Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong

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Abstract

Ambient VOCs samples were collected at three locations (PolyU campus (PU), Kwun Tong (KT), Hok Tsui (HT)) in Hong Kong during the periods of November 2000–February 2001 and June 2001–August 2001. Also the concentrations of VOCs in Cross Harbor tunnel in Hong Kong were obtained in order to determine the vehicular sources of VOCs. Toluene was the most abundant VOC detected in Hong Kong. At the PU station, which is close to a main road, the concentrations of most VOCs were higher in summer than in winter. However, at the background location HT, the concentrations of all VOCs except tetrachloroethene were higher in winter than in summer. Regional physical dispersion/transportation and mixing depth may be the reasons for higher VOC concentrations in winter at HT. The BTEX (benzene:toluene:ethylbenzene:xylene) ratios of PU and KT during winter period were (1.9:10.1:1.0:1.8) and (1.9:10.4:1.0:1.5), and (0.9:8.3:1.0:2.2) and (0.8:29.6:1.0:1.8) for summer season, respectively. The xylene/ethylbenzene (X/E) ratio was used to assess the relative age of the air parcels in this study. The concentrations of VOCs in the atmosphere in Hong Kong were mainly affected by direct emissions from vehicles, evaporation of fuels, photochemical reactions and few industrial emissions. The BTEX ratio in the tunnel was 2:10.4:1:3.2. The BTEX ratios at PU and KT during the winter period were similar to that in tunnel (except for xylenes). The X/E ratio in the tunnel was higher than that in the ambient air. This indicated that the freshly emitted xylenes in the tunnel decayed at different rates from OH-oxidation in the atmosphere. Good BTEX correlations ($r >$ 0.8) were found at PU and KT in winter (**$P < 0.01$). Vehicular exhaust was the dominant source at PU and KT stations, and less evaporation of fuel or additive occurred at low temperature in winter. Diurnal variations of mean BTEX concentrations at the roadside monitoring station (PU) showed two peaks associated with traffic density and vehicle type.
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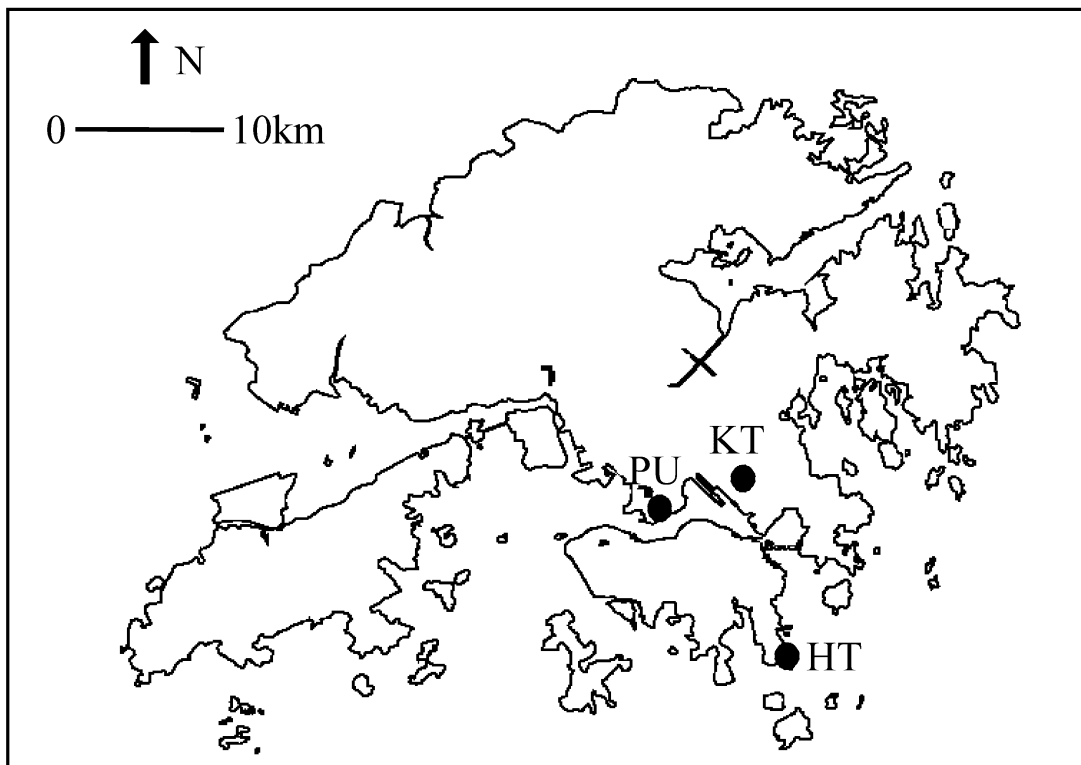*E-mail address:* ceslee@polyu.edu.hk (S.C. Lee).

Fig. 1. Sampling sites in Hong Kong.

1. Introduction

Hong Kong is a densely populated city. In 2001, there were 6.76 million people crowded into 1098.04 km^2 of land, resulting in an average density of 6156 people per square kilometre (The Census and Statistics Department of Hong Kong, 2001). Large amounts of air pollutants are released from both mobile and stationary sources everyday. The main VOC sources in Hong Kong are motor vehicle exhausts. There were 525 000 registered vehicles on 1904 km of roads in 2001 (The Census and Statistics Department of Hong Kong, 2001). The result of the heavy traffic in Hong Kong is poor air quality. Other than those traditional air pollutants such as carbon monoxide, sulphur dioxide, oxide of nitrogen, ozone and particulates, the toxic air pollutants (TAPs) have become of increasing concern in the past few decades due to their adverse impacts on human health. VOCs are one of the major groups of TAPs.

Many researches (Chan et al., 2002; Lee et al., 2002; Barletta et al., 2002; Mohamed et al., 2002) have focused on the urban levels of VOCs, especially aromatic and chlorinated organic compounds, due to the known and suspected carcinogenic nature of these species (Hanson, 1996). However, VOCs play an important role in the formation of ground-level ozone and photochemical oxidants associated with urban smog (Monod et al., 2001). One study showed that the toluene concentration in Hong Kong was relatively higher than that in other cities (Chan et al., 2002). Most VOCs identified in Hong Kong were mainly emitted from motor vehicles and gasoline evaporation.

Some of the VOC species are commonly used as indicators of the age of the air mass and tracers

for emission sources (Hsieh and Tsai, 2003). Nelson and Quigley (1984) used the ratio between ($m+p$)-xylene and ethylbenzene (X/E) to investigate the extent of photochemical reactivity in the atmosphere. The calculated lifetimes of ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene are 1.6 days, 11.8 h, 19.4 h and 20.3 h, respectively (Atkinson 1994; Monod et al., 2001) (assuming [OH] $= 10^6$ rad cm^{-3}). The relatively longer lifetime of benzene indicated that it has lower reactivity or is more stable in the atmosphere (Hsieh and Tsai, 2003). Xylenes are considered a more reactive species while ethylbenzene is considered a less-reactive species. A lower X/E ratio implies an aged air parcel (Hsieh and Tsai, 2003). Monod et al. (2001) showed that the X/E ratio was a useful tool to estimate the photochemical age of the air mass. Samples collected from the ambient air are difficult to differentiate between different pollution sources, and thus it is difficult to predict the true impacts of different emission sources. Few studies regarding motor emissions in tunnels have been published in Asian cities to investigate the characteristics of vehicle emissions (Chiang et al., 1996; Na et al., 2002; Hwa et al., 2002). Chiang et al. (1996) characterized different pollutants in the air of a roadway tunnel in Taiwan and established base-line information on vehicle exhausts. The study showed that the age of vehicle exhaust, temperature and the composition of fuel used by vehicles could affect the pollutants emitted. In the VOC measurements, the average BTEX ratio obtained inside the tunnel was 3:5:1:4.

Liu Chunming et al., 2000 presented the first available data and temporal variation of VOCs in Changchun, China. It showed that the VOC concentrations were not only affected by traffic volume and meteorological factors such as wind direction, but also by the emissions from other sources. Diurnal variations of total VOCs displayed two peaks (08:00–10:00 and 15:00–17:00 h) in traffic peak hours, indicating the effect of traffic volume; and the diurnal variations of total VOCs displayed a single peak in the industrial area, showing the effect of other emission sources.

The study reported here focused on the investigation and interpretation of seasonal variations of VOCs at three sampling locations (roadside, mixed urban and rural area). Diurnal variations of VOCs at the roadside environment were observed and finally vehicular emissions collected in a tunnel were used to determine their impact on the atmosphere of Hong Kong.

2. Methods

2.1. Sampling and analysis

2.1.1. Sampling

The climate in Hong Kong is sub-tropical and the seasons of autumn and spring are usually short. Therefore the winter season we defined includes November, December, January and February, while the summer season includes May, June, July and August. Strong monsoon wind and dry weather characterize winter seasons. In the summer, it is hot and humid with occasional showers and thunderstorms. The prevailing winds in Hong Kong are mainly north-easterly especially in winter time.

Sites were selected for VOC monitoring according to their different landuse categories, populations and traffic densities. Three sampling locations (PolyU campus, Kwun Tong and Hok Tsui) were chosen to represent the areas of urban traffic, industrial and commercial mixed, and rural background, respectively. The three sampling sites were PolyU campus (PU), Kwun Tong (KT) and Hok Tsui (HT), with their locations shown in Fig. 1. VOC samples were collected during the periods of November 2000–February 2001 (winter) and June 2001–August 2001 (summer). Sampling was carried out every 6 days and lasted for 24 h at the PU station, while 10 samples and six samples were collected for 24 h during each period at KT and HT, respectively.

To observe the diurnal variations in VOC concentrations (BTEX), samples were collected at the roadside PolyU station (~ 8 m away from the traffic road) in a 3-h interval from 09:00 to 21:00 h once a week from February 2002–March 2002. In all, nine sets of data were collected. The morning period (09:00–12:00 h) represents the period of high traffic activity with less photochemical reaction. The noon period (12:00–15:00 h) represents the period of high photochemical activity and the time for the most intense vertical

mixing. The afternoon period (15:00–18:00 h) represents another high traffic activity and the later period of photochemical reactions. The evening period (18:00–21:00 h) represents the period after photochemical reaction.

Also 12 grab VOC samples were collected inside the Cross-Harbor Tunnel of Hong Kong during November 2001 for vehicular emission source analysis.

The field descriptions are as follows:

PolyU campus (PU): It is situated at approximately 6 m above ground level, and approximately 8 m away from the main traffic road. The station is adjacent to Hong Chong Road, which leads to the Cross Harbor Tunnel. The traffic volume of the road is extremely high with more than 170 000 vehicles per day. Moreover, the site faces the Victoria Harbor with a strong wind from the sea providing good air dispersion. Thus the VOC levels at the site are mainly influenced by vehicle emission and wind direction.

Kwun Tong (KT): Most industries in Hong Kong, mainly metal and printing industries, are located in this area. They are close to the residential buildings and most of the vehicles are light and heavy goods vehicles. Kwun Tong is one of the Hong Kong Environmental Protection Department (HKEPD) air quality monitoring locations, representing a mixed residential/commercial/industrial area chosen for data comparison. The samples were collected on a 25-m high rooftop.

Hok Tsui (HT): It is situated at the tip of Southern Hong Kong (approximately 20 m above sea level), where the least anthropogenic pollution is expected. This is considered a background monitoring station.

Cross Harbor tunnel: It is a two-bore tunnel with two lanes per bore with a length of approximately 1990 m. The daily patronage of this tunnel was approximately 120 000 during 2000. Under the Road Tunnels (Government) Ordinance and Regulations, the speed limit of the Cross Harbor Tunnel is 70 km/h. Private car and taxi are the major types of vehicle ($>60\%$) that travel through this tunnel (Transport Department, 2002).

2.1.2. Analysis

Pre-cleaned and pre-evacuated 6-l SUMMA stainless steel canisters were used to collect sam-

ples. Flow rates of around 50 ml/min were used for 3-h sampling. All canisters were cleaned using humid zero air with at least five filling/evacuating cycles before sampling to ensure that the concentration of all compounds inside the canister was below 0.02 ppbv. Sampling and analysis of the samples were in accordance with U.S. EPA Compendium Method TO-14A, 1997. VOCs sampled in the canister were concentrated in a NUTECH 3550A cryogenic concentrator and were injected into a HP5890A gas chromatograph coupled to a HP5973 mass-selective detector (GC/MSD). A RESTEK RTX-1 capillary column, 60 m$\times$320 μm$\times$3 μm, was used in this system. The initial temperature was held at -30 °C and immediately raised to 80 °C at 10 °C/min, and then raised from 80 to 220 °C at 5 °C/min and held at 220 °C for 5 min. Most of the VOCs in the ambient samples were below the detection limit of 0.02 ppbv for the 39 compounds monitored. A total of 37 VOC species were identified by this GC/MSD system, and the target VOCs were identified from the mass spectra and quantified by multipoint calibration.

2.1.3. Quality assurance/quality control

The quality assurance and quality control (QA/QC) procedure included laboratory and field blanks, parallel samples and duplicate measurements of samples. Before each sampling with a canister, blank sample (zero air) was analyzed to ensure that the concentration of all compounds inside was below 0.02 ppbv. Parallel samples and duplicate measurements of samples were analyzed to test the precision of the sampling and analytical techniques, respectively. The mean relative standard deviations (R.S.D.) for all the compounds were less than 10%. A new calibration curve was determined each time. The detection limit of each compound was calculated from the data of seven replicate measurements of low concentration samples and observed from their standard deviation. The standard deviation ranged from 1 to 10%. The calibration system used standard gas at nominal concentrations of 1 ppmv in nitrogen to be diluted with nitrogen using Dynamic Dilution Calibrator-Model 700 (Advanced Pollution Instrumentation, Inc.). A dilution factor of 1.902 liter per minute

Table 1
Concentrations of selected VOCs at three stations in Hong Kong (24-h average)

Unit: $\mu g/m^3$	PU winter	PU summer	KT winter	KT summer	HT winter	HT summer
Methyl chloride	2.38 ± 0.70	1.84 ± 0.46	2.84 ± 0.45	1.70 ± 0.31	2.25 ± 0.24	1.27 ± 0.12
Methylene Chloride	2.12 ± 1.58	3.06 ± 2.01	1.94 ± 1.19	2.41 ± 1.14	1.56 ± 1.27	1.08 ± 2.00
Benzene	5.07 ± 2.28	2.97 ± 1.10	4.92 ± 2.01	$1.74 \pm .0.69$	2.07 ± 0.62	0.32 ± 0.17
Carbon tetrachloride	1.00 ± 0.25	0.80 ± 0.14	0.99 ± 0.22	0.89 ± 0.09	0.78 ± 0.05	0.58 ± 0.06
Toluene	26.44 ± 10.71	26.22 ± 8.48	26.42 ± 18.55	64.34 ± 36.77	3.23 ± 2.58	1.05 ± 1.31
Tetrachloroethene	1.31 ± 0.73	0.90 ± 0.48	1.56 ± 2.35	4.10 ± 2.91	ND	0.27 ± 0.33
Ethylbenzene	2.61 ± 1.67	3.18 ± 2.11	2.53 ± 2.34	2.17 ± 0.78	0.24 ± 0.19	ND
m,p-xylene	2.78 ± 1.30	3.99 ± 1.82	2.23 ± 1.76	2.31 ± 0.66	ND	ND
o-xylene	2.03 ± 0.96	3.06 ± 1.99	1.66 ± 1.19	1.61 ± 0.47	ND	ND
1,3,5-trimethylbenzene	0.79 ± 0.49	1.39 ± 2.75	0.40 ± 0.21	0.44 ± 0.10	ND	ND
1,2,4-trimethylbenzene	2.15 ± 0.98	2.59 ± 2.45	1.60 ± 0.79	1.54 ± 0.32	ND	ND

ND non-detectable (below detection limit); $\pm$ S.D.

(LPM) was used and the actual flow of standard gas was approximately 0.1 LPM into a 6 l precleaned canister. After dilution, the concentration was further diluted to 50 ppbv and it was then mixed with a humidified zero air stream and pressurized to 16.7 psig. The final concentration of the diluted calibration gas was 25 ppbv. A multipoint dynamic calibration (three levels plus humid zero air) was performed before each sample analysis. Three different volumes of standard gas of 50, 125 and 250 ml were used in the multipoint calibration. Correlation coefficients ranged from 0.9823 (methylene chlorine) to 0.9999 (toluene). Response linearity tests showed that the response signal was proportional to injection volume (50–250 ml) or VOC concentrations (0.1–12 ppbv). During the analysis periods, four-point calibration was performed every month and one-point calibration was carried out everyday.

3. Result and discussion

3.1. VOC concentrations in the atmosphere of Hong Kong

In this study, 60 ambient samples were collected during the monitoring period and a total of 37 species of VOCs were measured. As shown in Table 1 11, selected VOCs compounds were detected and quantified by GC-MSD analysis of ambient air samples collected at the three monitoring stations. Toluene was the most abundant

atmospheric aromatic hydrocarbon, followed by benzene in both PU and KT stations. The introduction of unleaded and particularly 'super unleaded' fuel has significantly increased the levels of aromatic compounds in petrol and has led to changes in fuel composition involving olefins, and the use of oxygenates (Perry and Gee, 1994). However, the increased aromatics, olefins and other organic compounds in fuels used in vehicles, which are not fitted with catalytic converters have been shown to increase emissions of aromatic VOCs (Perry and Gee, 1994; Singh et al., 1985). The concentrations of toluene at PU ranged from 14.4 to 54.3 $\mu g/m^3$ in winter and 11.6 to 39.2 $\mu g/m^3$ in summer, respectively. According to Table 1, significant variations (all *t* values are smaller than the critical $|t| = 2.02$, $P = 0.05$) existed for all aromatic VOC data between the urban areas (PU and KT) and the rural area (HT) sampling location. The distributions of these VOC compounds were different, with high concentrations of benzene, toluene, ethyl benzene and xylenes (BTEX).

The PU station has the heaviest traffic in Hong Kong. BTEX and 1,2,4-trimethylbenzene came mainly from traffic emissions and fuel evaporation. However, at the KT station, tetrachloroethene was sometimes found to be as high as 7.7 $\mu g/m^3$ and the average concentration was 2.8 $\mu g/m^3$ (winter = 1.6 $\mu g/m^3$; summer = 4.1 $\mu g/m^3$). The possible source of these tetrachloroethene could be cleaners,

especially the dry-cleaning shops along the streets. The VOC spectrum at the KT site was distinctively different from the other stations. There is a mixture of industrial buildings, commercial buildings and restaurants in this area. As shown in Table 1, KT has the highest toluene concentrations (mean= 64.3 $\mu g/m^3$), especially in summer. The KT site has high traffic volume and its BEX concentrations are only slightly lower than those in PU. At HT, which is classified as background, toluene, benzene, methylchloride and methylene chloride were found to be the top four species in winter and their concentrations were 3.2 $\mu g/m^3$, 2.3 $\mu g/m^3$, 2.1 $\mu g/m^3$ and 1.6 $\mu g/m^3$, respectively. Other VOC concentrations were less than 1.0 $\mu g/m^3$ since there were no significant anthropogenic sources.

3.2. Seasonal variations

Temperature in winter is usually between 10 and 20 °C, and between 25 and 33 °C in the summer. Table 1 illustrates the seasonal variations of VOCs between the winter and summer months among the three locations.

At the PU site, some VOC concentrations were slightly higher in summer than in winter, including methylene chloride, xylenes and 1,3,5-trimethyl-benzene. Some had similar concentrations such as carbon tetrachloride, ethylbenzene, toluene and 1,2,4-trimethylbenzene (all *t* values are below critical $|t| = 2.06$, no significant differences). Methylchloride, benzene and tetrachloroethene, however, had lower concentrations in summer than in winter. Most of the VOCs were emitted to the atmosphere from anthropogenic activities at this station, such as motor vehicle exhausts and evaporation of petrol vapors from motor vehicles. Some VOCs had higher concentrations simply because there is more evaporation in the summer. However, at the HT station, all VOCs (except tetrachloroethene) had higher concentrations in winter. Regional physical dispersion/transportation could explain higher concentrations in winter at HT. As the prevailing winds in Hong Kong are north-easterly, especially in winter time, the transportation of pollutants from the north-east area was one of the possible source for the background site. Several factors that could affect the concentrations of

VOCs are common in the winter and in the summer: dilution due to the increase in the mixing depth in summer; more rains in the summer, which cause a washout of pollutants and thus less accumulation of VOCs compared to the dry winter; removal of VOCs by particulate matter by dry and wet deposition; and chemical removal, especially by OH radicals, during the summer. VOC removal is faster in summer than in winter as more sunlight and higher temperatures produce higher chemical removal reaction rates. Therefore the winter VOC concentrations were higher than those in the summer, as found in many other cities (Wathne, 1983; Hartwell et al., 1987; Baek et al., 1997). Generally speaking, except for toluene and tetrachloroethene, all other VOCs at KT in winter had higher or similar concentrations in summer. Higher concentrations of toluene might be due to the construction work nearby (e.g. painting) and more evaporation from restaurants as well as industrial areas during summer time.

3.3. BTEX ratios

BTEX ratios were calculated to compare the VOC emissions among the three sampling sites. The BTEX ratios of PU and KT during the winter period were (1.9:10.1:1.0:1.8) and (1.9:10.4:1.0:1.5), and (0.9:8.3:1.0:2.2) and (0.8:29.6:1.0:1.8) for the summer season, respectively. The ratios at KT reflected that there might be different sources between winter and summer. However, as the BTEX ratios in PU and KT were similar during winter, both stations might be affected by the same sources. In the summer there should be other sources for toluene at KT, thus a high T/B ratio was observed (T/B=37). Generally speaking, the range of T/B ratios at PU was 3–8 in winter and 5–14 in summer. As the concentrations of ethylbenzene and xylenes were too low at HT during both seasons, only T/B ratios were calculated, 2 and 3 in winter and summer, respectively. The results indicate that the sources of benzene and toluene at HT were different from that at PU and KT. There are many factors that influence the VOC profiles in Hong Kong, a complex scenario that requires more data and intensive measurements. Mainly high toluene

to benzene ratios were found in other Asian cities, and higher ratios have been observed in Asian cities such as Manila (T/B=10), Bangkok (T/B=10), Korea (T/B=6) (Gee and Sollars, 1998; Na and Kim, 2001). T/B ratios were high in these cities because they are located in areas with large industrial emissions, possibly with additional sources of toluene. Gee and Sollars (1998) suggested that either there were large additional sources of toluene in these cities or there were major differences in the fuels or vehicles used. It is clear that the kind of unleaded fuels widely used in Asian cities contain a very high aromatic level (45%), and toluene is one of the most popular compounds added to unleaded fuels in order to increase the octane index. The level of toluene in gasoline in Hong Kong is much higher than that in the USA. According to one of the fuel supplier in Hong Kong, the level of toluene in gasoline is around 20%. But for other aromatic compounds such as ethylbenzene and xylene, their percentages are less than 10% (Caltex Oil (Hong Kong) Ltd. 2001), and the percentage of benzene is less than 5%. This confirms the high proportion of toluene in these fuels. Gasoline evaporation may well be one of the sources that lead to extremely high toluene concentration in Hong Kong. However, seasonal variations of xylene/ethylbenzene (X/E) ratios were observed at both PU (X/E=1.84 in winter; 2.22 in summer) and KT (X/E=1.54 in winter; 1.80 in summer) stations. Generally speaking, the X/E ratio is slightly lower at KT station due to reaction/degradation of the more reactive isomers of xylene at the receptor, which is far from the sources (Monod et al., 2001).

3.4. VOCs in tunnel

Generally, the VOCs in tunnels may come from two major sources, which include vehicular emission and evaporative emissions (from fuel tank, engine, etc.) (Kourtidis et al., 1999). Samples were collected at the Cross Harbor Tunnel in order to study the characteristics of VOCs emitted directly from motor vehicles. As this tunnel is a closed system, the pollutants should not have been affected by meteorological factors, and the results should be most representative of the vehicular emissions.

Table 2
VOCs concentrations in tunnel

Unit: $\mu g/m^3$	Tunnel
freon 12	3.41 ± 2.30
methyl chloride	1.17 ± 0.74
freon 114	ND
chloroethene	ND
bromoethane	ND
ethyl chloride	ND
freon 11	1.33 ± 0.86
1,1-dichloroethene	ND
methylene chloride	1.54 ± 1.52
freon 113	0.45 ± 0.29
1,1-dichloroethane	3.71 ± 10.39
cis-1,2-dichloroethene	1.62 ± 4.09
chloroform	0.19 ± 0.13
1,2-dichloroethane	ND
1,1,1-trichloroethane	0.21 ± 0.14
benzene	30.51 ± 9.16
carbon tetrachloride	0.45 ± 0.28
1,2-dichloropropane	15.63 ± 44.20
trichloroethene	1.09 ± 1.34
cis-1,3-dichloropropene	ND
trans-1,3-dichloropropene	ND
1,1,2-trichloroethane	0.14 ± 0.19
toluene	200.82 ± 99.82
1,2-dibromoethane	ND
tetrachloroethene	0.43 ± 0.53
chlorobenzene	0.09 ± 0.12
ethylbenzene	15.07 ± 6.22
m,p-xylene	27.12 ± 13.94
styrene	2.48 ± 1.84
o-xylene	18.55 ± 8.55
1,3,5-trimethylbenzene	7.05 ± 6.18
1,2,4-trimethylbenzene	32.46 ± 25.92
1,4-dichlorobenzene	0.13 ± 0.13
1,3-dichlorobenzene	0.13 ± 0.13
1,2-dichlorobenzene	ND
1,3,5-trichlorobenzene	ND
hexachlorobutadiene	ND

ND non-detectable (below detection limit).

The concentrations of most vehicular related VOCs obtained inside the tunnel were much higher than those obtained at the PU station (Table 2). The maximum concentrations of benzene, toluene, ethylbenzene, m,p-xylene, o-xylene and 1,2,4-trimethylbenzene were 40.1 $\mu g/m^3$, 397.4 $\mu g/m^3$, 25.9 $\mu g/m^3$, 53.5 $\mu g/m^3$, 28.0 $\mu g/m^3$ and 91.2 $\mu g/m^3$, respectively. The average BTEX ratio inside the tunnel was 2:10.4:1:3.2. The ratio of BTEX reported in the other studies for vehicle exhaust was (3:4:1:4) (Chiang et al., 1996), while

Table 3
Summary of BTEX correlation coefficients (r) at PU and KT during summer and winter

Tunnel	benzene	toluene	ethylbenzene	*m,p*-xylenes	*o*-xylene
PU winter					
benzene	1.00	–	–	–	–
toluene	0.81	1.00	–	–	–
ethylbenzene	0.90	0.94	1.00	–	–
m,p-xylene	0.83	0.88	0.93	1.00	–
o-xylene	0.80	0.83	0.91	0.98	1.00
PU summer					
benzene	1.00	–	–	–	–
toluene	0.57	1.00		–	–
ethylbenzene	0.33	0.45	1.00	–	–
m,p-xylene	0.26	0.47	0.78	1.00	–
o-xylene	0.23	0.30	0.97	0.76	1.00
KT winter					
benzene	1.00	–	–	–	–
toluene	0.95	1.00	–	–	–
ethylbenzene	0.93	0.99	1.00	–	–
m,p-xylene	0.93	0.98	0.99	1.00	–
o-xylene	0.93	0.99	0.99	0.99	1.00
KT summer					
Benzene	1.00	–	–	–	–
Toluene	0.09	1.00	–	–	–
ethylbenzene	0.55	0.07	1.00	–	–
m,p-xylene	0.52	0.06	0.99	1.00	–
o-xylene	0.67	0.20	0.96	0.97	1.00

in the study in the tunnel in Taiwan (Taipei city), the ratio was (3:5:1:4) (Chiang et al., 1996). The ratios of BTEX in Hong Kong were different from the ratios of other countries, especially for benzene and toluene emissions. Moreover, the X/E ratio (3.2) in the tunnel was higher than that in the ambient air (1.54–2.22). This indicates that the freshly emitted xylene in the tunnel decayed at different rates from OH-oxidation in the atmosphere. Therefore the X/E ratio decreased after xylene emitted to the ambient air and reacted with some oxidants in the atmosphere.

3.5. BTEX correlation analysis

As shown in Table 3, BTEX correlations were evaluated at the PU and KT monitoring sites during winter and summer. Good BTEX correlations ($r > 0.8$) were found at PU and KT during wintertime (**$P < 0.01$). During wintertime, vehicular exhaust was the dominant source at PU, and

less evaporation of fuel or additive occurred at low temperature. Also at KT, the traffic emissions were the major sources in winter. However, poor correlations of benzene with TEX and toluene with BEX were found during summer at both sites. More evaporation in the summer season, especially for toluene (high proportion in gasoline), and photochemical reactions under high solar radiation were the major factors affecting the correlation of BTEX. At KT, as discussed above, poor correlations of toluene with BEX might be due to the higher emission from construction work nearby (e.g. painting) during the summer. Ethylbenzene, *m,p*-xylene and *o*-xylene were well correlated with each other during both seasons, suggesting that they came from the same sources during both seasons. At the background site HT, although no nearby sources affected the correlation, higher concentrations of BTEX observed in winter might be due to the transportation of pollutants from the northeast area. However, the concentrations of

Table 4
BTEX correlation coefficients (r) at tunnel

Tunnel	benzene	toluene	ethylbenzene	xylenes
benzene	1.00	–	–	–
toluene	0.78	1.00	–	–
ethylbenzene	0.86	0.80	1.00	–
xylene	0.96	0.76	0.95	1.00

ethylbenzene and xylenes were low (sometimes below the detection limits) and with the small sampling size no correlation analysis was done for HT.

Table 4 shows the correlation coefficients (r) for the BTEX concentrations in tunnel. Strong correlations between EX were found with significance levels <0.01. However, benzene in the tunnel only showed fair correlation with TEX with a significance level of 0.05. This is because the benzene content is the lowest (when compared with TEX) in the petrol fuel, therefore, the evaporation of benzene to the atmosphere is the lowest. The major emission of benzene was from vehicular exhaust.

3.6. Diurnal variations

The VOC concentrations were not the same throughout the day. Concentrations of most VOC species were lower outside the tunnel due to a dilution effect. The concentrations of benzene, toluene, ethylbenzene and xylene were four to six times higher inside the tunnel than outside. Samples were collected at the PU station intensively from 09:00 to 21:00 h, and in total four 3-h averaged samples were collected each day. The diurnal variations of BTEX concentrations were different for benzene compared with toluene, ethylbenzene and xylenes (Fig. 2). The concentrations of toluene, ethylbenzene, m,p-xylene and o-xylene followed the same pattern: increased at 09:00–12:00 h, then decreased at 12:00–15:00 h, followed by a peak at 15:00–18:00 h, and finally decreased slightly at 18:00–21:00 h. It was observed that the concentrations of TEX reflected the traffic flow (peak at 09:00–12:00 and 15:00–18:00 h) and vehicle types. However, benzene concentrations were higher at 09:00–12:00 and 18:00–21:00 h than that at 12:00–15:00 and
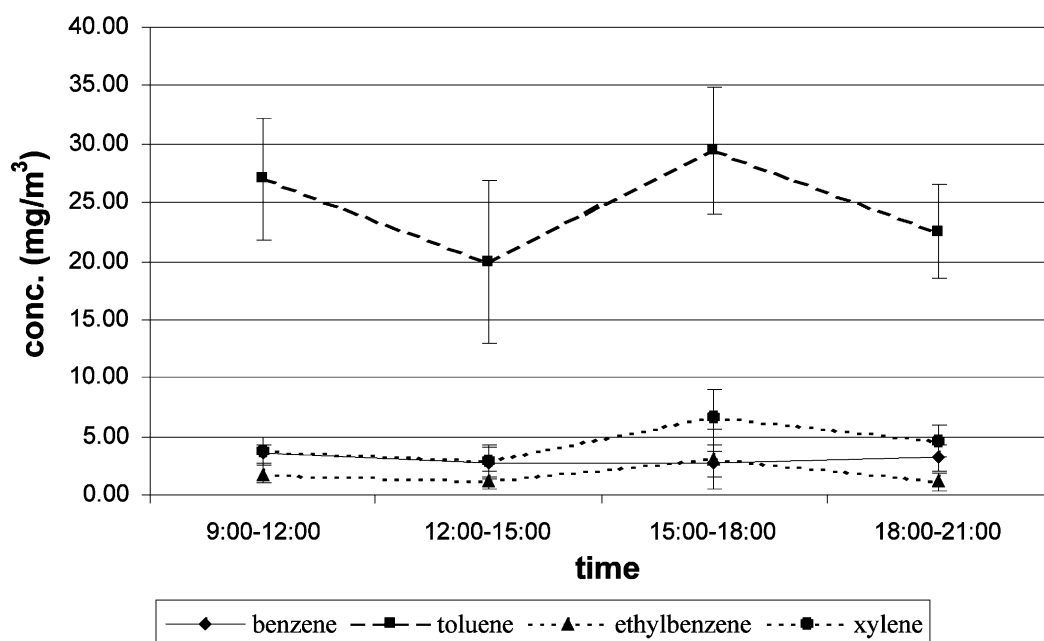

Fig. 2. Temporal variation of benzene, toluene, ethylbenzene and xylenes at PolyU station.

15:00–18:00 h. But the variations were not significant (*t*-test for benzene concentrations during 09:00–12:00, 18:00–2100 h and 12:00–15:00, 15:00–18:00 h = 1.47, cf. critical $|t| = 2.07$)

The traffic volume on the Hong Chong Road started to increase from 05:00 h and reached its maximum value at 08:00 h, while at 19:00 h it started to decrease (Traffic Annual Census 2000). Although there was only a slight increase in the traffic volume during the morning and evening rush hour, it was noted that there were changes in the vehicle types during the day. The percentages of private cars and taxis were much higher at night than in the morning, while percentages of medium and heavy vehicles were higher in the morning. In the morning 50% of the total traffic flow was private cars/taxis and 17% were medium/heavy vehicles, while at night 64% of the total traffic flow was private cars/taxis and only 7% was medium/heavy vehicles.

Benzene is mainly emitted from vehicular exhaust (less from gasoline evaporation) and has less reactivity with the OH radical. The slight decrease of benzene concentrations during 12:00–15:00 and 15:00–18:00 h periods were due to the dilution effects caused by an increase of the mixing depth during the daytime (Na et al., 2003). The peaks of TEX species in the morning (09:00–12:00) may be due to the high traffic volume in that period. After that period, the concentrations started to decrease due to the decrease of traffic volume and the dilution effects caused by an increase of the mixing depth. At 15:00–18:00 h, the concentrations of TEX reached their maximum because the traffic volume (especially the gasoline vehicles) and other evaporative emissions (Na et al., 2003) increased. Finally, TEX decreased because the traffic volume and the manufacturing activities (painting and coating) decreased.

3.7. Diurnal variations of BTEX ratio

The X/E ratios were similar during the whole sampling periods, with the average ratio ranging from 1.2 to 1.7. The similar EX suggested a common source of the two pollutants, namely the vehicular exhaust, and the photochemical reaction was not significant because the sampling location was close to the road. The T/B ratios were similar in the periods 09:00–12:00 h, 12:00–15:00 h and 18:00–21:00 h, with the average ratio ranging from 7.1 to 7.6, respectively. But an increase in the T/B ratio (10.9) during 15:00–18:00 h suggested that the contributions of evaporative emission increased. The different BT ratio at 15:00–18:00 h meant that there were different sources of pollution during this time. The possible sources responsible for this difference could be the decrease of diesel vehicles and increase of gasoline vehicles, and/or the evaporation of the gasoline from manufacturing activities. However the T/B ratio decreased again during 18:00–21:00 h because the evaporation of fuels declines due to the temperature drop.

4. Conclusion

In a 1 year seasonal VOC monitoring study carried out at PU, KT and HT monitoring sites in Hong Kong from November 2000–February 2001 and June 2001–August 2001, high ambient concentrations were recorded for toluene (24-h average concentrations of toluene at PU ranged from 14.4 to 54.3 $\mu g/m^3$ in winter and 11.6 to 39.2 $\mu g/m^3$ in summer, respectively). In addition, the most abundant toxic organic compounds in urban air were aromatic hydrocarbons. Vehicular emission is one of the most important pollutant sources in Hong Kong, leading to the high concentrations of aromatic compounds in the atmosphere. However, the concentrations of aromatic compounds were low at the background station, HT. Most VOCs had higher concentrations in summer except at the HT station, where all VOCs (except tetrachloroethene) had higher concentrations in winter than in summer, possibly the result of regional physical dispersion/transportation at HT. The PU and KT sites had similar BTEX ratios during winter, suggesting that both vehicular exhaust and evaporative emissions of gasoline (composition of aromatic hydrocarbon in gasoline: toluene approx. 20%, ethylbenzene and xylene <10%; benzene < 5%) are the major sources. In the summer there were other sources for toluene in KT, resulting in a high T/B ratio of 37. Good BTEX correlations ($r > 0.8$) were found at PU and KT during winter

(**$P < 0.01$). In winter, vehicular exhaust was the dominant source at PU, along with less evaporation of fuel or additive at low temperature.

The concentrations of most VOCs obtained inside the tunnel were much higher than those at PU station. The average BTEX ratio inside the tunnel was 2:10.4:1:3.2, which was different from the ratios found in other countries. Moreover, the comparison of the X/E ratios between tunnel and ambient air implied the photochemical reactivity of xylenes. The X/E ratio (3.2) in the tunnel was higher than that in the ambient air (1.54–2.22). This indicated that the freshly emitted xylene in the tunnel decayed at different rates from OH-oxidation in the atmosphere.

The 3-h average samples collected showed that benzene exhibited a different variation pattern when compared with toluene, ethylbenzene, *m,p*-xylene and *o*-xylene. Benzene concentrations were higher between 09:00–12:00 and 18:00–21:00 h than at 12:00–15:00 and 15:00–18:00 h; while the concentrations of toluene, ethylbenzene, *m,p*-xylene and *o*-xylene were high at 09:00–12:00 h, then decreased at 12:00–15:00 h, peaked at 15:00–18:00 h, then decreased again at 18:00–21:00 h. The X/E ratios were similar during 09:00–21:00 h but there was a slight difference in the T/B ratio during 15:00–18:00 h. This may be due to the change of the vehicle type from diesel vehicle to gasoline vehicle at that period and the increase of manufacturing activities. Evaporation of the gasoline and the use of solvents for industrial purposes were possible causes of the peak at 15:00–18:00 h.

Acknowledgments

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