene	0.88			
<i>o</i> -xylene	0.88			
1,3,5-Trimethylbenzene			0.82	
1,2,4-Trimethylbenzene			0.85	
1,2,3-Trimethylbenzene			0.86	
Sources of VOC	Vehicle emission	Gasoline evaporation/ industrial sources	Solvent usage	Biogenic sources
(d) YL				
CO		0.89		
Ethane		0.91		
Ethene	0.57	0.79		
Ethyne		0.93		
Propane		0.85		
Propene	0.80	0.54		
<i>i</i> -butane	0.68	0.68		
<i>n</i> -butane	0.65	0.72		
1-butene	0.81	0.52		
<i>i</i> -butene	0.87			
<i>i</i> -pentane	0.84			
<i>n</i> -pentane	0.79	0.52		
Isoprene		−0.71		
Benzene		0.83		
Toluene	0.63	0.73		
Ethylbenzene	0.58	0.75		
<i>m</i> -xylene	0.64	0.71		
<i>p</i> -xylene	0.66	0.68		
<i>o</i> -xylene	0.69	0.68		
1,3,5-trimethylbenzene	0.89			
1,2,4-trimethylbenzene	0.90			
1,2,3-trimethylbenzene	0.90			
Sources of VOC	Gasoline evaporation/ solvent usage/industrial emissions	Vehicle emission		

Extraction method: Principal component analysis.

Rotation method: Varimax with Kaiser normalization.

Only factor loadings with an absolute value ≥ 0.50 are listed, except for CO in (b) (0.46 in F2 at C/W).

Only factors with eigenvalue ≥ 1.00 are shown.

highest in the world. The total road length is about only 1900 km, i.e. 275 vehicles km^{−1} (HKEPD, 2006). In addition, about 30% of these vehicles use diesel fuel which is relatively more polluting,

contributing to about 70% of the vehicle mileage in Hong Kong. The relative contribution of vehicular emission to ambient VOCs in urban Hong Kong is comparable to that in Beijing, China, and Santiago,

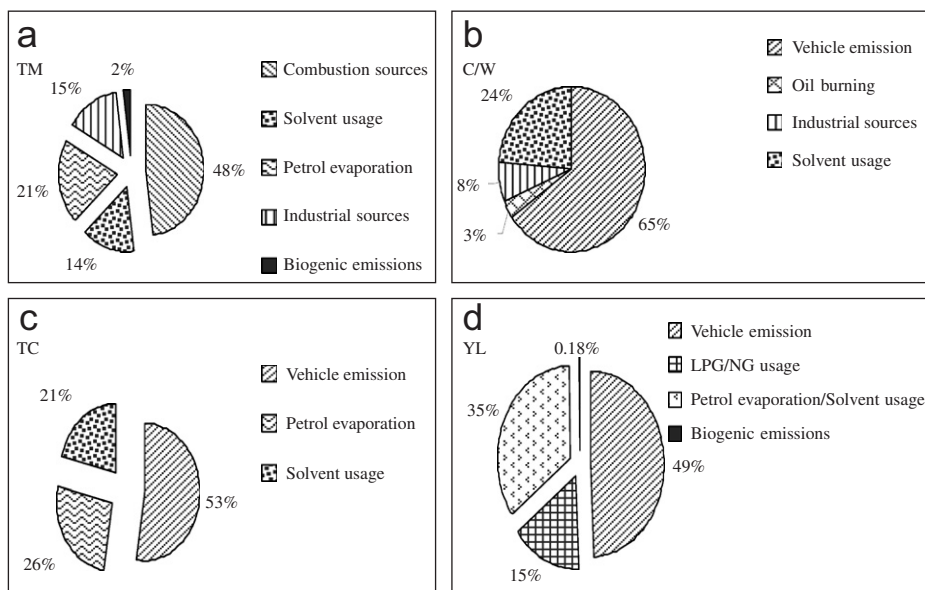


Fig. 6. Source contributions to the total NMVOCs at (a) TM, (b) C/W, (c) TC and (d) YL.

Chile, where the vehicle exhaust contributed on average 57.7% and 40–62%, respectively (Jorquera and Rappenglück, 2004; Liu et al., 2005). The similar contributions in major developing cities indicate the dominance of vehicular emission in urban areas.

Other major sources at the urban/sub-urban sites were gasoline evaporation, solvent usage and industrial emissions. At CW, solvent usage and industrial sources accounted for $24 \pm 16\%$ and $8 \pm 11\%$ of the total NMVOCs, respectively (Fig. 6b). At TC, a combination of gasoline evaporation and industrial sources contributed $26 \pm 32\%$ to the total NMVOCs and solvent usage accounted for the rest ($21 \pm 27\%$) (Fig. 6c). At YL, $35 \pm 14\%$ of the total NMVOCs were attributed to gasoline evaporation and solvent usage, whereas industrial emissions accounted for $15 \pm 14\%$ (Fig. 6d). A quite different profile from that at CW, TC and YL is obtained at the rural site. At TM $48 \pm 30\%$ of the total NMVOCs were due to combustion sources; $21 \pm 19\%$, $15 \pm 14\%$ and $14 \pm 19\%$ were attributed to gasoline evaporation, industrial emissions and solvent usage, respectively (Fig. 6a). In connection with the site characteristics, biogenic emissions also contributed $2 \pm 1\%$ to the ambient NMVOC levels.

It is of interest to compare our source apportionment results in 2001 (Guo et al., 2004b) to those of 2002/2003 (this study) at the same site (C/W) to learn about the possible changes in VOC emissions

during the intervening period. It is worth mentioning that the NMVOCs selected for source apportionment analysis in these two studies are similar, and that the total NMVOC levels changed little over the period ($43 \pm 19 \mu\text{g}/\text{m}^3$ in 2001 vs. $40 \pm 18 \mu\text{g}/\text{m}^3$ in 2002/2003). Bearing in mind the uncertainties associated with these calculations, the results indicate that there has likely been a change of emission sources at C/W during these years. In 2001, about 40% of the ambient NMVOCs came from vehicular emissions and 35% from solvent usage. By comparison, the contribution of vehicular emissions increased to 65% while solvent usage decreased to 25% in 2002/2003. In addition, 20% of NMVOCs were attributed to LPG/natural gas leakage in 2001 whereas no such activity was found in 2002/2003. The contribution of industrial emissions does not show any change (6% in 2001 versus 8% in 2002/2003). The increase in the vehicular fraction could be attributed to the reduction of solvent usage and significant control of LPG or natural gas leakage in 2002/2003. The comparison reveals that there are no obvious changes in major source types at the site but their relative contributions appear to be changing because of the implementation of relevant VOCs control programmes.

It is noteworthy to discuss the potential uncertainty in estimation of the contribution of sources to NMVOCs. Sampling strategies may affect the

source apportionment, as the results of any PCA depend on the averaging time period taken for the basic data elements, the number of pollutants and data points included (Derwent et al., 1995). Choice of particular sampling time, sampling duration and sampling frequency may emphasize or exclude specific emission sources (Derwent et al., 1995). In this study, 24-h integrated samples were taken which minimized the uncertainty of source apportionment. Moreover, the samples were taken regularly (per sample every 6 days), which would also reduce the bias caused by sampling.

Under certain circumstances, the receptor model itself may generate uncertainty in the source apportionment. The model may not be able to separate sources that are strongly correlated, such as the gasoline evaporation was co-located with solvent usage at TC site (Table 4c). Uncertainty may also be generated if the collected air samples are not well mixed with species from different sources. To maximize the representativeness of air samples, we took well-mixed 24-h integrated samples on individual sampling days. In addition, some very short-lived species such as isoprene could hamper the model since they may be lost in photochemical reactions during the transport to the receptor site. In this study, most NMVOCs selected for source apportionment had relatively long lifetimes considering the distance between source regions and the receptor site, and those species with short lifetimes had very low mixing ratios compared to the relatively long-lived species. Thus, we believe the uncertainty caused by the receptor model has been minimized.

4. Summary and conclusions

Selected trace gases and 22 VOCs at four different sites of Hong Kong were measured from September 2002 to August 2003. The VOC levels in Hong Kong were on the low side as compared to other overseas cities. The average VOC levels at suburban YL were the highest, while the average levels at rural TM were the lowest. The elevated VOC levels at YL were mainly attributed to local anthropogenic sources (in particular vehicles and nearby industrial estates) as well as regional influences. Analysis of temporal variations of the selected VOCs indicates that higher VOC levels were observed in wintertime with lower levels during summertime, in response to air circulation patterns driven by the Asian mon-

soons. In contrast, isoprene level was higher at the rural site in summer because of its biogenic sources.

Ratios between VOCs with different photochemical reactivities showed the mix of emission sources and the increase of atmospheric processing from urban to rural areas. Compared to respective results in overseas rural areas, a relatively high ethyne/CO ratio (of 5.6 pptv/ppbv at TM) showed that the subtropical city was influenced by a rather fresh mix of local and regional pollution. The results of the PCA/APCS indicated that anthropogenic sources such as vehicular exhaust, gasoline evaporation, solvent usage and industrial emissions made major contributions to ambient VOC levels at the four sites. This study yielded useful and comprehensive information on the distribution, air mass ages and source apportionment of VOCs in a subtropical Asian city. The results provided a useful reference for the control of VOCs and photochemical pollution in the study region.

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