Characteristics of Volatile Organic Emissions from Hong Kong Traffics

by

Yu Yuen Shan

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Department of Civil and Structural Engineering
The Hong Kong Polytechnic University
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DECLARATION

I hereby declare that this thesis entitled "Characteristics of Volatile Organic Emissions from Hong Kong Traffics" has not been previously submitted to any other institution for a degree or other qualification, and contains no material previously published or written by another person, except where due reference is made in the text.

YU Yuen Shan

ABSTRACT

This research project studies the characteristics of volatile organic emissions from vehicular sources in Hong Kong. It covers the volatile organic emissions from vehicular sources, fuel evaporation and characteristics of volatile organic compound (VOC) in tunnels and ambient atmosphere. Through this research project, a better understanding of the impact of VOC to the air pollution problem in Hong Kong can be achieved. In the tunnel study, results demonstrate that alkenes and alkanes are the most abundant hydrocarbon groups in the selected tunnels. Also, these two groups of hydrocarbon are mainly from vehicle exhaust. Moreover, grab air samples were collected from different vehicular sources in Hong Kong to explore the emission characteristics of each vehicular source. The most abundant VOCs in the exhaust of diesel-powered vehicles and gasoline-powered vehicles are alkenes and aromatic hydrocarbons respectively. In the exhaust of LPG-powered vehicles, the most abundant VOCs are saturated hydrocarbons. For the ambient VOCs in Hong Kong, toluene contributions are high, which may due to gasoline evaporation from vehicles or solvent evaporation. In addition, 3 factors were extracted using the data collected by the multivariate statistical method of Principle Component Analysis (PCA). Results indicate that

the VOCs in ambient air are highly influenced by gasoline evaporation, vehicle exhaust emissions and solvent evaporation.

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LIST OF ABBREVIATION

$\mu g/m^3$	:	Microgram per cubic metre
2-L	:	Two Litres
APCO	:	Air Pollution Control Ordinance
Ar	:	Argon
B	:	Benzene
BT	:	Benzene-to-Toluene Ratio
C_2-C_5	:	Light Hydrocarbons
C_2Cl_4	:	Tetrachloroethylene
CH_2Cl_2	:	Methylene Chloride
cm^3/min	:	Cubic centimeter per minute
CW	:	Central/Western Monitoring Station
E	:	Ethylbenzene
ECD	:	Electron-catpure Detector
EE ratio	:	Ethyne-to-Ethene Ratio
F-11	:	Freon 11
F-12	:	Freon 12
FID	:	Flame-ionization Detector
GC/MS	:	Gas Chromatography / Mass Spectrometry
HAPs	:	Hazardous Air Pollutants
HGV	:	Heavy Goods Vehicles
HK	:	Hong Kong
HKEPD	:	Hong Kong Environmental Protection Department
HKSAR	:	Hong Kong Special Administrative Region
HPCL	:	Health Protection Concentration Levels
i-butane	:	Isobutane
i-pentane	:	Isopentane
KCR	:	Kowloon Cantoon Railway
kPa	:	KiloPascal
LPG	:	Liquefied Petroleum Gas
LR	:	Light Rail
mg/m^3	:	Milligram per cubic metre
MGV	:	Medium Goods Vehicles
mL/min	:	Millilitre per minute
MSD	:	Mass Spectrometric Detector
MTBE	:	Methyl Tertiary Butyl Ether
MTR	:	Mass Transit Railway
m-xylene	:	Meta-xylene
N	:	Number of Sample
N_2	:	Nitrogen
n-butane	:	Normal Butane
NOx	:	Nitrogen Oxides
n-pentane	:	Normal Pentane
O_2	:	Oxygen
o-xylene	:	Ortho-xylene
PAHs	:	Polycyclic Aromatic Hydrocarbons
PAN	:	Peroxyacetyl Nitrate
PCA	:	Principle Component Analysis
PCRF	:	Per-Carbon-Response-Factor
ppb	:	Part per billion
PRD	:	Pearl River Delta

PRDEZ	:	Pearl River Delta Economical Zone
p-xylene	:	Para-xylene
QA/QC	:	Quality Assurance and Quality Control
r	:	Correlation Coefficient
RSPs	:	Respirable Suspended Particulates
T	:	Toluene
Taiwan EPA	:	Taiwan Environmental Protection Agency
TO	:	Toxic Organic
TS	:	Tsuen Wan Monitoring Station
ULSD	:	Ultra Low Suphur Diesel
US	:	United States
US EPA	:	United Stated Environmental Protection Agency
VKT	:	Vehicle Kilometers Traveled
VOC	:	Volatile Organic Compound
WHO	:	World Health Organization
wt %	:	Weight Percentage
X	:	Xylenes

CHAPTER 1 OVERVIEW

1.1 Aim and Objectives of Study

The aim of this research project is to get a better understanding of the impact of traffic-emitted VOCs to air pollution problem in Hong Kong through the study of the characteristics of the volatile organic emissions from vehicular sources in Hong Kong.

The objectives of this research are:

(1) To identify the volatile organic fingerprints of various vehicular exhaust;

(2) To investigate the relationship between the volatile organic emissions in tunnels and vehicular exhaust;

(3) To study the contribution of vehicular volatile organic emissions upon air pollution in Hong Kong;

1.2 Structure of Report

In Chapter 2, characteristics VOC from vehicular emission sources in tunnels and in the atmosphere were reviewed. The background information on traffic and vehicular emissions and related information were introduced in Chapter 3. The sampling methods, chemical analysis, quality control and assurance of the field study are described in Chapter 4. Results and discussion are shown in the next three chapters. These include a tunnel study in Chapter 5; an examination of vehicular emissions in Hong Kong in Chapter 6; and the contribution of the vehicular emissions on ambient VOC in Hong Kong in Chapter 7. Overall conclusion and recommendations are shown in Chapter 8 and 9.

CHAPTER 2 LITERATURE REVIEW

2.1 Volatile Organic Compounds in General

2.1.1 Volatile Organic Compounds in the Atmosphere

Volatile organic compounds (VOCs) are an important class of air pollutants, which include species with different physical and chemical behaviors. There are many hundreds of compounds that come within the category of VOCs and the different definitions and nomenclatures yet further complicate the situation. Strictly speaking, VOCs refers to those organic compounds, which are present in the atmosphere as gases, but which under normal conditions of temperature, and pressure would be liquids or solids (Derwent, 1995). A volatile organic compound is by definition an organic compound whose vapor pressure at say $20^{0}C$ is less than 760 torr (101.3kPa) and greater than 1 torr (0.13kPa) (Derwent, 1995). And it is commonly found in the atmosphere at ground level in all urban and industrial centres, which are released during the combustion or evaporation of solvents, paints, glues, and fossil fuels. Apart from industrial emissions, the exhaust of gasoline and diesel automobiles also contains significant concentrations of VOC. In the urban atmosphere, the most important VOCs are benzene, 1,3-butadiene, m&p-xylenes, o-xylenes, ethylbenzene, toluene and formaldehyde (Friedrich and

Obermerier, 1999).

Moreover, natural biogenic processes such as emissions from plants, trees, wild animals and natural forest fires also give rise to substantial ambient concentrations of organic compounds. In addition, the oceanic sources of VOCs have been investigated in seawater and it is found that alkanes and alkenes are significantly supersaturated in seawater compared to their atmospheric burden (Lamontagne et al., 1974).

2.1.2 Impacts of Volatile Organic Compounds

VOCs are of great concern in urban air pollution because of their roles in stratospheric ozone depletion, ground level photochemical ozone formation, enhancement of the global greenhouse effect as well as accumulation and persistence in the environment. Moreover, VOCs which belong to the air toxic category, are widely distributed in the ambient atmosphere and may have important impacts on human health such as leukaemia, nasal cancer and lung cancer (Derwent, 1995). Concern is particularly expressed about those VOCs present in the ambient atmosphere that are toxic or having carcinogenic human health effects. The US EPA has designated many VOCs, including those typically found in auto pollution, as air toxic or hazardous air pollutants (HAPs) which are known or suspected to cause serious health hazards. Both benzene and 1,3-butadiene are known carcinogens and also potential leukemia-inducing agents (Derwent, 1995). In addition, through complex photochemical reactions, VOCs contribute to the formation of toxic oxidants (Finlaysons-Pitts and Pitts, 1986; Lioy and Daisey, 1986; Atkinson et al., 1988; Shah and Singh, 1988; Mohamed et al., 2002) such as tropospheric ozone, and peroxyacetyl nitrate (PAN), which are detrimental to health and are phytotoxic.

2.1.3 VOC Regulation and Standards

In the Pearl River Delta Region, there are no air quality objectives or standards for volatile organic compounds although VOCs play an important role in photochemical reaction and ozone formation (HKEPD, 2002).

Under the Ordinance for the Purpose of Public Health Protection, the Health Protection Concentration Levels (HPCL), which is the action level are specified. In setting the HPCL, the primary concern was the carcinogenic risk. For easy enforcement, the HPCLs have been transformed and stipulated as hourly limits. They are protecting the public to below a practical intermediate target theoretical risk of $1x10^{-4}$ μg/m^3 (1-hr average). In the long term, $1x10^{-6}$ μg/m^3 (1-hr average), which is already the target for large manufacturing processes having wider impact on the population, should be the ultimate goal (Pang et al., 1994). The Hong Kong Environmental Protection Department (HKEPD) may issue an air pollution abatement notice to require the owner to reduce the emissions of air pollutants under Section 10 of the Air Pollution Control Ordinance (APCO) if the air pollution caused by the premise is not in compliance with the HPCL. Among the 38 air pollutants, 36 are classified as toxic air pollutants and only 10 VOCs are listed in the TO14 VOC compound list. Their HPCLs are shown in Table 2.1.

Air quality standard for VOCs is also regulated in the United Kingdom. The Expert Panel on Air Quality Standards (EPAQS) in the United Kingdom has produced recommendations for standards for benzene and 1,3-butadiene, which are known as carcinogens. EPAQS has recommended an air quality standard of 16 μg/m^3 as annual average concentrations for benzene, while 2.4 16 μg/m^3 as annual average for 1,3-butadiene (Dollard et al., 1995). According to the New Zealand

Ambient Air Quality Guidelines 2002, the recommended annual benzene concentration is 3ppb. The air quality standards of VOCs in other countries are referred to Table 2.2.

2.1.4 Characteristic Ratios for Vehicular VOC Emissions

Previous studies indicated that benzene, toluene, ethylbenzene and xylenes (BTEX) were the major photochemical reactive organic pollutants emitted from automobiles (Sigsby et al., 1987). Therefore, the characteristic BTEX ratios based on the four typical aromatic hydrocarbons were used to characterize the vehicular emission sources of VOCs. The BTEX ratios are usually used to characterize the VOC emissions in tunnels (Duffy and Nelson, 1996; Chiang et al., 1996, Zielinska and Fung, 1994). The BTEX ratios found in the Sydney Harbour Tunnel (Australia) and the Hsin-Hai Tunnel (Taiwan) were 5 : 8 : 1 : 5 and 3 : 5 : 1 : 4 respectively.

Apart from BTEX ratio, benzene and toluene (BT) ratio, ethyne/ethene (EE) ratio, m,p-xylenes/benzene ratio, m,p-xylenes/toluene ratio were used to characterize vehicular emissions (Zielinska and Fung, 1994; Gertler et al., 1996; Fraser et al., 1998; Rogak et al., 1998; Grosjean et al., 1999; Sagebiel et al., 1996). The BT ratios in the tunnels in Taiwan, Australia, USA and Hungary ranged from 0.6 to 0.7 (Chiang et al., 1996; Duffy and Nelson, 1996; Zielinska and Fung, 1994; Haszpra and Szilagyi, 1994; Scheff et al., 1989). Ambient urban air BT ratios in various cities have been reported ranging from 0.7 to 4.0 (Evan et al., 1992, Chan et al., 1991; Baek et al., 1997). BT ratios found in the Latin American cities (Gee and Sollar, 1998) and Rome (Brocco et al., 1997) ranged from 2 to 3.3. Bangkok and Manila had greater BT ratio of 10. Thus, there may be additional sources of toluene in these cities. Also, the BT ratio in a fresh air mass is expected to be about 0.4 (0.3-0.5), whereas, in an aged air mass it exceeds this number (USEPA, 1996). The EE ratios found the tunnels in California, Maryland and New Jersey were the same, which was 0.4. The EE ratio in Pennsylvania was 0.3 (Zielinska et al.. 1994; Scheff et al., 1989). The similar EE ratios indicate that the compositions of fuels used in the USA are close. Also, a study found that the higher EE ratio indicate a higher contribution of high emitting (or non-catalyst) vehicles (Sagebiel et al., 1996). The m,p-xylenes/benzene ratios ranged from 0.3 to 2.1 with an average of 1.1 while the m,p-xylenes/toluene ratios ranged from 0.2 to 1.6 with an average of 0.5 at urban areas (Grosjean et al., 1999). According to USEPA, the ratio of the m&p isomers of xylene to benzene is about 1.5 in a fresh air mass, but in an aged sample it is less than 1.5 (USEPA, 1996).

2.2 Volatile Organic Emissions in Tunnels

Road traffic emissions can be determined by exhaust measurements of driving vehicles (Bailey et al., 1990) or in tunnel measurements. However, tunnel study has been widely used to determine the hydrocarbon speciation of vehicular emission, as tunnel is a relatively homogeneous atmosphere (Haszpra and Szilagyi, 1994; Duffy and Nelson, 1996). In the past decade, a considerable number of tunnel studies had been performed. Kebbekus et al. (1983) examined the levels of airborne pollutants in the Lincoln and Holland Tunnels. The result indicated that the pollution levels of vehicle exhausts in the tunnels were ten to twenty times higher than those measured in nearby urban air. Hsieh et al. (1999) carried out a tunnel study in two vehicle tunnels in Taipei. They found that toluene and xylenes were the most predominant VOCs in the two vehicle tunnels, which were 410.2 and 109.1$\mu g/m^3$. It was also found that the characteristic ratios of the VOC concentrations were similar in the two tunnels although the traffic volume and types of vehicles were not exactly the same. Another tunnel study in Taiwan found that the most abundant species from the traffic-emitted VOCs in Taipei road tunnel are toluene, ethene and 1,2,4-trimethylbenzene on the weight basis (Hwa et al. 2002). Moreover, a few studies found that i-pentane, toluene, m,p-xylene and benzene were the major components of VOCs measured in Fort McHenry, Tuscarora, Gubrist and Chung-Cheng Tunnels (Pierson et al., 1996; John et al., 1999; Hsu et al., 2001)

2.3 Sources of Volatile Organic Compounds

2.3.1 Vehicular Emission

Vehicular emission contributes significantly to urban air pollution problems in most metropolitan cities all over the world. Concern about auotmobile as a source of air pollution has been expressed periodically, but national concern was first evidenced in the 1960s when California established the first new car emission standards. Exhaust from tailpipe of motor vehicles is a complex mixture that contains hundreds of chemicals in the form of gases as well as solid and liquid aerosols. The composition of the mixture depends on the fuel, the type and operating conditions of the engine and the effects of any emission control devices (Bates et al. 1988). Recent studies proposed that the major source of VOCs in urban areas is from motor vehicles (Chiang et al., 1996; Jones et al., 1998; Na et al., 2002). In the past decade, unleaded fuel has been used widely all over the world. However, the removal of lead as an additive in fuel has its side effect. Changes in the mixing of the petrol to increase the octane number may increase the emission of aromatic hydrocarbons e.g. benzene. Benzene concentrations have increased in many urban atmospheres with the introduction of catalytic converters, which is used to increase oxidation. However, many chemical reactions are involved at the same time and benzene is one of the pollutants emitted (Richter and Williams, 1998). Jones et al. (1998) found that evaporative and exhaust emissions contributed an estimated 30 % of total VOC emissions in the UK. Also, studies on vehicular emissions on roadways and car exhaust pipes have been published. Mugica et al. (2001) carried out a study to characterize the VOC emissions from tunnels, crossroads, truck and bus terminals. The results indicated that the most abundant VOCs are ethene, ethyne, i-pentane, toluene, xylenes and methyl tertiary butyl ether (MTBE) from all the sampling sites. As from diesel powered vehicles, a higher contribution of aromatic compounds was found i.e. ethylbenzene, toluene and xylenes. Referring to the study carried out by Doskey et al. (1992), the major components of the gasoline headspace vapor were the saturated hydrocarbons 2-methylpropane, n-butane, 2-methylbutane and n-pentane. The study also found that the aromatic content increased with octane level and largely due to an increase in the toluene content. Schifter et al. (2000) found that the major composition of LPG exhaust is lighter alkanes, which were enriched in propane, n-butane and i-butane.

2.3.2 Other Sources of Volatile Organic Compound

Other than vehicle emission, VOCs are present in the atmosphere as a result of solvent usage, industrial processes, oil refining, petrol storage and distribution, landfilled wastes, food manufacture, and agriculture. Although solvents from paints and industrial uses form large components of all reactive organic gases inventories, their reported profiles are few (Kitto et al., 1997; Guo et al., 1998, 1999). Seila et al. (2001) reported that the evidence of industrial solvent was suggested by the presence of elevated levels of xylenes, styrene, and trimethylbenzenes. Brocco et al. (1997) indicated that toluene, ethylbenzene and xylenes have the largest portion in solvents. Similarly, the compounds that characterize the painting applications are xylenes and toluene (Watson et al., 2001). Evaporative losses from the dry cleaning industry are suspected to represent a significant portion of releases of tetrachloroethylene to the air (ATSDR, 1997). Taback et al. (1978) reported that propane, n-butane and i-butane are abundant in asphalt roofing. For petroleum refinery emissions, the most abundant VOCs include propane, n-butane and i-pentane (Taback et al., 1978; Western Oil & Gas Association, 1977). For the architectural coatings emissions, it was characterized by high contribution of toluene (Scheff et al., 1989). In landfill, tetrachloroethylene, ethylene chloride and trichloroethylene existed in relatively higher concentrations in the air. Also, landfills are sometimes identified as large total organic gases emitters. Brosseau and Heitz (1994) found acetone, alpha terpinene, benzene, butyl alcohol, dichlorobenzene, dichloromethane, ethylbenzene, ethyl mercaptan, limonene, furans, terpenes, toluene, vinyl acetate, vinyl chloride and xylene to be among the most abundant components of landfill reactive organic gases.

2.4 Other Related Studies

Recently, the Hong Kong Environmental Protection Department (2002) carries out a study on the air quality in Hong Kong and the PRD Region. It found that both the local air pollution sources and the worsening regional air quality in the PRD

Region are causes for our deteriorating air quality. There are four major emission sources that contribute to at least 90 % of the regional emission. They include energy, industry, transportation and VOC containing product. It was found that the regional emissions for all the concerned pollutants are dominated by PRDEZ. Moreover, transportation is the largest contributor to VOC emissions in Hong Kong and the PRD Region.

Recently, there are a few VOC studies carried out in Hong Kong. Ho et al. (2002) suggested that emissions from motor vehicles have been one of the primary pollution sources in the metropolitan area of Hong Kong and many of ambient VOC concentrations are originated from the same sources as particulate PAHs and carbonyls compounds. In urban air, benzene, toluene, ethylbenzene, m,p-xylenes and o-xylenes (BTEX) were the major VOC compounds for mobile sources. Toluene was found to be the most serious VOC pollutants compared to the other four species. The average and maximum concentrations of toluene were 28.8 and 136.6 $\mu g/m^{-3}$ respectively. In addition, the characteristics and concentrations of VOCs in the roadside microenvironments were investigated by Chan et al. (2002). The VOC concentrations, especially toluene, benzene and chlorinated VOCs in

Hong Kong were high when compared with those in most developed cities. The average and maximum concentrations of toluene were 74.9 and 320.0 μg/m^{-3} respectively. The respective values for benzene were 25.9 and 128.6 μg/m^{-3}. Trichloroethylene and tetrachloroethylene dominated the chlorinated VOCs with the maximum concentrations reached 248.2 and 144.0 μg/m^{-3} respectively. Also, there were strong variations in the spatial fluctuation and characteristic of VOC concentrations. The highest VOC concentrations were found in the industrial areas followed by those in the commercial areas and residential areas.

On the other hand, Qin et al. (1993) suggested that vehicular activity was on the rise and the combustion exhaust has gradually changed from coal limited to one with vehicle dominance in the 90s in South China (Qin et al., 1993; Elliott et al., 1997). As one of the most abundant components in vehicular exhaust, volatile organic compounds are of great concern in urban air pollution due to its physical and chemical properties. Therefore, obtaining different source profiles from South China is very helpful to the investigation of the change during these years, especially at present vehicle exhaust has become the dominant VOC source in South China. However, there are only limited studies on VOCs in Mainland China.

In a recent study carried out in the northeast of China where the concentrations of VOCs were monitored at five different function zones in Changchun, Liu et al. (2000) found that i-pentane was the most abundant alkane, which came from both exhaust and evaporative emissions. Besides, 2-butene was the most abundant alkene, which can be mostly attributed to vehicular sources. Apart from alkane and alkene, toluene and benzene were the most abundant VOCs in the aromatic fraction. In addition, the total average concentration of VOCs in downtown was about four times as high as that in the rural area.

Table 2.1 Health Protection Concentration Levels (HPCL) (Pang, 1994)

Air Pollutants	**HPCL (μg/m^3, 1-hr average)**
Benzene	185
1,3-Butadiene	19
Carbon tetrachloride	30.4
Chloroform	55.5
Dichloromethane	311
1,2-Dichloroethane	58
Hexachlorobutadiene	0.6
1,1,2,2-Tetrachloroethane	22
Trichloroethane	311
Vinyl chloride	472

Table 2.2 Air Quality Standards of VOCs in Other Countries (Pang, 1994)

Air Quality Standards	**VOCs**	**Standards (μg/m^3)**	**Average Time**
Hong Kong Technical Memorandum	Dichloromethane	311	1 hour
	Trichloromethane	55.5	1 hour
	Trichloroethene	311	1 hour
	Benzene	185	1 hour
European WHO Guideline	Dichloromethane	3000	24 hours
	Trichloroethene	1000	24 hours
	Tetrachloroethene	5000	24 hours
	Toluene	7500	24 hours
Occupational Safety and Health Administration (OSHA) (Occupational limit)	Dichloromethane	173800	8 hours
	Trichloromethane	9789	8 hours
	Trichloroethene	270000	8 hours
	Tetrachloroethene	170000	8 hours
	Benzene	3100	8 hours
	Toluene	375000	8 hours

CHAPTER 3 BACKGROUND INFORMATION

3.1 Background of Traffic and Vehicular Emissions in Hong Kong

Hong Kong is a densely populated city in South China with over 6.8 million people. However, the total land area of Hong Kong is just under 1,100 km^2, which covers Hong Kong Island, the Kowloon Peninsula and the New Territories, including 235 outlying islands. It is one of the fastest growing cities in South China. Unfortunately, air pollution also causes great concern in Hong Kong due to the increasing emission of air pollutants from vehicles and various industries. The poor air quality at street level in Hong Kong is caused primarily by the high volume of traffic. For the driving pattern in Hong Kong, the proportion of idling is large while the proportion of cruise is small. High-rise buildings close to each other, and when combine with heavy traffic-flow, cause serious air pollution in Hong Kong (Chan et al., 2001). Due to heavy atmospheric pollution, acid rain was widely recorded (Cheng et al., 2000).

3.1.1 Transport Statistics in Hong Kong

In year 2001, the total length of public roads in Hong Kong was 1,911 kilometers, which has increased 10% approximately over year 1996 (Census and Statistics

Department, 2002). At the same time, the number of vehicle has increased rapidly in the past few years, which leads to more serious urban air pollution. In year 2001, the total number of licensed vehicles exceeded 540,000 and it had increased more than 9% over year 1996 (Transport Department, 2002). Among various types of motor vehicles in Hong Kong, the number of private cars in year 2001 has increased 16% approximately over year 1996 (Transport Department, 2002). The number of licensed motor vehicles by type is shown in Table 3.1.

On the other hand, the traffic growth can be expressed in terms of vehicle kilometers traveled (VKT). The VKT of different types of motor vehicles in Hong Kong is shown in Table 3.2. In Table 3.2, the annual VKT of private car was the highest among different vehicle types in year 1997 and 2001, followed by light and heavy-duty vehicle. According to the Transport Department in Hong Kong, over 10 million passenger journeys are made on public transport system everyday. The public transport system in Hong Kong is mainly composed of the underground Mass Transit Railway (MTR), the Kowloon Cantoon Railway (KCR) and Light Rail (LR), buses, taxis, trams and ferries. Figure 3.1 shows the busy traffic condition in a commercial area in Hong Kong.

In addition, the number of licensed vehicles in Hong Kong can be classified by fuel types. In general, there are four major types of auto fuel used in Hong Kong, which include gasoline, diesel, electric, and light petroleum gas (LPG). The number of licensed vehicles by fuel type up to March 2002 is shown in Table 3.3 (Transport Department, 2002). According to Table 3.3, more than 70% of vehicles in Hong Kong are gasoline-powered, which are mainly private cars. Besides, only about 25% of vehicles are diesel-powered, which are mainly light goods vehicles. The Hong Kong Environmental Protection Department had been trying for years to find an alternative to diesel, at least for small vehicles such as taxis, but earlier attempts to switch them to gasoline fuel met with vigorous opposition. Finally, the Hong Kong Government strongly encourages the conversion of diesel taxis into LPG taxis. At the moment, there are more than 80% of taxis powered by LPG. LPG is strongly recommended because it is virtually free of smoke and emits small amounts of other pollutants. If the entire taxi fleet switched to LPG, Hong Kong's high particulate emissions would drop by 30 per cent (HK EPD, 1999). Table 3.4 shows the differences in emissions between LPG and diesel taxi. The Hong Kong Government requires all newly-registered taxi to be LPG taxis since the end of the year 2000. Also, the rest of the fleet will be encouraged to switch to

LPG by the year 2005.

3.1.2 Traffic Air Pollution Control in Hong Kong

In Hong Kong, there are two main air pollution problems, which are street-level pollution and smog. The major source of street-level pollution is emissions from diesel vehicles. Therefore, the Hong Kong Special Administrative Region Government gives high priority to controlling air pollution by implementing a wide range of measures to control emissions from motor vehicles. Motor vehicles, especially diesel vehicles, are the main cause of high concentrations of respirable suspended particulates (RSPs) and nitrogen oxides (NOx) at street level in Hong Kong. In order to solve the problems, a comprehensive programme was introduced in year 2000, which is aimed to reduce RSPs and NOx from motor vehicles by 80% and 30% respectively by the end of 2005. The key strategies include: 1) adopt tighter fuel and vehicle emission standards, 2) adopt cleaner alternatives to diesel where practicable, 3) control emissions from remaining diesels vehicles with devices that trap pollutants, 4) strengthen vehicle emission inspections and enforcement against smoky vehicles and 5) promote better vehicle maintenance and eco-driving habits (HK EPD, 2002).

Since 1995, emission standards for newly-registered vehicles have been progressively tightened. Recently, Euro III emission standards is implemented in step with the European Union. A Euro III diesel vehicle emits 90% less particulates and 40% less nitrogen oxides as compared to a pre-Euro vehicle manufactured 6 years ago.

As of at 1st April 1991, all petrol stations have been required to sell unleaded gasoline in Hong Kong. To encourage the switch, the government charged a lower duty on unleaded gasoline. In year 1999, leaded gasoline has totally changed into unleaded gasoline. In year 2000, benzene content in unleaded gasoline has reduced from 5% to 1%. Also, the quality of gasoline has upgraded to meet the current European standards since January 2001. Moreover, Hong Kong is the first place in Asia to introduce ultra low suphur diesel (ULSD). The suphur content is only 0.005%, which is the only motor diesel fuel available at petrol refilling stations in Hong Kong. Furthermore, the Hong Kong Government is strongly encouraging to switch 18,000 diesel taxis to environmentally cleaner vehicle by using LPG. By early 2002, more than 75% of taxis had switched to LPG. Apart from LPG taxis, a trial of LPG and electric public light buses was completed in

2001. The trial confirmed that both alternatives are less polluting than diesel and are feasible options for light bus operation in Hong Kong (HK EPD, 2002).

3.2 Meteorology of Hong Kong

Hong Kong is a rapidly changing subtropical and coastal metropolis in the western Pacific Rim, which is located at the southeast edge of the Asian continent. The climate in Hong Kong is governed by the Asian monsoon system (Ramage, 1971). A monsoon is induced by the different rates of cooling and heating of land and water. Usually, large temperature differences occur between continents and oceans.

The monsoon climate gives rise to four fairly marked seasons in Hong Kong. In autumn and winter, a northwesterly wind prevails in North China, Korea and Japan while a northeasterly wind prevails in South China and the South China Sea including Hong Kong. The cool and dry air masses from the Asian continent as far as Siberia usually travel southeasterly over the Asian continent and the Yellow Sea to South Korea and southern Japan. These air masses then curve southwesterly across the East Sea and southeastern China to Hong Kong (Cheng et al., 1991). In summer, the southwesterly wind becomes the prevalent wind in South China, the South China Sea and Hong Kong. The warm and damp marine air masses that originate from the South China Sea are carried to Hong Kong by a southwest wind. In spring, the northeast monsoon changes into the southwest monsoon (Qin. et al., 1997).

Table 3.1 Number of Licensed Motor Vehicles from 1996-2001

Type	1996	1997	1998	1999	2000	2001
Motor cycles	22650	23511	23343	24258	25500	27116
Private Cars	293381	314833	318137	321617	332379	340568
Taxis	17789	17918	18053	18008	17983	18045
Buses	10290	11063	11819	12076	12523	13033
Public Light Buses	4313	4335	4343	4343	4340	4340
Private Light Buses	2303	2230	2158	2101	2051	2012
Light Goods Vehicles	79162	78876	75899	73527	72429	70891
Medium Goods Vehicles	35611	36968	36551	37526	38945	38513
Heavy Goods Vehicles	2018	2435	2601	2717	2903	3181
Special Purpose Vehicles	316	370	406	433	487	550
Government Vehicles	7282	7689	7363	7368	7242	7127
Trailers	21661	20583	18474	19278	19723	18394
Rickshaws	8	7	5	4	4	4
Total Number of Vehicles	496784	520818	519425	523256	536509	543774

Source: Transport Department (2002)

Table 3.2 Annual VKT in Hong Kong (100 Million Kilometers)

Vehicle Type		1997	2000
Hong Kong	Taxi	17	22
	Motorcycle	3	4
	Private car	42	59
	Light duty vehicle[1]	28	35
	Heavy duty vehicle[2]	18	24
	Total	*108*	*144*

1: Include passenger van, public light bus and light goods vehicle,

2: Include heavy goods vehicle, non-franchised bus, single & double deck franchised bus;

Source: Hong Kong Environment Department 2002

Table 3.3 Licensed Vehicles by Fuel Type – March 2002

	Gasoline	Diesel	Electric	LPG	Others*	Total
Motor cycles	26963	0	5	0	0	26968
Private Cars	337564	2357	11	0	36	339968
Taxis	0	3270	0	14819	0	18089
Buses	0	13120	1	0	0	13121
Public Light Buses	0	4284	0	54	0	4338
Private Light Buses	7	1986	1	10	0	2004
Light Goods Vehicles	3543	66762	2	0	3	70310
Medium Goods Vehicles	0	38164	0	0	1	38165
Heavy Goods Vehicles	0	3195	0	0	0	3195
Special Purpose Vehicles	64	432	23	22	22	563
Total Number of Vehicles	368141	133570	43	14905	62	516721

*Including various vehicles with power plants such as hybrid engine, turbine engine, fuel cell vehicle etc. which fuel type cannot be further classified

Source: Transport Department (2002)

Table 3.4 Differences in Emissions between LPG and Diesel Taxi (in mg/m^3)

	LPG Taxi	Diesel Taxi
Carbon Monoxide	0.33-0.41	0.59-1.00
Hydrocarbons	0.19	0.38-1.00
Nitrogen Oxides	0.01-0.04	0.73-1.00
Particulate Matters	Negligible	0.57-1.00
Smoke	Negligible	0.48-1.00

Source: HK EPD (1999)

Figure 3.1 Busy Traffic in a Commercial Area in Hong Kong (Wan Chai)

CHAPTER 4 METHODOLOGY

4.1 Sampling Method

Canister-based grab sampling of volatile organic compounds is used in this research project. It is a viable and widely used approach that is based on research and performance over the past several years. The method is described as part of the US EPA *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* under the title, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Polished Canister Sampling and Gas Chromatographic (GC) Analysis". It is usually referred to as Compendium Method TO-14. This method is applied under most conditions encountered in sampling of ambient air into canister (Winberry et al., 1988).

The canisters employed for whole air sampling were manufactured by the Blake/Rowland group at the University of California (UCI), Irvine. The canisters are currently a seventh generation design and are conditioned and tested regularly to ensure reliability. In this research project, subatmospheric pressure sampling mode was adopted by using evacuated 2-L stainless steel canisters (Figure 4.1). Sub atmospheric sampling is to collect air sample without the assistance of a sampling pump. The canister is filled as internal canister pressure increases to ambient or near ambient pressure. After sampling, the canisters were sealed and returned to Irvine for subsequent chromatographic analysis.

4.2 Canister Cleaning and Preconditioning

Preconditioning involved cleaning the electro polished canister with hexane and acetone, then heating in an oven to 140°C overnight. Then the canisters were cleaned by evacuated and pumped overnight before being treated with distilled water vapor. In every two years, the canisters begin to grow certain gases. The gases given off at highest concentrations are ethene, propene, benzene and toluene. In order to reduce the growth effect to insignificant concentration levels, canisters are baked followed by flushing with very clean ambient air. During the baking procedure, the valves of the canisters are removed to prevent malfunctioning of the valves under very high temperature. The canisters are then reassembled into snakes and transported to a site in the Sierra Nevada Mountains, which is about 500 miles from the University of the California, Irvine and it is at an elevation of about 4 km. The site is in the free troposphere and has very low aerosol levels thus it is ideal for flushing canisters. The canisters will be pressurized to 40 psi and then vented. This procedure will be repeated 15 times. After the final filling, the valves will be closed (leaving 40 psi in the canisters) and the canisters will be transported back to the laboratory in UCI. Finally, the canisters will be allowed to sit for approximately one month and then 1 or 2 canisters will be assayed to determine that the canisters are ready for use. Whenever a canister is brought back from the field, the canisters were cleaned, verified free of contamination and returned to the air laboratory of the Hong Kong Polytechnic University.

4.3 Chemical Analysis

4.3.1 GC/MS System

Full details of the chromatographic analysis can be referred to Colman et al. (2001). A brief description of the operation procedure of the gas chromatography/mass spectrometry system is shown as below.

The grab air samples were analyzed by gas chromatography/mass spectrometry technique. Figure 4.2 shows an example of GC/MS system. The chromatographic systems remained in operation 24 hours a day. Continuous operation helps to stabilize the analytical systems and thus to produce an internally consistent data set.

Two separate but equal analytical systems were employed in this research project. Approximately 800 torr of air from each canister was introduced into the system manifold. Subsequently 700.0 torr of this sample was passed over glass beads (1/8" diameter, washed with acetone and heated at 350° C overnight) maintained at liquid nitrogen temperature, the rest was discarded. This procedure corresponds to a 1519 cm^3 sample aliquot at standard temperature and pressure. A Brooks Instrument mass flow controller model 5850E was used to regulate the flow, which was kept below 500 cm^3/min to ensure complete trapping of the relevant components and to prevent freeze-up. This procedure has the effect of pre-concentrating the relatively less-volatile components of the sample (such as halocarbons and hydrocarbons) while allowing volatile components (such as N_2, O_2, and Ar) to be pumped away. The less volatile compounds were then re-volatilized by immersing the sample loop in hot water (~80° C), and subsequently flushed into a helium carrier flow (head pressure 48 psi). This sample flow was then reproducibly split into five streams at a 1 to 6 port union (Valco Instruments, 1/16" manifold 1 to 6 ports, 0.75 mm inlet bore, 0.25 mm outlet bore, with one outlet port capped off). Each stream was chromatographically separated on an individual column and sensed by a single detector.

Three Hewlett-Packard 6890s Gas Chromatographs (GC) form the core of each analytical system. There are three types of detector included: electron-capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), flame-ionization detectors (FID, sensitive to hydrocarbons), and quadrupole mass spectrometers (MSD. for unambiguous compound identification and selected ion monitoring) were used.

The first HP-6890 (GC-1) system contains two columns. The first column is a J&W DB-5 (30 m; i.d., 0.25 mm; film, 1 μm) connected in series to a RESTEK 1701 (5 m; i.d., 0.25 mm; film, 0.5 μm), which was output to an ECD detector. The second column is a DB-5ms (60 m; i.d., 0.25 mm; film 0.5 μm), which was output to an MSD detector (HP-5973). The second HP-6890 (GC-2) contains a J&W DB-1 column (60 m; i.d., 0.32 mm; film, 1 μm) output to an FID detector. The third HP-6890 (GC-3) contains a J&W GS-Alumina PLOT column (30 m; i.d. 0.53 mm) connected in series to a DB-1 (5 m; i.d. 0.53 mm, film 1 μm), which was output to a FID detector, and a RESTEK 1701 (60 m; i.d. 0.25 mm, film 0.50

μm), which was output to an ECD detector. The oven parameters employed for each GC are listed in Table 4.1. Moreover, liquid nitrogen was used to achieve subambient initial temperatures.

The signal from each FID and ECD detector was output to a Spectra Physics 4400 integrator, which produced hardcopies of the analogue responses, and to a personal computer, where it was recorded digitally. Each MSD detector was output to a dedicated personal computer and digitally recorded. Each resulting chromatogram was manually modified, and each peak shape was individually checked.

Zero-air and nitrogen for use in the FID and ECD detectors were generated in the lab. House air was passed through a homemade glass wool filter, and then through a Whatman 64-02 air dryer equipped with a 100-12 BX prefilter. This removes oil, water. and any particulates from the air stream, which is then split and directed into a Domnick Hunter nitrox-nitrogen generator (NG7-0) and a Praxair zero-air generator (model Airlab WHA 76803). The output from these devices was then split further and directed into gas regulators for head pressure regulation. Before entering the analytical system, all gases employed were passed through a homemade graphite/molecular sieve trap to remove any remaining contaminants; in the case of helium and hydrogen (ultra-pure, purchased by the cylinder) an identical trap that was kept immersed in liquid nitrogen was connected in series. These traps were preconditioned (and regenerated) by flowing hydrogen gas through them at a temperature of 350°C for at least 24 hours. Both of the FIDs operate at a detector temperature of 250°C with a zero-air flow of 450 mL/min, an $H_{2(g)}$ flow of 40 mL/min, and a detector makeup gas flow of 20 mL/min $N_{2(g)}$. The ECDs operate at a detector temperature of 250°C with a detector makeup flow of 50 mL/min $N_{2(g)}$.

4.3.2 Calibration

Multiple standards were employed on each system. Working standards were run roughly every two hours, and calibrated standards were run at least twice daily. Pressurized cylinders of air are regularly collected from different environments and calibrated in lab for use as standards. The primary reference standard for halocarbons was previously calibrated from static dilutions of standards prepared in the lab. For hydrocarbons, a propane standard purchased from the National Bureau of Standards (SRM 1660A) was used to calculate a

Per-Carbon-Response-Factor (PCRF) for the FIDs. This was compared to PCRFs calculated from more readily available (and economical) commercial standards (NIST and Scott Marin) to check the absolute accuracy of the commercial standards, as well as the appropriateness of using the same PCRF for different compounds. Then from analysis of the commercial standards, a different PCRF was assigned for each alkane from ethane to octane. This PCRF was then used for any compound with an equivalent number of carbons. The calibration scheme has been cross-checked against absolute standards from other group for both hydrocarbons and halocarbons.

4.3.3 Systematic Temporal Drift

The calibrated standards were employed to put all of the measurements on the same absolute scale, and as a check of the working standard. The working standard was employed because of the difficulty involved in calibrating and maintaining a set of "absolute" standards. Thus, their use is minimized whenever possible. The working standard was used to correct the data for drift (on a time-scale of tens of hours) in the detector response.

4.3.4 Experimental Precision Analysis

Once the working standard values have been detrended for systematic temporal drift, they can be used to give an estimate of the precision of the experimental apparatus. The mean and standard deviation values extracted from the frequency distribution plot can be used to estimate the precision of the experimental apparatus. The relative error in the standards was calculated for each detrended temporal section for each detector for each compound.

Although this represents a reasonable way to estimate the precision of the apparatus, it only tells us how precisely a component of a specific mixture of compounds can be measured. That is, because each standard always has the same mixing ratio of an individual compound any error due to a variable coelutor, or due to being on the tail of a variable compound, will not be captured. On the other hand, if the compound is present in low abundance in the working standard(s), then the precision may be underestimated by this procedure.

4.3.5 Homogenous Airmass Values

Another approach to estimating experimental precision is to calculate the relative standard deviation of samples thought to have been collected in a homogeneous airmass. The concept of a homogeneous airmass depends on both the residence time of the compound in question and how precisely it can be quantified.

Occasionally, a sample is rerun a number of times to obtain an estimate of precision and this is more or less equivalent to the homogeneous airmass estimate of precision. To arrive at the lab's working-standard-derived precision, the sample would have to be run periodically. However, this is impossible because each sample canister can only be analyzed a couple of times due to the limited volume of the canister.

4.4 Statistical Analysis

4.4.1 Pearson's Correlation

A statistical technique, Pearson's correlation, is used in this study. Pearson's correlation reflects the degree of linear relationship between two variables. It involves the calculation of a coefficient, which ranges from +1 to –1. When two variables with a correlation coefficient *(r)* approaching +1, it is apparent that a near "perfect positive" relationship occurs. When *r* approaching -1, it is apparent that a near "perfect negative" relationship occurs.

4.4.2 Principle Component Analysis (PCA)

The multivariate statistical method of Principle Component Analysis (PCA) is the best known and one of the earliest descriptive techniques (Pentecost et al., 1999). It is widely used in atmospheric science. The aim of PCA is to clarify the variation within a series of multivariate samples and display samples in a scatter-graph so that similar samples appear close together and dissimilar samples far apart. Therefore, it is a very useful tool for reducing the number of variables in a data set. In order to determine the number of factors to be retained, two most commonly used criteria were utilized to assess the calculated eigenvalues.

Latent Root: This criterion was used in almost all statistical software packages. This rule is very simple that all factors with eigenvalues less than 1 are considered insignificant and are disregarded.

Scree Test: The rule directs one to examine the graph of eigenvalues (Scree Plot), and discard factors beyond the point where the eigenvalues begin to level off forming a straight line with an almost horizontal slope.

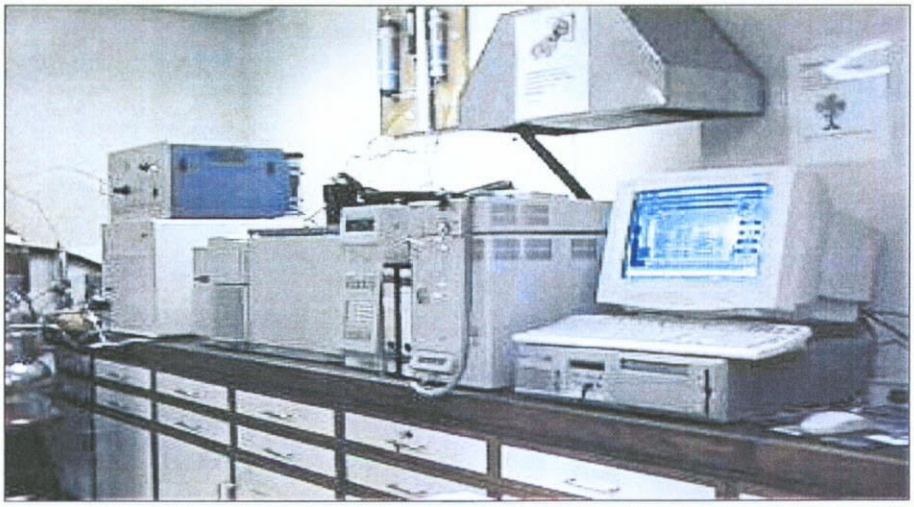
Table 4.1 Oven Parameters

	GC-1	GC-2	GC-3
Initial Temperature	-30°C	-50°C	-20°C
Initial Time	1.50 min	1.50 min	1.50 min
Rate 1	15°C/min	18°C/min	20°C/min
Final Temperature 1	50°C	30°C	200°C
Final Time 1	0	0	4.70 min
Rate 2	10°C/min	13°C/min	–
Final Temperature 2	110°C	145°C	–
Final Time 2	0	0	–
Rate 3	20°C/min	25°C/min	–
Final Temperature 3	200°C	200°C	–
Final Time	0.00 min	0	–
Run Time	17.33 min	16.99 min	17.20 min

Note: The designations GC-1, GC-2, and GC-3 are described in the text.

Figure 4.1 Stainless Steel Canister

Figure 4.2 An Example of GC/MS System (Hewlett Packard)



CHAPTER 5 TUNNEL STUDY

5.1 Introduction

Tunnel study has been widely used to determine the hydrocarbon speciation of vehicular emission as tunnel is a relatively homogeneous atmosphere (Haszpra and Szilagyi, 1994; Duffy and Nelson, 1996). However, tunnel measurements do have some limitations such as no cold start emission and bias in fleet distribution. But the compositions of the hydrocarbon species in the tunnel are still broadly representative of a large number of vehicles and fuel types used in the metropolitan area (Duffy and Nelson, 1996). Tunnels are usually constructed to overcome topographic constraints or to minimize traffic congestion in urban areas. Except for short tunnels (less than 300m), mechanical ventilation is required to decrease the concentration of pollutants emitted from vehicles to acceptable levels. Several types of ventilation system are used to achieve this purpose, which include longitudinal ventilation type, semi-transverse type and full transverse type. For those tunnels less than 300m, natural ventilation is used where pollutants are not expected to accumulate (Raton, 2001; Hsieh et al., 1999)

Apart from the study of the characteristics of VOC emissions in Hong Kong tunnels, we also compare the VOC emissions in different vehicle tunnels in Hong Kong, Guangzhou and Shenzhen (Figure 5.1) so that the vehicular emissions can be differentiated from other possible sources in the atmosphere.

5.2 Field Study

Five tunnels in three major cities in the PRD region were selected for measurements. These three major cities are Guangzhou, Shenzhen and Hong Kong, which are the fastest growing cities in South China. Two tunnels in Hong Kong i.e. the Cross Harbour Tunnel (Figure 5.2), Western Harbour Tunnel (Figure 5.3); two tunnels in Guangzhou i.e. the Bai Yun Tunnel (Figure 5.4), Zhu Jiang Tunnel (Figure 5.5); and one tunnel in Shenzhen i.e. Wu Tong Shan Tunnel are measured. The microenvironment condition and the daily patronage of individual tunnels are shown in Table 5.1.

In this study, grab sampling method is used where the average sampling time ranges from 30-40 seconds in tunnels. A total of twelve air samples (Cross Harbour Tunnel: 3; Western Harbour Tunnel: 3; Bai Yuen Tunnel: 2; Zhu Jiang Tunnel: 2 and Wu Tong Shan Tunnel: 2) were collected in the evacuated 2-L electropolished stainless steel canisters from 2nd to 9th June 2000. The canister was connected to a Teflon tube, which was extended outside the windows. The samples were collected during peak hours (8:00-9:00am and 6:00-7:00pm) when traveling through all the tunnels at around 40 kilometers per hour (km/h) on a private car. Also, the vehicle was kept at about 6 meters apart from the vehicle ahead during the sampling period.

Under the Road Tunnels (Government) Ordinance and Regulations, the speed limits of the Cross Harbour Tunnel and the Western Harbour Tunnel are 70 and 80 kilometers per hour (km/h) respectively. Private car and taxi are the major types of vehicle (>60 %) that travel through the two selected tunnels in Hong Kong (Transport Department, 2002). The other vehicle types include bus, motorcycle and goods vehicle. For the tunnels in Guangzhou and Shenzhen, the speed limit in the tunnels is 50 kilometers per hour (km/h). Since the Zhu Jiang Tunnel is situated at the urban area, heavy goods vehicles are not allow traveling through the tunnel during most of the day (China Infobank, 2002). For the other two tunnels, they links the urban area to the suburban / rural area. Therefore, there is no limitation on heavy goods vehicle travel through the tunnels.

5.3 Result and Discussion

In this study, a total of 55 species of VOC were measured in the five tunnels. The 55 VOCs were divided into five hydrocarbon groups, which include alkanes, alkenes, alkynes, aromatics and chlorinated hydrocarbons.

5.3.1 Characteristics of VOC Emissions in Hong Kong Tunnels

The top 10 species of VOCs in the Hong Kong tunnels are listed in Table 5.2. The most commonly found VOCs in these tunnels are mainly composed of light hydrocarbons (C_2-C_5) such as ethene, ethyne, propene, i-pentane, i-butene plus aromatic hydrocarbons such as toluene and benzene. The concentration of the top 10 species of VOC ranged from 3.7 to 92.0 ppb with ethene having the highest concentration. Among the top 10 species, ethene and ethyne were the most abundant species in both tunnels of Hong Kong. Similar results were found in the Caldecott Tunnel in U.S.A. where ethene and ethyne were the most abundant light hydrocarbons in the tunnel, which were 164.9 and 65.16 ppb respectively (Zielinska et al., 1994). Stoeckenius et al. (1994) also found that ethene and ethyne are mainly emitted from vehicle exhaust or in air, which has high contribution from vehicular exhaust emissions. In Hong Kong, the number of vehicle is increasing every year. So, high concentrations of ethene and ethyne may emit from vehicle exhaust. Other than light hydrocarbons, toluene and benzene were among the top 10 species, and they are mainly from combustion processes and mobile sources. Thus, it shows that the VOCs emissions in tunnels are mainly from vehicles.

For the two tunnels in Hong Kong, the concentration ranking of the top 6 VOCs are the same. The ranking is (1) ethene, (2) ethyne, (3) toluene, (4) i-pentane, (5) propene and (6) benzene. Since the exhaust gas composition reflects to a large extent the characteristics of the fuel used, the ranking of the VOC species confirmed the consistency of fuel used in Hong Kong. Comparing the VOC concentrations, we found that the Cross Harbour Tunnel VOC concentrations nearly doubled the Western Harbour Tunnel for the top 10 VOC species. As seen from Figure 5.6, which presents the concentration of VOC groups and the total VOC concentration in different tunnels, the total VOC concentration in the Cross Harbour Tunnel was 331.7 ppb, which approximately doubled the Western Harbour Tunnel (154.3 ppb). Total VOC is defined as the sum of the concentrations of the quantified species in this study. The higher VOC concentration in the Cross Harbour Tunnel may due to the higher traffic volume (Table 5.1). The daily patronage of the Cross Harbour Tunnel in 2000, which is the busiest tunnel in Hong Kong, approximately tripled the Western Harbour Tunnel. Except different traffic volume, the two tunnels have different number of lanes. The Cross Harbour Tunnel is a dual two-lane tunnel while the Western Harbour Tunnel is a three-lane tunnel. The Western Harbour Tunnel is wider than the Cross Harbour Tunnel and the VOC concentration may be diluted more in the Western Harbour Tunnel. Therefore, it is reasonable that the VOC concentrations in the Cross Harbour Tunnel were higher than that of the Western Harbour Tunnel.

From Figure 5.7, which presents the percentage of VOC groups in different tunnels. We found that the percentages of different hydrocarbon groups in the two tunnels in Hong Kong were almost the same. Similar percentages of hydrocarbon groups reflect that the compositions of vehicle emission in both the tunnels are very similar, indicating the consistent use of fuel in Hong Kong. In addition, alkenes and alkanes were the most abundant hydrocarbons in tunnels. The high percentage of alkenes and alkanes indicated that the VOCs collected are vehicular exhaust oriented.

Toluene and benzene were abundant in both tunnels in Hong Kong. According to previous studies, toluene and benzene are recommended to use as the tracers for vehicle exhaust (Stoeckenius et al., 1994). Both toluene and benzene are aromatic hydrocarbons. They have detrimental effects on human and contribute to photochemical smog formation (Na and Kim, 2001). According to the U.S. Environmental Protection Agency, benzene is classified as one of the carcinogens, which represent a serious threat to human health and can cause cancer on human (Guicherit. 1997). On the other hand, toluene is classified as a suspected carcinogen. Thus, the concentration level of aromatic hydrocarbons is very important in assessing the health impact of tunnel air quality. The contributions of aromatic VOC in the Cross Harbour Tunnel and the Western Harbour Tunnel were 17.0 % and 17.5 % respectively. The high percentage of aromatic VOCs can be explained by the alteration of fuel used in Hong Kong recently. In 1999, the local gasoline formulation totally changed from leaded gasoline to unleaded gasoline. Aromatic compounds and oxygenated compounds are commonly added into unleaded gasoline to increase the octane index during fuel reformulation. According to the statistics provided from the Census and Statistics Department of Hong Kong, the aromatics percent weight composition of unleaded gasoline has increased about 10 % (Sin et al., 2001). Thus, the impacts of the emission of aromatic VOCs become greater. Aromatic contribution, in particular high level of benzene, is a great concern in tunnel air quality since it proves a threat to human health.

5.3.2 Comparison of VOC Emissions in Hong Kong, Guangzhou and Shenzhen Tunnels

From Table 5.2, the most commonly found VOCs in Guangzhou and Shenzhen tunnels are mainly light hydrocarbons (C_2-C_5) The finding is the same as the tunnels in Hong Kong. Among the top 10 species, ethene and ethyne were the most abundant species in all the tunnels in the Pearl River Delta. The ethene and ethyne concentrations ranged from 49.2 to 92.0 ppb and 37.1 to 72.8 ppb respectively. Other than light hydrocarbons, toluene and benzene were also abundant in the top 10 species. Their concentration ranged from 10.8 to 24.7 ppb and 8.2 to 18.5 ppb respectively.

By comparing the two tunnels in Guangzhou (Bai Yun and Zhu Jiang), it was found that the VOC concentrations in Zhu Jiang Tunnel were higher than that in the Bai Yun Tunnel for the top 10 VOC species. According to Table 5.1, the length of Zhu Jiang Tunnel is 1239m, which is much longer than that of the Bai Yun Tunnel (242m). Therefore, VOCs may accumulate more in Zhu Jiang Tunnel. On the other hand, the Bai Yun Tunnel is a short tunnel with a length of 242m. Usually, the air exchange in a short tunnel is induced by natural wind and the piston effect created by the vehicle movement (Raton, 2001). Thus, the lower VOC concentration in Bai Yun Tunnel may due to the dilution by the action of natural wind. Moreover, the Zhu Jiang Tunnel is located at urban area with heavy traffic nearby while the Bai Yun Tunnel is located at rural area. Therefore, the background concentrations of VOCs should be higher in the Zhu Jiang Tunnel. In addition, vehicle types and fleets may also affect the VOC concentrations.

In Wu Tong Shan Tunnel in Shenzhen, VOC species were found similar to the Guangzhou tunnels. The ethene concentration (92.0 ppb) was the highest followed by ethyne (70.2 ppb), i-pentane (25.5 ppb), propene (25.2 ppb) and toluene (14.9 ppb). As shown in Table 5.2, these species also ranked in the top 5 VOCs in Bai Yun and Zhu Jiang Tunnel. This reflects that the exhaust gas compositions in Guangzhou and Shenzhen are quite similar.

Among the three tunnels in the Pearl River Delta, the highest total VOC concentration occurred in Zhu Jiang Tunnel. It may be due to higher traffic volume, higher background level of VOC and different fuel used in this tunnel. However, there is no statistics available for the daily patronage of Zhu Jiang Tunnel.

On the other hand, if comparing the total VOC emissions from the Western Harbour Tunnel in Hong Kong to the Wu Tong Shan Tunnel in Shenzhen, the VOC emission for the latter is higher although the daily patronage is much lower. Besides, there is no ventilation system in Wu Tong Shan Tunnel so that VOCs may accumulate inside the tunnel. Therefore, higher VOC concentration was found in the Wu Tong Shan Tunnel. Referring to Figure 5.7, comparing the percentage of different hydrocarbon groups in the two tunnels in Guangzhou, it was found that the concentrations of alkanes, aromatics and alkynes were very similar with differences no more than 1 %. However, the chlorinated hydrocarbons in the Zhu Jiang Tunnel were approximately 8 times higher than that in the Bai Yun tunnel. Generally, the chlorinated hydrocarbons are mainly from solvent or paint evaporation. So, the only reason, which may explain the unexpectedly high percentage of chlorinated hydrocarbons in Zhu Jiang Tunnel, is the solvent leakage from the goods vehicles when traversing the tunnel on the sampling day. The higher emissions in the tunnels of Guangzhou and Shenzhen may be due to more heavy vehicles passing through them. Also, poor maintenance or vehicle deterioration may affect the efficiency of the emission control system and lead to higher emission in these cities. The use of inferior fuel may also be a cause. Similar to the tunnels in Hong Kong, alkenes and alkanes were the most abundant hydrocarbons in these tunnels. In Wu Tong Shan Tunnel, the percentage of alkanes was approximately the same as alkynes with 20 %. Other than alkanes and alkynes, alkenes was the most abundant group of VOC in Wu Tong Shan Tunnel with 51.4 %.

In a recent tunnel study in Seoul (South Korea), alkanes (46.3 %) was the most abundant hydrocarbon group, followed by aromatics, alkenes, alkynes and naphthenes in the Sangdo Tunnel in all seasons. Among the 45 compounds analyzed in the study, ethene (65.5 ppb) was the most abundant compound observed in the tunnel (Na and Kim, 2002), which is the same as both tunnels in Hong Kong. In our study, alkene was the most abundant hydrocarbon group, followed by alkanes in all the five tunnels in Hong Kong, Guangzhou and Shenzhen.

In the tunnel study, ethyne and ethene were the most abundant species among all the VOCs and both are the tracers for vehicle exhaust (Stoeckenius et al., 1994). Therefore, the characteristic ratio of ethyne-to-ethene (EE ratio) is used as the indicator of vehicle exhaust. The EE ratios of tunnel in Hong Kong, Shenzhen and Guangzhou were shown in Table 5.3. The EE ratios in the two tunnels in Hong Kong were 0.6. For the tunnels in Guangzhou and Shenzhen, the EE ratios ranged from 0.8-1.0. It is clear that the characteristic ratios of ethyne-to-ethene in Hong Kong, and the other two cities are different. Among the three tunnels in South China, the EE ratio of Zhu Jiang Tunnel in Guangzhou was 1.0, which was higher than that in the other tunnels. According to Table 5.2, it is because of the higher ethyne concentration in this tunnel. The higher EE ratios in these two South China cities indicate a higher contribution of high emitting (or non-catalyst) vehicles (Sagebiel et al., 1996). Also, such difference between Hong Kong, Guangzhou and Shenzhen tunnels may due to the different fuel used and the exhaust gas compositions in Hong Kong and these South China cities. Moreover, different vehicle types and age of vehicle may lead to different emission of VOCs. By comparing the EE ratios with other cities in Table 5.2, the EE ratio in Paris was the same as that in Hong Kong (Touaty and Bonsang, 2000). So, the exhaust gas composition in Paris and Hong Kong may be similar. Other than Paris, the EE ratios in California, Maryland and New Jersey were the same, which was 0.4 (Zielinska et al., 1994; Scheff et al., 1989). The EE ratio in Pennsylvania was 0.3 (Zielinska et al., 1994). The similar EE ratios indicate that the compositions of fuels used in the USA are close. However, it is obvious that the EE ratios in USA were lower than that in Hong Kong and South China. It reflects that each country may have its own characteristic ratios due to different vehicular fleets, exhaust control devices or composition of fuel used.

Apart from EE ratios, the characteristic ratio of benzene and toluene (BT ratio) is used to study vehicular emissions since benzene is a well-known tracer for combustion such as motor vehicle exhaust (Stoeckenius et al., 1994). The relative composition of VOCs in the ambient air has been used as an indicator of different source contributions to the atmosphere, such as using the ratio of toluene-to-benzene concentration to distinguish the contributions from automobile exhaust to VOCs measured in urban air (Hsieh et al., 1999). Table 5.4 listed the BT ratios of the tunnels in HK, Guangzhou and Shenzhen. In this study, the BT ratios found in the three Guangzhou and Shenzhen tunnels ranged from 0.7 to 0.8. However, the BT ratios in the tunnels in Hong Kong were only 0.3. The significant difference between the tunnels in Hong Kong and South China was due to the high toluene concentration in Hong Kong. It is possible that the low BT ratio in Hong Kong is due to the local gasoline reformulation in 1999. The BT ratios found in other countries are also shown in Table 5.4. Generally, the BT ratios in the tunnels in Taiwan, Australia, USA and Hungary ranged from 0.6 to 0.7, which were more close to the BT ratios found in South China (Chiang et al., 1996; Duffy and Nelson, 1996; Zielinska et al., 1994; Haszpra and Szilagyi, 1994; Scheff et al., 1989). The comparisons of BT ratios highlight the problem of high toluene concentration in Hong Kong.

5.4 Conclusion

This study was aimed to obtain the characteristics of the VOC emissions in different vehicle tunnels in Hong Kong and to compare them with other major cities in the PRD region. We would also like to differentiate the emissions from other possible sources in the atmosphere. VOC measurements were carried out in five tunnels in Hong Kong, Guangzhou and Shenzhen using electropolished stainless steel canisters. In this study, the total VOC concentrations of tunnel range from 154.3 (Western Harbour Tunnel) to 501.5 ppm (Zhu Jiang Tunnel). Results demonstrate that alkenes (i.e. ethene, ethyne) and alkanes (i.e. i-pentane, n-butane, n-pentane) are the most abundant hydrocarbon groups in all of the five tunnels and these two groups are mainly from vehicle exhaust. The EE ratio in the two tunnels in Hong Kong were 0.6 while there in Guangzhou and Shenzhen ranged from 0.8-1.0. The BT ratio in Hong Kong is 0.3 while those in Guangzhou and Shenzhen ranged from 0.7-0.8. In all tunnels, ethene and ethyne were the predominant VOC species within the top 10 VOCs, which are recommended to be used as the tracer for vehicle exhaust. The EE and BT ratios in Hong Kong and the other two South China cities indicate that the vehicular fleets and composition of fuels used in the two areas are different. Also, the higher EE ratios in Guangzhou and Shenzhen indicate a higher contribution from high emitting vehicles; and the low BT ratio in Hong Kong indicates a pattern of high toluene contribution in Hong Kong.

Table 5.1 Background of Different Tunnels

Tunnel	Length (m)	Daily Patronage in 2000	Microenvironment condition
Cross Harbor	1900	120,000	Dual two-lane, immersed tube, uni-direction, links between two urban commercial areas, cross-harbour tunnel
Western Harbor	2000	43,000	Dual three-lane, immersed tube, uni-direction, links urban residential area and urban mixed residential/commercial area, cross-harbour tunnel
Bai Yun	242	*	Dual three-lane, uni-direction, links rural area and urban mixed residential/commercial/partial industrial areas, traverse mountain tunnel
Zhu Jiang	1239	*	Triple two-lane (include one for mass transit railway), immersed tube, uni-direction, links industrial area to urban area, cross-river tunnel
Wu Tong Shan	2493	26,046	Dual two-lane, uni-direction, links rural area and urban mixed residential/commercial/industrial area, traverse mountain tunnel

* No statistics available

Table 5.2 Top 10 VOCs in Different Tunnels (Average Concentration in ppb)

	Cross Harbour (Hong Kong)	ppb	Western Harbour (Hong Kong)	ppb	Bai Yun (Guangzhou)	ppb	Zhu Jiang (Guangzhou)	ppb	Wu Tong Shan (Shenzhen)	ppb
1	Ethene	74.7	ethene	36.2	Ethene	49.2	ethyne	72.8	ethene	92.0
2	Ethyne	44.4	ethyne	23.3	Ethyne	37.1	ethene	71.7	ethyne	70.2
3	Toluene	44.3	toluene	20.6	i-pentane	28.9	i-pentane	50.0	i-pentane	25.5
4	i-pentane	27.8	i-pentane	11.5	Propene	12.2	toluene	24.7	propene	25.2
5	Propene	19.6	Propene	10.1	Toluene	10.8	propene	20.0	toluene	14.9
6	Benzene	12.0	benzene	6.5	2+3-methylpentane	8.5	benzene	18.5	i-butene	12.2
7	n-butane	11.3	i-butene	4.4	Benzene	8.2	2+3-methylpentane	16.4	benzene	11.8
8	n-pentane	8.9	n-pentane	3.9	2-methyl-2-butene	8.1	n-butane	14.8	2+3-methyl pentane	10.9
9	2+3-methyl pentane	8.4	ethane	3.8	n-butane	6.3	2-methyl-2-butene	14.3	ethane	9.5
10	Ethane	6.9	2+3-methylpentane	3.7	n-pentane	6.2	propane	11.5	2-methyl-2-butene	8.6

Table 5.3 Ethyne/Ethene Ratios of the Tunnels in HK and the PRD Cities

Tunnel	Location	EE Ratio	Reference
Cross Harbor	Hong Kong	0.6	This study
Western Harbor		0.6	
Bai Yun	Guangzhou	0.8	
Zhu Jiang		1.0	
Wu Tong Shan	Shenzhen	0.8	
Thiais	Paris (France)	0.6	Touaty, 2000
Sydney	Sydney (Australia)	1.1	Duffy, 1996
Caldecott	California (USA)	0.4	Zielinsla, 1994
Fort McHenry	Maryland (USA)	0.4	Zielinska, 1994
Tuscarora	Pennsylvania(USA)	0.3	Zielinska, 1994
Lincoln	New Jersey (USA)	0.4	Scheff, 1989

Note: EE —ethyne-to-ethene

Table 5.4 BT Ratios of the Tunnels in HK and the PRD Cities

Tunnel	Location	BT ratio	References
Cross Harbor	Hong Kong	0.3	This study
Western Harbor		0.3	
Bai Yun	Guangzhou	0.8	
Zhu Jiang		0.7	
Wu Tong Shan	Shenzhen	0.8	
Hsin-Hai	Taipei (Taiwan)	0.6	Chiang,1996
Sydney Harbour	Sydney (Australia)	0.7	Duffy, 1996
Caldecott	California (USA)	0.6	Zielinska, 1994
East-west	Budapest (Hungary)	0.6	Haszpra, 1994
Lincoln	New Jersey (USA)	0.7	Scheff, 1989

Note: BT — benzene-to-toluene

Figure 5.1 Map of the Pearl River Delta (PRD)

Figure 5.2 Cross Harbour Tunnel in Hong Kong

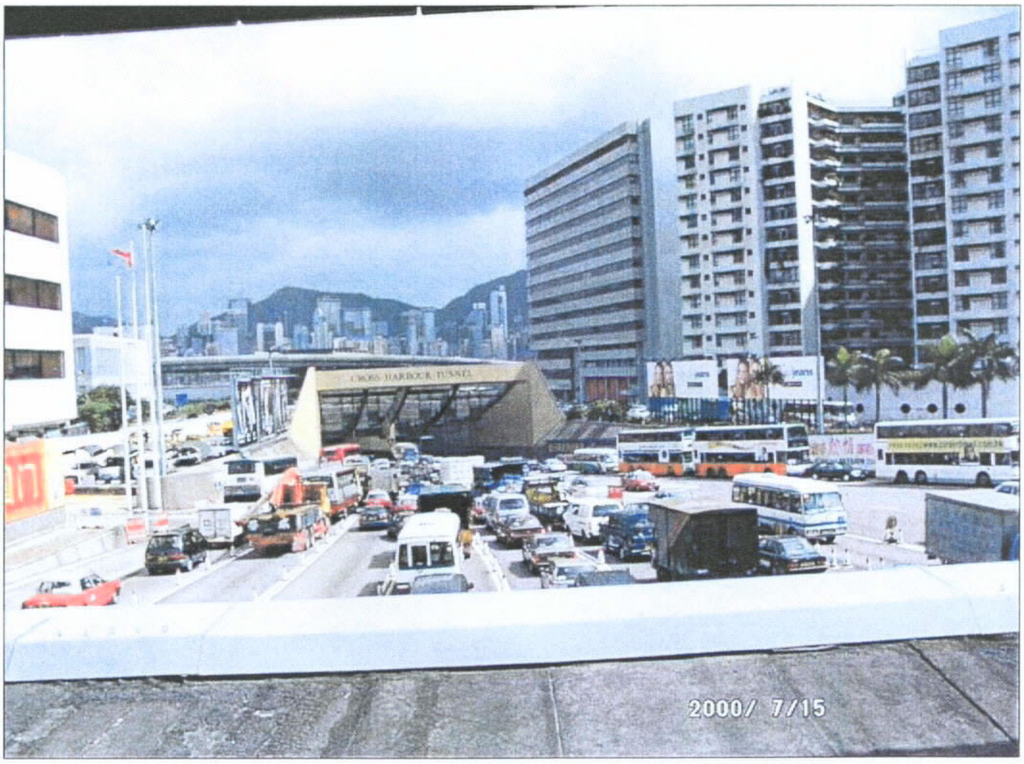


Figure 5.3 Exit of the Western Harbour Tunnel in Hong Kong

Figure 5.4 Bai Yun Tunnel in Guangzhou

Figure 5.5 Zhu Jiang Tunnel in Guangzhou

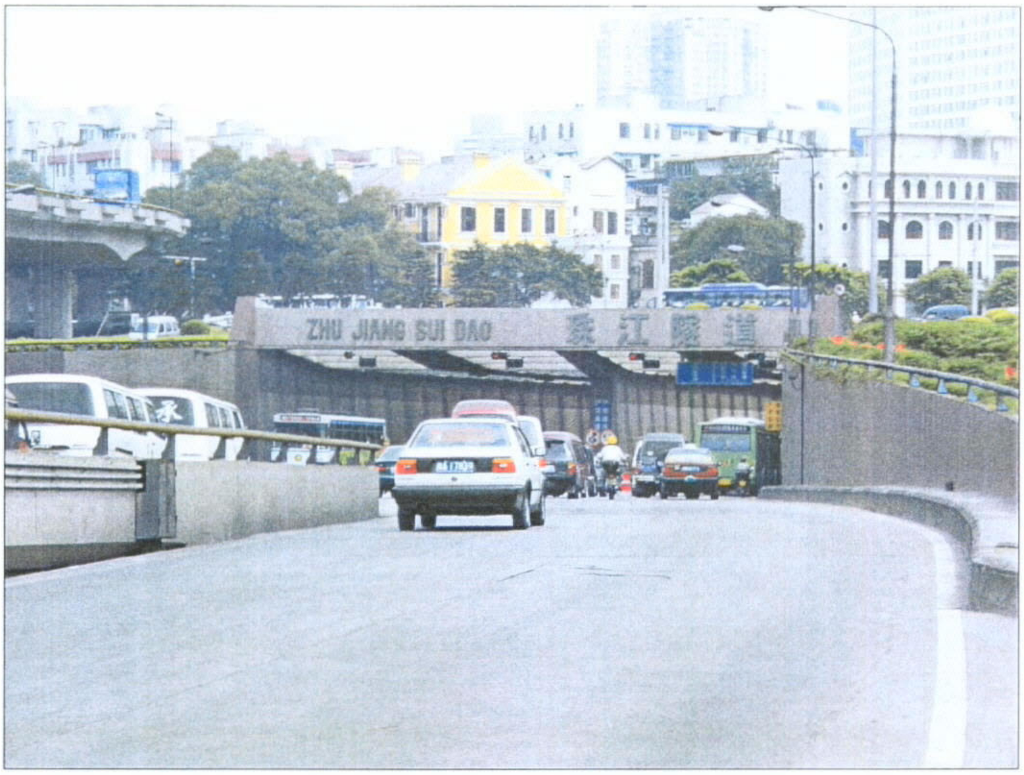


Figure 5.6 Concentration of VOC Groups in Different Tunnels

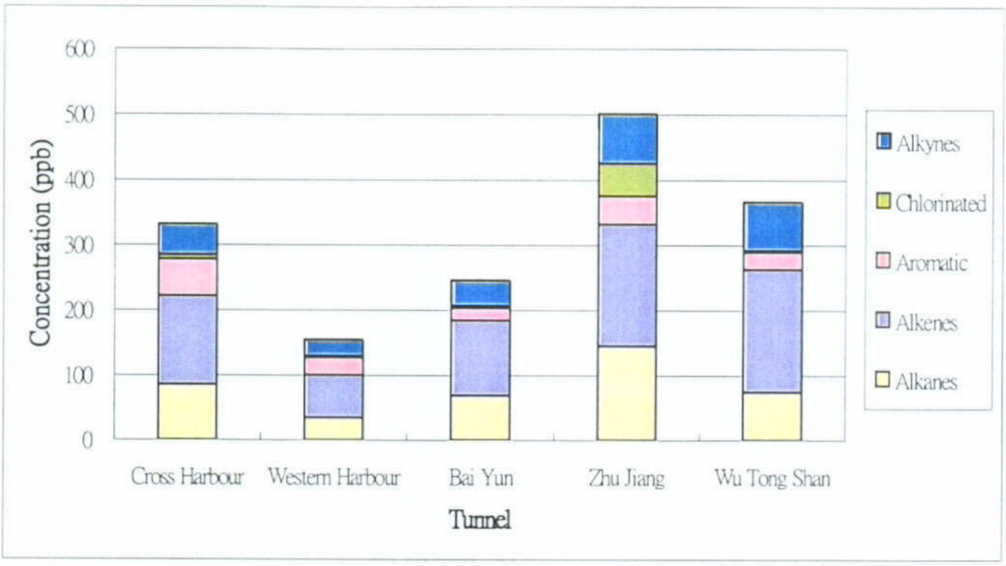
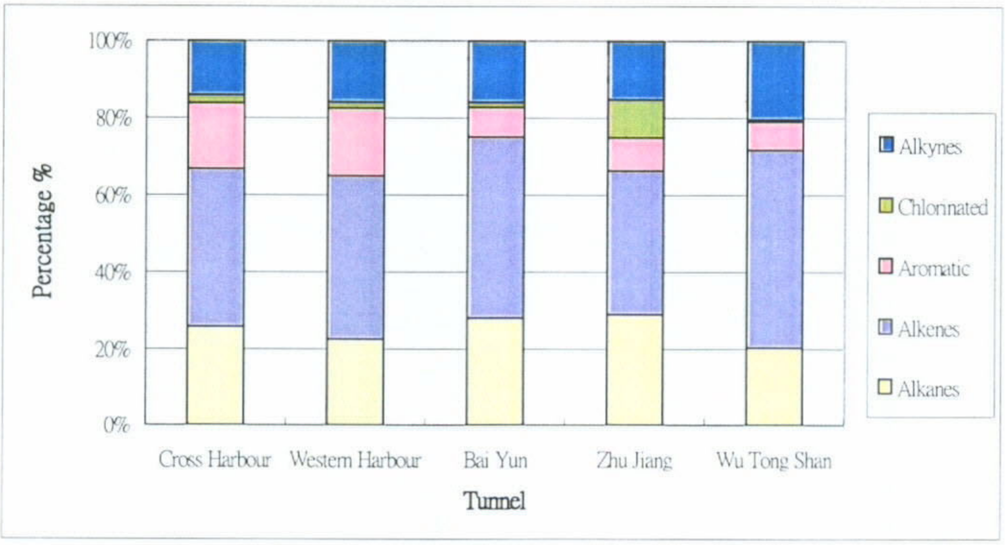


Figure 5.7 Percentage of VOC Groups in Different Tunnels



CHAPTER 6 TRAFFIC RELATED VOC EMISSIONS IN HONG KONG

6.1 Introduction

The predominant source of volatile organic compounds (VOCs) is vehicular emission in Hong Kong (Ho et al., 2002). The composition of the emission depends on the fuel, the type and operating conditions of the engine, and the effects of emission control devices. In general, the air pollution problems in Hong Kong are caused by several factors: high population density, high-rise buildings that hinder or prevent the circulation of air at street level, combined with high traffic volume and poor awareness of the public about the pollution situation. Among those factors, the high traffic volume is the most significant factor that leads to the poor air quality in Hong Kong. The total number of licensed vehicle exceeded 500,000 in 2000 and it had increased over 45% in the past decade. According to the Transport Department in Hong Kong, over 10 million passenger journeys are made on public transport system everyday. Therefore, vehicular emission is the major source of air pollution in Hong Kong like other metropolitan cities.

In this study, VOC source profiles were collected from different vehicular emissions in Hong Kong (Fig. 6.1). It is aimed to find out the VOC fingerprints of different vehicular emissions in Hong Kong. Moreover, we have prepared a comparison of VOC source profiles between different vehicular emissions.

6.2 Vehicular Emission Sampling

6.2.1 Tunnels in Hong Kong

In this study, the tunnels selected include the Cross Harbour Tunnel and the Shing Mun Tunnel. Relevant information and the daily patronage of individual tunnels are shown in Table 6.1. A total of six air samples were collected from 4th to 6th July 2001, which include three samples from the Cross Harbour Tunnel and three samples from the Shing Mun Tunnel. Sampling methodology is presented in Chapter 5.

6.2.2 Vehicular exhaust

Vehicular exhaust samples were collected from the exhaust pipe of different types of vehicle when they are temporally stopping for loading and unloading on roadside from 1st to 14th July 2001. A total of 41 air samples were collected in the evacuated 2-L electropolished stainless steel canisters. The average sampling time ranges from 30-40 seconds. Various transport modes include bus, light bus, taxi, goods vehicle and private car. Grab air samples were collected from eleven diesel buses, four diesel public light bus, four diesel taxis, four LPG taxis, seven diesel medium goods vehicles, three diesel heavy good vehicles and eight gasoline private cars. In this study, various types of vehicles are divided into 3 groups, which include gasoline-powered vehicle, diesel-powered vehicle and LPG-powered vehicle. In Hong Kong, all buses and medium/heavy goods vehicles are powered by diesel. More than 99% of private cars are powered by gasoline. Since the Hong Kong Government strongly encourages the conversion of diesel taxis into LPG taxis, more than 80% of taxis are now powered by LPG. In general, more than 70% of vehicles are powered by gasoline and around 25% of vehicles are powered by diesel in 2001 (Transport Department, 2002).

6.2.3 Refueling emission

At petrol stations, grab air samples were collected close to the oil tank of the vehicle during refueling process. A total of six air samples were collected in the evacuated 2-L electropolished stainless steel canisters from 16th to 18th July 2001. Two grab air samples were collected from each petrol station, which include Shell, Caltex and Esso. The average sampling time ranges from 30-40 seconds. The refueling emission profiles represent the commonly used regular unleaded gasoline in Hong Kong. Gasoline is now the most commonly used fuel in Hong Kong and it is one of the sources of VOC emission. So, it is significant to investigate the VOC emissions in Hong Kong by obtaining the gasoline refueling emission profile.

6.3 Results and discussion

In this study, a total of 40 species of VOCs were measured for the vehicular sources in Hong Kong. Measured concentrations of individual organic species showed a significant variation from canister to canister. So, individual VOC species concentrations were normalized to the total measured VOC. Table 6.2 shows a summary of all the vehicular emission profiles in percentage. In order to investigate the VOC emission characteristic of different vehicular sources, the 40 species of VOC were further divided into four hydrocarbon groups, which include alkanes, alkenes, alkynes and aromatics.

6.3.1 Further Analysis of Vehicular Emissions in Hong Kong Tunnels

In general, the VOC in tunnels come from two major sources, which include vehicular exhaust emission and evaporative emissions (from fuel tank, engine etc.) (Kourtidis et al., 1999). The compositions of VOC in tunnels represent a composite of many on-road vehicles and fuel types used broadly in urban areas. For the tunnel measurement, the emission profiles of the two selected tunnels were very similar. The major components in both tunnels were ethene, ethyne, i-pentane and toluene, which ranged from 8.13 to 16.32% (Figure 6.2). The results match the previous tunnel study in Chapter 5. Similar results were found in the Caldecott Tunnel in U.S.A. In the tunnel, ethene, i-pentane and toluene were the most abundant light hydrocarbons, which ranged from 6.63 to 8.76% (Zielinska et al., 1994). Stoeckenius et al. (1994) also found that ethene and ethyne have high contribution from vehicular exhaust emissions. Moreover, i-pentane was found abundant in gasoline powered vehicle exhaust (Mugica et al., 2001).

The VOC concentration of different hydrocarbon groups is shown in Table 6.3 in ppb level. The total VOC concentration is defined as the sum of the concentration of the quantified species in this study. The total VOC concentration in the Cross

Harbour Tunnel was 399.7ppb, which is 2.36 times the Shing Mun Tunnel. The difference may be due to the variation in the composition of the vehicular fleet in the two tunnels. By further comparing the two tunnels, the concentration ratios within each hydrocarbon groups were closely related to the total VOC ratios. As shown in Table 6.1, the daily patronage of the Cross Harbour Tunnel (120,350) in year 2000 was 2.22 times the Shing Mun Tunnel (54,199). Therefore, the total VOC concentrations in the two tunnels correlated well with traffic volume. Moreover, the pattern for the contribution of different hydrocarbon groups in the two tunnels was similar, which may be due to the consistent fuel used in Hong Kong.

In Figure 6.3, alkane was the most abundant hydrocarbon group in both tunnels, which were around 35.1%, followed by alkene (29%), aromatic (25.2%) and alkyne (10.7%). This meant that alkane is the major composition of hydrocarbons in tunnels. Also, the percentages between the four hydrocarbon groups in the two tunnels were close, which reflect that the vehicular source profiles in both tunnels were similar. A recent study in a Seoul tunnel also found that alkane was the most abundant hydrocarbon group with 48.6%, which was higher than that of the two tunnels in Hong Kong (Na et al., 2002).

Previous studies indicated that toluene, benzene, ethylbenzene and xylene were the major photochemical reactive organic pollutants emitted from automobiles (Sigsby et al., 1987). Hence, the characteristic ratios based on this four typical aromatic hydrocarbons i.e. benzene, toluene, ethylbenzene and xylene (BTEX) were used to further compare and characterize the emission sources of VOCs inside the two tunnels. As shown in Table 6.4, the BTEX ratio of the Cross Harbour Tunnel and the Shing Mun Tunnel were 1.3 : 6 : 1 : 4.2 and 2.9 : 6.3 : 1 : 4.3 respectively. It is clear that the characteristic ratios are similar in both tunnels except benzene. According to Table 6.2, the contribution of benzene was higher in the Cross Harbour Tunnel. Also, percentage of benzene in private car exhaust was found the highest among various vehicle types. Therefore, the higher benzene contribution may due to the higher proportion of private cars using the Cross Harbour Tunnel. According to the public transport statistic in year 2001, there were 40% of private car used the Cross Harbour Tunnel (Transport Department, 2002).

The BTEX ratios of tunnels in other countries are shown in Table 6.4. The BTEX ratio in the Sydney Harbour Tunnel (Australia) was 5.3 : 8 : 1 : 5. It is clear that the contribution of toluene was higher than Hong Kong. The BTEX ratios in the Hsin-Hai Tunnel (Taiwan) and the Caldecott tunnel (U.S.A.) were 3 : 5 : 1 : 4 and 3.5 : 5.8 : 1 : 5.7 respectively. By comparing with the BTEX ratios of the two tunnels in Hong Kong, it is obvious that each country has its own characteristic ratios. It may due to different composition of the vehicular fleets and composition of fuel use.

6.3.2 Characteristics of Diesel Emissions

In this study, the diesel-powered vehicles include bus, public light bus, goods vehicle and taxi. The grab samples were collected from the exhaust pipes of vehicles. Therefore, the emission profiles can represent the characteristics of each vehicle type. From Figure 6.2, we found that the most abundant VOCs in the exhaust of diesel-powered vehicles were unsaturated hydrocarbons. Among all diesel-powered vehicles, the contribution of ethene was the highest with an average of 51.24%, followed by ethyne (16.68%), propene (10.96%) and benzene (3.33%). In general, the characterized emissions of these types of vehicles were quite similar, but there were differences as shown in Table 6.2. The contributions of ethane and toluene were a little higher in the bus exhaust than in other diesel-powered vehicles. Variation can be due to differences in engine type and emission control devices of each type of vehicle. Also, different brands of diesel used can lead to differences in emission profiles.

In Figure 6.3, the pattern for the contribution of different hydrocarbon groups in diesel powered vehicle exhaust was similar. Among the four hydrocarbon groups, alkene (67.8%) was the most abundant hydrocarbon, followed by alkyne (16.7%), aromatic (10.1%) and alkane (5.4%). Thus, alkene is the major composition of hydrocarbon in diesel powered vehicle exhaust.

However, heavier alkanes were determined to be more characteristic of diesel emissions according to a previous study (Chiang et al., 1996). Diesel exhaust also contains toxicologically relevant compounds such as benzene, toluene, ethylbenzene, xylene etc. In the hydrocarbon fraction, benzene and toluene are present in relative concentrations of 11 and 4% by weight respectively. In Guangzhou, the most abundant VOCs found in diesel exhaust include ethene.

propene and trans-2-butene (Wang et al., 2001), which is similar to that in Hong Kong. Although different results were found in different studies, the amount and composition of diesel exhaust are more related to fuel specification and engine condition.

6.3.3 Characteristics of Gasoline Emissions

Private car is the only gasoline-powered vehicle type in this study. The grab samples were collected from the exhaust pipes of private cars. In Hong Kong, almost 100% of private car are powered by gasoline. Moreover, gasoline is the most popular fuel used in Hong Kong and the number of gasoline powered vehicles accounted for 71% of the total number of vehicle. The most abundant VOCs in the exhaust of private car were toluene with 15.01%, followed by ethane (10.17%), m-xylene (9.77%) and i-pentane (7.72%). By comparing the most abundant VOC in the exhaust of private car with diesel-powered vehicles, we found that the contribution of ethene (51.83%) in the exhaust of diesel-powered vehicles was much higher than the contribution of ethene (6.03%) in the exhaust of private car. It reflects that the single VOC species, ethene, accounted for very large proportion of the total VOC concentration of the diesel powered exhaust.

In Figure 6.3, the pattern for the contribution of different hydrocarbon groups in private car exhaust was quite distinguishes from those of the diesel powered vehicles. Aromatic hydrocarbon was the most abundant hydrocarbon with 47%, followed by alkane (39.5%), alkene (13.1%) and alkyne (0.5%). The results reflect that the composition of the gasoline in Hong Kong is rich in aromatic hydrocarbons. The high composition of aromatic hydrocarbons can be explained by the local gasoline reformulation. In 1999, leaded gasoline has totally changed into unleaded gasoline. Aromatic compounds are commonly added into unleaded gasoline to increase the octane index during fuel reformulation. According to the statistics provided from Census and Statistics Department of Hong Kong, the aromatics percent weight of unleaded gasoline has increased about 10% (Sin et al., 2001). Therefore, the high concentrations of aromatic hydrocarbons, especially toluene and m-xylene were found in the exhaust of gasoline-powered vehicles.

Comparing the results of a study conducted by Montells et al. (2000), toluene and m+p-xylene were the dominant VOCs in gasoline exhaust, which is similar to the results that found in Hong Kong. Other than the two aromatic compounds, the gasoline exhausts were enriched in prop-1-ene, n-but-1-ene, benzene, 2,2,4-trimethylpentane, ethylbenzene and o-xylene. In a gasoline powered vehicle dominated tunnel in Mexico (Mugica et al. 2001), the most abundant VOCs include i-pentane, toluene, xylenes, propane and n-butane, which were also the most abundant VOCs in the gasoline exhaust in Hong Kong. Moreover, Stoeckenius et al. (1994) found that n-butane can be used as the tracer of gasoline use. This also can be applied on Hong Kong as high contribution of n-butane was found, which indicated the use of gasoline.

The characteristic ratio BTEX of private car was 2.1 : 4.9 : 1 : 6. It is clear that the contribution of benzene to private car was lower than that of toluene. On the other hand, the contributions of benzene to diesel-powered vehicles were higher than that of toluene. Also, the benzene contribution to private car was found at least two times lesser than that of diesel powered vehicles.

6.3.4 Characteristics of LPG Emissions

In Hong Kong, taxi is the only type of vehicle that is powered by LPG. Recently, the Hong Kong Government strongly encourages the conversion of taxis using diesel fuel into taxis using the cleaner fuel, LPG (Transport Department, 2001).

Due to this reason, there are more than 80% of taxis (12,590) in Hong Kong are powered by LPG instead of diesel as at end of March 2001. According to the Shell Gas Company in Hong Kong, LPG is a mixture of butane and propane (Shell International Ltd., 2002). In Figure 6.3, we found that the most abundant VOCs in the exhaust of LPG taxis were saturated hydrocarbons. The major components in LPG taxis include propane (27.98%), n-butane (27.05%), i-butane (18.93%) and ethane (16.35%). These four VOC species already accounted for more than 90% of the total VOC concentration. Other than saturated hydrocarbons, ethene, was the most abundant unsaturated hydrocarbon in the exhaust of LPG taxis, which was 4.78%.

Among the four hydrocarbon groups (Figure 6.3), alkane was the most abundant hydrocarbon, which accounted for 91% of the total VOC concentration. Following by alkene (7.4%), aromatic (1.4%) and alkyne (0.1%). Therefore, the LPG exhaust is characterized by the extremely large proportion of alkane when compare with other vehicular sources.

Similar to Hong Kong, the Taiwan EPA encourages the use of LPG in a small fleet of taxis as an alternative fuel in Taipei in order to improve the urban air quality. In Taiwan, the LPG exhausts were enriched in propane, n-butane and i-butane, which were similar to the composition of LPG exhaust in Hong Kong (Chang et al., 2001). Furthermore, similar composition of LPG exhausts was found in Mexico, which was enriched in propane, n-butane and i-butane (Schifter et al., 2000). In general, the major composition of LPG exhaust is lighter alkanes due to more complete combustion in engines than diesel and gasoline. According to previous studies, the weight fractions of propane in vehicle exhausts are small, ranging from 0.8 to 6.7% (Aronian et al., 1989; Nelson & Quigley, 1984; Wadden and Scheff, 1994) and propane is not present in gasoline and diesel fuels. However, the behaviors of LPG emissions may affect by the changes of ratios of propane to $C_2 \simeq C_5$ VOC (Na & Kim, 2001). Therefore, the compositions of LPG directly affect the contents of LPG exhaust. Since only LPG and butane fuel compose of $C_2 - C_5$ VOC, those VOC can be used as markers such as propane, i-butane, n-butane.

6.3.5 Characteristics of Petrol Station Emissions

Gasoline is the major automotive fuel used in Hong Kong. It is a low viscosity petroleum mixture with high vapor pressure, which would evaporate easily. The major components of the gasoline headspace vapor are the saturated hydrocarbons. In Table 6.2, the most abundant VOCs include i-pentane (51.67%), 2,3-dimethylbutane (12.43%), n-hexane (9.32%) and n-butane (6.78%). The contribution of i-pentane to evaporated gasoline is more than 50%. However, the contribution of i-pentane has dropped to 7.72% in the gasoline exhaust after combustion.

Alkane is the most abundant hydrocarbon among the four hydrocarbon groups, which accounted for 88% of the total VOC concentration (Figure 6.3). It is followed by alkene (21.6%), aromatic (5.6%) and alkyne (1.4%). By comparing with the aromatic proportion in gasoline exhaust (47%), the aromatic contribution was much lower in evaporated gasoline. Therefore, the gasoline exhaust can be characterized by large proportion of aromatic hydrocarbons, while the evaporated gasoline can be characterized by large proportion of alkane.

The characteristic ratio BTEX of the petrol stations was 6 : 189.2 : 1 : 5. It is clear that the contribution of toluene to gasoline evaporation was particularly high.

According to a previous study in USA, the BTEX ratio of gasoline evaporation was 4.2 : 6.4 : 1 : 2.1 (Doskey P.V., 1992). It is clear that the toluene proportion of the gasoline in Hong Kong is quite high. It reflects the characteristic of the gasoline content in Hong Kong. According to one of the fuel supplier in Hong Kong, the composition of toluene in gasoline is in the range of 20%. But for other aromatic compounds such as benzene, ethylbenzene and xylene, their percentages only range from 5 to 10% (Caltex Oil (Hong Kong) Ltd., 2001). Data from the Hong Kong Environmental Department shows that the BTEX ratio of the ambient air in Central West (2000) was 2 : 10 : 1 : 2. The ambient BTEX ratio also reflects the problem of high toluene concentration in the atmosphere of Hong Kong.

Moreover, Hong Kong's climate is sub-tropical, the mean temperature in year 2000 was 23.3°C. The high temperature in Hong Kong especially in the summer enhances evaporation of gasoline. Furthermore, the vapor pressure of gasoline (>400 mmHg at 20°C) is much higher than that of diesel fuel (<0.1 mmHg at 20°C) (Exxonmobil Oil Corporation, 2001). Thus, gasoline is easier to vaporize than diesel. Therefore, gasoline evaporation may be a possible source that leads to extremely high toluene concentration in Hong Kong other than vehicular exhaust.

Furthermore, the high concentration of toluene in tunnels may be caused by gasoline evaporation from fuel tanks or engine.

6.4 Characteristic Ratios of Vehicular Sources

The characteristic ratio BTEX is usually used to characterize vehicular emissions since benzene, toluene, ethylbenzene and xylenes are the most abundant VOCs in vehicular emissions (Chiang et al., 1996). Moreover, it is due to their relevance as potential health hazards, and because they are markers for vehicle emissions (Chan et al., 1991). However, the toluene contribution to the ambient air in Hong Kong is extremely high. As mentioned in the previous section, the ambient BTEX ratio of in Central West (2000) was 2 : 10 : 1 : 2, which reflects the high toluene concentration in ambient air. A recent study of air quality in the Pearl River Delta Region indicated that the VOC emission from motor vehicle accounted for 25% of the anthropogenic emissions in Hong Kong (HKEPD, 2002). Thus, high toluene contribution in the ambient may be from motor vehicles especially in busy trafficked commercial districts.

Also, the characteristic ratio of ethyne-to-ethene (EE ratio) is used as the indicator of vehicle exhaust in Hong Kong because it is closely related to diesel-powered vehicles. Other than BTEX, ethene and ethyne were the most abundant VOCs among vehicular sources in this study. The EE ratio of the diesel exhausts ranged from 0.3-0.5. The EE ratio of the gasoline and LPG exhausts were 0.08 and 0.03 respectively. We found that the EE ratios of gasoline and LPG exhausts were lower than 0.1 while that of diesel exhaust were higher than 0.1 in Hong Kong. Thus, the EE ratios may be used to characterize the different types of fuel used in Hong Kong. Moreover, the EE ratio of both tunnels was 0.7, which was higher than that of the vehicular exhausts. A previous study found that the higher the EE ratio, the higher contribution of high emitting vehicles (Sagebiel et al., 1996). In general, the air inside the tunnel is mixed with different types of vehicular exhaust from a large number of vehicles and fuel types. There may be high contribution of high emitting vehicles in tunnels. Therefore, it is reasonable that the EE ratio in tunnels were higher than that of vehicle exhaust from tailpipes.

6.5 Conclusion

This study measured the VOC concentrations of different vehicular sources in Hong Kong. The results show the emission characteristic of different vehicular sources. The major components in both tunnels were ethane, ethyne, i-pentane and toluene, which ranged from 8.13 to 16.32%. In the two selected tunnels in Hong Kong, alkane was the most abundant hydrocarbon group. By further comparing the total VOC concentration in the two tunnels, the Cross Harbour Tunnel was 2.36 times the Shing Mun Tunnel. The difference is due to the differences in the volume and composition of the vehicular fleet in the two tunnels.

In the diesel powered vehicle exhaust, unsaturated hydrocarbons - alkene is the most abundant hydrocarbon, which was 67.8%. Among all diesel-powered vehicles, the contribution of ethene was the highest with an average of 51.24%. In the gasoline-powered vehicle exhaust, aromatic hydrocarbon was the most abundant hydrocarbon group with 47%. The most abundant VOC in gasoline exhaust was toluene with 15.01%. The pattern for the contribution of different hydrocarbon groups in gasoline powered vehicle exhaust was quite distinguishes from those of the diesel powered vehicles. The results reflect that the composition of the gasoline in Hong Kong is rich in aromatic hydrocarbon. In the exhaust of LPG-powered vehicle, saturated hydrocarbons - alkane is the most abundant hydrocarbon group, which was 91%. The most abundant VOCs include propane, n-butane, i-butane and ethane.

At petrol stations, the contribution of i-pentane to evaporated gasoline was more than 50%. Therefore, the evaporated gasoline can be characterized by large proportion of alkane. The BTEX ratio of the petrol stations was 6 : 189.2 : 1 : 5. It is clear that the contribution of toluene to gasoline evaporation was particular high. Since the toluene concentration is extremely high in Hong Kong when compared with other countries, it is not suitable to use as an indicator for vehicular exhaust. Apart from BTEX ratio, EE ratios may be a better indicator of vehicular exhaust in Hong Kong. The EE ratios of the gasoline and LPG exhausts were lower than 0.1 while that of diesel exhaust were higher than 0.1 in Hong Kong.

Table 6.1 Background of Different Tunnels

Tunnel	Approx. Length (m)	Daily Patronage in 2001	Microenvironment condition
Cross Harbour	1900	120,444	Dual two-lane, immersed tube, uni-direction, links between two urban commercial areas, cross-harbour tunnel
Shing Mun	2600	53,794	Dual two-lane, uni-direction, links residential area and urban mixed residential/industrial area, traverse mountain tunnel

Table 6.2 Vehicular Emission Profiles

%	Cross Harbour Tunnel	Shing Mun Tunnel	Bus	Public Light Bus	Diesel Taxi	MGV	HGV	Private Car	LPG Taxi	Petrol Refilling
Ethane	2.14	1.95	3.62	1.98	2.33	1.82	1.34	10.17	16.35	0.29
Propane	2.14	1.68	1.08	0.51	0.49	0.51	0.41	0.37	27.98	0.34
i-butane	2.15	2.65	0.27	0.05	0.17	0.12	0.09	0.69	18.93	1.50
n-butane	4.84	5.11	0.59	0.13	0.25	0.27	0.17	2.37	27.05	6.78
i-pentane	8.13	10.06	0.53	0.03	0.11	0.19	1.32	7.72	0.16	51.67
n-pentane	2.90	3.09	0.22	0.03	0.11	0.11	0.04	2.70	0.04	12.43
2,3-dimethyl butane	1.54	2.04	0.49	0.00	0.03	0.04	1.19	1.02	0.03	9.32
n-hexane	1.34	1.29	0.28	0.07	0.05	0.36	0.05	1.50	0.17	1.22
Cyclopentane	1.57	0.27	0.03	0.00	0.00	0.01	0.00	0.18	0.00	0.31
2-methylpentane	2.16	2.56	1.16	0.50	0.24	0.55	0.24	2.83	0.12	2.29
3-methylpentane	1.41	1.43	0.11	0.02	0.03	0.15	0.04	1.73	0.05	1.40
2,2,4-trimethyl pentane	2.57	2.32	0.15	0.04	0.07	0.07	0.04	5.62	0.02	0.27
2,3,4-trimethyl pentane	0.79	0.70	0.03	0.04	0.03	0.04	0.06	1.62	0.00	0.05
n-heptane	0.51	0.59	0.31	0.07	0.05	0.24	0.09	0.73	0.09	0.14
n-octane	0.14	0.17	0.32	0.12	0.02	0.18	0.27	0.19	0.01	0.01
Ethene	16.32	14.31	40.51	54.23	57.96	49.29	54.20	6.03	4.78	1.41
Propene	4.92	4.08	11.05	11.72	8.91	10.39	12.76	2.83	1.43	0.42
trans-2-butene	0.82	1.64	0.42	0.33	0.28	0.32	0.34	0.35	0.28	0.15
1-butene	1.38	1.44	2.63	2.69	1.71	2.31	3.01	0.35	0.23	0.19
i-butene	1.85	2.17	1.24	1.39	0.88	0.88	1.41	2.25	0.47	0.28
cis-2-butene	0.73	1.46	0.35	0.28	0.40	0.24	0.26	0.26	0.13	0.10
1,3-butadiene	1.17	0.97	0.09	0.06	0.18	0.07	0.05	0.05	0.00	0.03
1-pentene	0.46	0.80	0.92	1.20	0.58	0.90	1.29	0.54	0.08	0.54
Isoprene	0.99	0.46	0.03	0.00	0.01	0.01	0.01	0.04	0.00	0.04
trans-2-pentene	0.67	0.81	0.27	0.21	0.10	0.19	0.18	0.26	0.02	1.24
Cis-2-pentene	0.28	0.28	0.17	0.09	0.04	0.11	0.04	0.13	0.02	0.61
Ethyne	11.62	9.77	18.98	13.92	17.26	18.95	14.28	0.48	0.13	1.36
Benzene	4.35	2.31	4.28	3.07	3.36	3.62	2.33	6.22	0.13	0.17
Toluene	9.50	10.91	3.65	1.06	1.28	2.42	1.03	15.01	1.03	5.23
Ethylbenzene	1.51	1.81	0.76	0.35	0.33	0.48	0.36	3.03	0.03	0.03
m-xylene	3.27	3.90	1.20	0.85	0.81	0.88	0.61	9.77	0.05	0.07
p-xylene	1.41	1.66	0.60	0.43	0.38	0.44	0.34	3.81	0.02	0.03
o-xylene	1.74	1.99	0.87	0.84	0.67	0.72	0.63	4.58	0.02	0.03
Isopropyl benzene	0.06	0.07	0.13	0.09	0.03	0.12	0.07	0.08	0.01	0.00
Propylbenzene	0.12	0.16	0.14	0.11	0.04	0.14	0.08	0.20	0.01	0.00
3-ethlytoluene	0.45	0.70	0.56	0.51	0.17	0.60	0.30	1.12	0.02	0.01
4-ethyltoluene	0.22	0.32	0.30	0.21	0.08	0.30	0.14	0.47	0.01	0.01
1,3,5-trimethyl benzene	0.30	0.46	0.51	0.43	0.12	0.70	0.25	0.52	0.04	0.01
2-ethyltoluene	0.18	0.25	0.19	0.19	0.07	0.20	0.16	0.40	0.01	0.00
1,2,4-trimethyl benzene	1.37	1.39	0.99	2.12	0.36	1.08	0.50	1.78	0.05	0.02

Note: MGV – Medium Goods Vehicles, HGV – Heavy Goods Vehicles

Table 6.3 VOC Concentrations of Different Hydrocarbon Groups in Tunnels

Group	**Cross Harbour (in ppb)**	**Shing Mun (in ppb)**
Alkane	143.56	58.17
Alkene	104.15	46.08
Alkyne	39.04	19.69
Aromatic	112.98	45.51
Total VOC	**399.73**	**169.45**

Table 6.4 BTEX Ratios of the Tunnels in HK and Other Countries

Tunnel	Country	BTEX ratio	References
Cross Harbour	Hong Kong	1.3 : 6 : 1 : 4.2	This study
Shing Mun		2.9 : 6.3 : 1 : 4.3	
Sydney Harbour	Australia	5.3 : 8 : 1 : 5	Duffy, 1996
Hsin-Hai	Taiwan	3 : 5 : 1 : 4	Chiang, 1996
Caldecott	U.S.A.	3.5 : 5.8 : 1 : 5.7	Zielinska, 1994

Figure 6.1 Different Vehicular Emission Sources in Hong Kong

Bus

Public Light Bus

Taxi

Petrol Station

Figure 6.2 Comparison of Diesel, Gasoline & LPG Powered Vehicle Emission Profiles

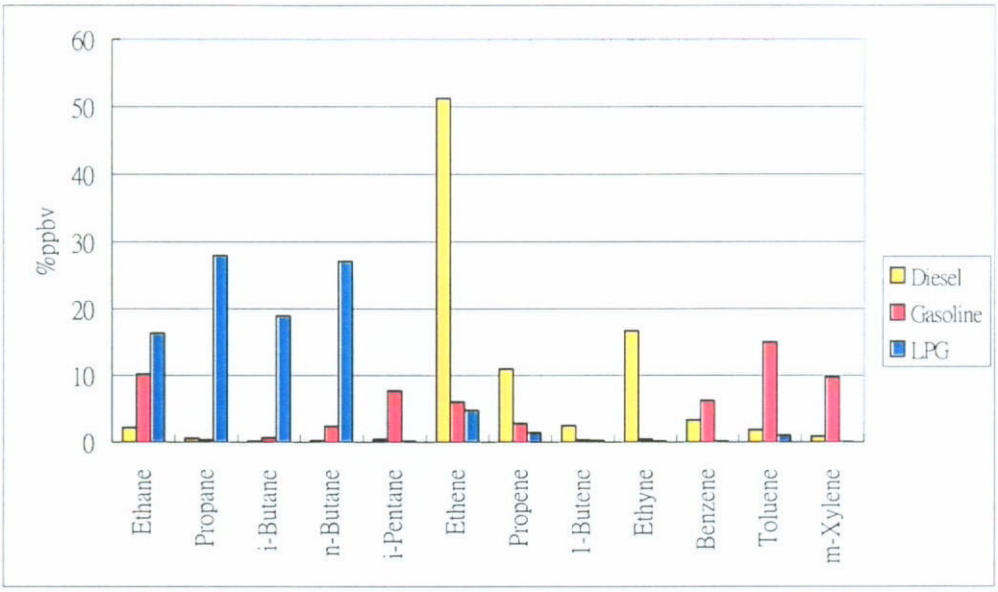
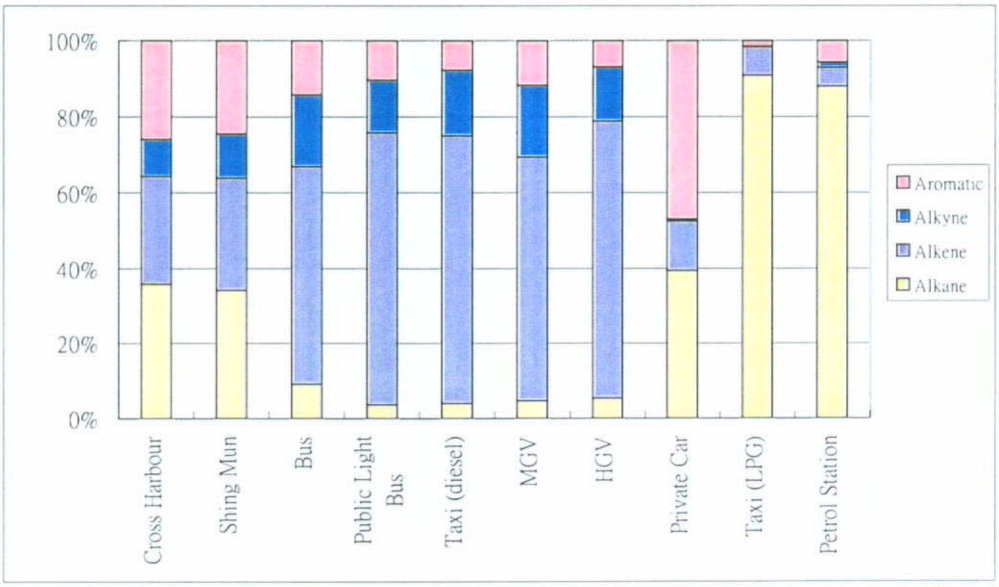


Figure 6.3 Percentage of Different Hydrocarbon Groups



CHAPTER 7 CONTRIBUTION OF TRAFFIC-RELATED SOURCES TO VOC LEVEL IN HONG KONG

7.1 Introduction

The poor air quality in Hong Kong has become a focal point for many Hong Kong people. Over the past few years, smog has visibly worsened and daily air pollution indices have reminded people that the air may be bad for their health. Ten years ago, the major source of pollution in Hong Kong was from industry. Nowadays, the air pollution in Hong Kong quickly changed to pollution from vehicles with numbers increased dramatically in the 1990s. It is mainly caused by the high density of vehicles on the roads, coupled with the hilly geography and cavernous streets. Also, regional air pollution has increasingly affected visibility.

In order to tackle the problem, air quality is monitored through 14 fixed stations set up around Hong Kong by the Environmental Protection Department in year 1999 (Figure 7.1). The objectives for setting up the air quality monitoring network include: 1. To understand air pollution problems in order that cost-effective policies and solutions can be developed. 2. To assess how far standards and targets are being achieved or violated. 3. To assist the assessment of public's exposure to air pollution. 4. To provide public information on current and forecast air quality.

Among the 14 fixed air quality monitoring stations, there are 11 general stations and 3 roadside stations. The general stations are located at Tap Mun, Tai Po, Yuen Long, Shatin, Tsuen Wan, Kwai Chung, Sham Shui Po, Kwun Tong, Eastern, Central/Western and Tung Chung. The roadside stations are located at the most highly populated areas in Hong Kong, which include Mong Kok, Central and Causeway Bay.

7.2 Methodology

In this study, ambient VOC data was provided by the Hong Kong Environmental Protection Department. The ambient VOC measurements were carried out at the two fixed monitoring stations in Central/Western and Tsuen Wan throughout the year 2001. The Central/Western monitoring station (Figure 7.2) is a general station located at the rooftop of a police station, which is 18 meters above ground level. Central/Western is an urban/residential area. The Tsuen Wan monitoring station (Figure 7.3) is located at the rooftop of a community centre, which is 17 meters above ground level. The area is a densely populated urban residential area with mixed commercial/industrial developments. Air samples were collected by canister once per week. In year 2001, there were 61 and 59 air samples collected at Central/Western and Tsuen Wan monitoring stations respectively. The collected data was then analyzed to identify the main source groups for VOC using the statistical methods of Pearson Correlation and Principal Component Analysis (PCA). The contribution of vehicular VOCs is discussed.

7.3 Results and Discussion

In this study, 38 individual hydrocarbons of the atmospheric samples were selected from the Hong Kong Environmental Department database, which were mainly alkanes, alkenes, aromatic and chlorinated compounds. However, some species of our study are not available in the Hong Kong Environmental Department database such as ethane, ethene and ethyne.

7.3.1 Quantitative Analysis of the Hong Kong Air Samples

The average concentrations and standard deviation of selected VOCs and total VOCs are listed in Table 7.1. The selected VOCs were the twelve most abundant species found in the two monitoring stations in Hong Kong, which include n-butane, i-butane, 2-methylbutane, propane, pentane, 2-methylpentane, propene, benzene, toluene, methylene chloride (CH_2Cl_2), freon-11 and freon-12. The total

VOCs concentration is defined as the sum of the concentration of the 38 selected VOCs from the Hong Kong Environmental Department database.

Central / Western Monitoring Station

Central/Western is an urban/residential area located on the Hong Kong Island. The monitoring station is on the rooftop of a police station (1 High Street), which is 18 meters above ground level. Nearby the monitoring station, there are mainly residential buildings with a large park, few schools and a community center.

The average concentrations of the selected VOCs vary between 0.46 ppb (pentane) to 3.27 ppb (toluene). Among the twelve selected VOCs, toluene was the most abundant VOC at the Central/Western monitoring station. The average concentration of toluene was 3.27 ppb. According to previous studies, toluene may emit from vehicular emissions, which include vehicle exhaust and fuel evaporation. Also, toluene is present in various solvents. However, Central/Western monitoring station is located in an urban/residential area with no industrial source nearby. Thus, the high toluene concentration may come mainly from vehicular emissions. Moreover, we found that toluene concentration is usually high in Hong Kong throughout this research project. The reason for high toluene concentration in Hong Kong may due to the local gasoline reformulation in year 1999. Aromatic compounds are commonly added into unleaded gasoline to increase the octane index during fuel reformulation. Therefore, high toluene concentration found at the Central/Western monitoring station may come from gasoline-powered vehicles.

Other than toluene, the concentration of n-butane was high also with 2.14 ppb. According to previous studies, n-butane may come from gasoline evaporation and exhaust (Bond et al., 1986; Black et al., 1980). In Hong Kong, gasoline is the most commonly used automobile fuel. In year 2002, more than 70% of licensed vehicles are gasoline powered (Figure 7.5). Moreover, private car is the major vehicle type using gasoline. Since the Central/Western monitoring station is an urban/residential area with majority of residential buildings, there are mostly private cars and light duty vehicles on roads. Therefore, the major source of n-butane at the Central/Western monitoring station is gasoline evaporation or exhaust.

Tsuen Wan Monitoring Station

Tsuen Wan is a densely populated urban residential area with mixed commercial/industrial developments. The monitoring station is on the rooftop of Princess Alexandra community center (60 Tai Ho Road), which is 17 m above ground level. There are playgrounds, schools and residential buildings around the monitoring station. Within the district, there are many old industrial buildings.

The average concentrations of the selected VOCs vary between 0.63 ppb (Freon-11) to 3.41 ppb (n-butane). Among the twelve selected VOCs, n-butane was the most abundant VOC at the Tsuen Wan monitoring station. The average concentration of n-butane was 3.41 ppb. In previous studies, the major source of n-butane was from gasoline evaporation and exhaust (Black et al., 1980; Bond et al., 1986). As mentioned in the previous section, gasoline is the most commonly used automobile fuel in Hong Kong (Figure 7.5). Also, almost 100% of private car are powered by gasoline. Therefore, the high concentration of n-butane may possibly come from gasoline evaporation and exhaust. In addition, the average temperature in Hong Kong is high throughout the year. It makes gasoline easier to evaporate.

Other than n-butane, toluene concentration was also high at the Tsuen Wan monitoring station. Toluene is one of the most abundant VOCs in vehicular emissions (Chiang et al., 1996). As mentioned in the previous section, the high toluene concentration in Hong Kong may due to the local gasoline reformulation in year 1999 since aromatic compounds are added into unleaded gasoline. Thus, high toluene concentration may due to vehicular emissions (evaporation and exhaust) in the district.

In addition, propene concentration at Tsuen Wan monitoring station was high also. The average concentration of propene was 1.04 ppb. According to previous studies, propene is a marker for diesel emission (Fujita et al., 1997). The result reflects that diesel emission was abundant in Tsuen Wan. Tsuen Wan is a mixed commercial/industrial area with many industrial premises. Moreover, there is a container terminal near Tsuen Wan (Kwai Chung Container Terminal) and there are many heavy goods vehicles driving in and out the district everyday. In Hong Kong, all medium and heavy goods vehicles are diesel powered. Therefore, the high concentration of propene in Tsuen Wan may come mainly from diesel powered vehicles exhaust.

7.3.2 Comparison among the Monitoring Stations in Hong Kong

In comparing the concentrations of VOCs at the two monitoring stations in Hong Kong (Table 7.1), the higher concentrations of n-butane (3.41 ppb), i-butane (1.40 ppb), 2-methylbutane (1.45 ppb), propane (2.47 ppb), pentane (0.67 ppb), 2-methylpentane (0.69 ppb), propene (1.04 ppb), benzene (0.72 ppb), methylene chloride (1.03 ppb), freon-11 (0.63 ppb) and freon-12 (1.06 ppb) were found at the Tsuen Wan monitoring station. On the other hand, only toluene concentration was found higher at the Central/Western monitoring station.

As mentioned before, Tsuen Wan is a densely populated residential area with mixed commercial/industrial developments. There are many old industrial buildings located in the district. The concentrations of chlorinated compounds such as methylene chloride (CH_2Cl_2), freon-11 (F-11) and freon-12 (F-12) were higher at the Tsuen Wan monitoring station, which may due to industrial emissions in the district. Methylene chloride is predominately used as a solvent in paint strippers and removers. Also, it is used as a propellant in aerosols for products such as paints, automotive products and insect sprays. On the other hand, freon-11 and freon-12 are commonly used as refrigerants, solvents, and foam blowing agents (USEPA). Thus, it is reasonable that the concentrations of chlorinated compounds were found higher at the Tsuen Wan monitoring station where there is more industrial premises nearby. The high concentrations of chlorinated compounds may due to solvents use during manufacturing processes.

Moreover, pollution from vehicular emissions (evaporation and exhaust) was more serious at the Tsuen Wan monitoring station as higher concentrations of butanes and propane were found. Propane is not present in gasoline and is emitted from vehicle exhausts (Fujita et al, 1995; Na et al., 1998). According to a study in Korea, the major source of propane in urban area is known to be liquefied petroleum gas (LPG) for taxi fuel (Na et al., 2001). In Hong Kong, all new taxis have to run on LPG since January 2001 (HKEPD, 2000). On the other hand, butanes are mainly from gasoline evaporation and exhaust (Bond et al., 1986; Black et al., 1980). Therefore, higher concentrations of these VOCs reflect that vehicular emissions were more serious in Tsuen Wan. In addition, Tsuen Wan is a densely populated area with many residential buildings. People living in the district need to travel to work everyday. So, the number of vehicle travels to and from the district should be high everyday and it leads to higher vehicular emissions.

Furthermore, the concentration of propene was higher at the Tsuen Wan monitoring station. As mentioned before, propene is the marker for diesel emission (Fujita et al., 1997) and there are more diesel-powered goods vehicles travel to and from the district. Therefore, high concentration of propene in Tsuen Wan may come from diesel powered vehicle exhaust.

The total VOCs concentrations found at the two monitoring stations in Hong Kong were shown on Table 7.1. The total VOCs concentration in Tsuen Wan (21.84 ppb) was higher than that of Central/Western (17.87 ppb). The results indicated that the air pollution problem was more serious in Tsuen Wan as there is more vehicles travel around the district everyday. Also, air quality may affect by industrial emissions as many industrial buildings located in Tsuen Wan. Industrial solvent use is the major source of chlorinated VOCs in the district. On the other hand, Central/Western monitoring station is located at the urban/residential area where vehicular emission is the major pollution source. However, the population density in Central/Western is lower than that in Tsuen Wan. Thus, there must be lesser vehicles travel to and fro the district. Therefore, the air quality is better at Central/Western monitoring station.

7.3.3 Correlations of Selected VOCs

Correlations of selected VOCs were evaluated by regression analysis, which include pentane, butane, 2,3-dimethylbutane, 2-methylbutane, benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, 1,2,4-trimethylbenzene, tetrachloroethylene (C_2Cl_4) and methylene chloride (CH_2Cl_2). A few selected VOCs are the markers for different sources such as gasoline evaporation, vehicle exhaust and industrial emissions. Thus, good correlation between the markers and other VOCs can reflect that they may from the same source. The correlation coefficients (r) of the selected VOCs are shown in Tables 7.3 and 7.4.

In this study, the correlation coefficients of selected VOCs in Central/Western and Tsuen Wan were from 0.4 {*$P<0.01$} to 0.97 {**$P<0.001$} and 0.34 {*$P<0.01$} to 0.98 {**$P<0.001$} respectively. At both monitoring stations, correlations for pentane, butane and 2-methylbutane were high {r=0.85-0.96, **$P<0.001$}. The high positive coefficients strongly indicate that the primary origin of pentane, butane and 2-methylbutane are from the same source. According to previous studies, the major sources of butanes are known to be the evaporation of gasoline and LPG used as automobile fuel in urban areas (Na et al., 1998). Moreover, pentane is also known to be the representative compounds of gasoline evaporation (Na et al., 2001). In Hong Kong, gasoline is the most commonly used automobile fuel. Also, there are many refueling stations in urban areas. Thus, gasoline evaporation may come from refueling stations during the refueling process. Therefore, the source of pentane, butane and 2-methylbutane in Central/Western and Tsuen Wan is from gasoline evaporation.

At the Central/Western and Tsuen Wan monitoring stations, concentrations for toluene, ethylbenzene and m,p,o-xylenes were highly correlated, which were {$r=0.80\text{-}0.97$, **$P<0.001$} and {$r=0.78\text{-}0.97$, **$P<0.001$} respectively, which indicate that they are from the same source. Previous studies shown that benzene, toluene, ethylbenzene and xylenes (BTEX) were the major photochemical reactive organic pollutants emitted from automobiles (Sigsby, 1987). Therefore, these VOCs are usually used to characterize vehicular exhaust emissions. However, benzene was not highly correlated with the other vehicular emission markers. It may due to the Hong Kong Government has reduced benzene in unleaded gasoline from 5% to 1% since April 2000 in order to meet current European Standards (HKEPD, 2000). Thus, emission of benzene from gasoline exhaust is lowered.

Furthermore, concentrations for methylene chloride, pentane and butanes were significantly correlated {r=0.47-0.69, **$P<0.001$}, which implied that methylene chloride may also be contributed partially from vehicular emissions. Usually, methylene chloride is added into solvents. According to an automobile manufacturing company (Ford), methylene chloride is used as solvent for drawing paints and cleaning chemicals required in the manufacture of the starter components, including the copper ring of the commutator. Due to this reason, the methylene chloride left on the commutator after cleaning processes may evaporate into atmosphere when heating up the vehicles during driving.

7.3.4 Principle Components Analysis (PCA)

In this chapter, the multivariate statistical method of Principle Components Analysis (PCA) is used to analyze the relationship between the VOC compounds in Hong Kong. In the following, PCA was performed on the data set to investigate similarities and differences in the behavior of the concentrations of the selected VOCs in Hong Kong. The number of common factors and their loadings were found by factor analysis. The factor scores obtained for each VOC within the factors are a type of correlation coefficient. Higher values are therefore associated with greater significance. As mentioned in the previous chapter, a factor score of 0.6 was selected as the lowest level of significance within a factor (Ho et al., 2002)

The factors were extracted by PCA for the determination of the number of factors to be retained in the data matrices. Kaiser's criterion was adopted to fix the number of factors to be retained (only factors with eigenvalues >1). In Central/Western and Tsuen Wan, three factors were retained at both monitoring station. For easier interpretation, varimax with Kaiser normalization rotation method was employed (Kaiser, 1958). The result of the PCA and the possible sources of the species are listed in Table 7.5 and 7.6.

Table 7.5 shows the factor loadings of the three retained factors that account for

79.56% of the total variance at Central/Western monitoring station, which means that the selected VOCs are from these three possible sources. Factor 1 accounts for 41.14% of total variance, which contains the variable toluene, ethylbenzene, m,p-xylene, o-xylene and 1,2,4-trimethylbenzene. According to a previous study in Korea, toluene, ethylbenzene and xylenes (denoted as TEX) accounts for about 15wt% in vehicle emissions (Na et al, 2001). Also, they are the major photochemical reactive organic pollutants emitted from automobiles (Sigsby, 1987). Moreover, others studies also found toluene and m,p-xylenes to be the major components of VOCs from vehicular emissions (Pierson et al., 1996; John et al., 1999; Hsu et al., 2001). Therefore, the possible source of factor 1 is related to vehicle exhaust emissions.

On the other hand, table 7.6 shows the factor loadings of the three retained factors that account for 74.54% of the total variance at Tsuen Wan monitoring station, which means the selected VOCs are from three possible sources. Factor 1 accounts for 32.62% of total variance, which contains the variable toluene, ethylbenzene, m,p-xylene, o-xylene (denoted as TEX). As mentioned in the previous paragraph, TEX are the major photochemical reactive organic pollutants emitted from automobiles (Sigsby, 1987). Hence, the source of factor 1 at Tsuen Wan monitoring station is also related to vehicle exhaust emission.

Similarly, factor 2 of Central/Western and Tsuen Wan monitoring stations contains the same variables, which include pentane, butane, 2,3-dimethylbutane, 2-methylbutane and methylene chloride. At Central/Western monitoring station, factor 2 accounts for 28.4% of total variance. At Tsuen Wan monitoring station, factor 2 accounts for 31.64% of total variance. Among these VOCs, pentane and butane are known to be the representative compounds of gasoline evaporation (Na et al., 2001). Thus, the possible source of factor 2 is related to gasoline evaporation. The result also matches the previous correlation study.

Moreover, factor 3 of Central/Western and Tsuen Wan monitoring stations also contain the same variable, which is tetrachloromethylene. At Central/Western monitoring station, factor 3 accounts for 10.02% of total variance. At Tsuen Wan monitoring station, factor 3 accounts for 10.28% of total variance. In Hong Kong, tetrachloroethylene is used as a dry-cleaning agent because of its good cleaning power. However, about one third to one half of the existing dry-cleaning machines in Hong Kong are vented type, which means that they release tetrachloroethylene vapor directly into the atmosphere during the drying cycle. As many of these dry-cleaning facilities are close to residential premises, the emissions will affect the people nearby, a potential threat to their health in the long run (HKEPD, 2002). Therefore, the possible source of factor 3 is related to emission from dry cleaning.

According to the PCA results of Central/Western and Tsuen Wan monitoring stations, we found that VOCs at these two stations were mainly from three sources, which include vehicle exhaust emissions, gasoline evaporation and dry cleaning emissions.

7.4 Conclusion

This study compared the VOC emissions at the two monitoring stations in Hong Kong, which include Central/Western and Tsuen Wan. In order to characterize the VOC emissions at the two monitoring stations, statistical methods – Principle Components Analysis (PCA) and Pearson Correlation were used. In this study, 38 individual hydrocarbons of the atmospheric samples were identified. The results show that toluene (3.27 ppb) and n-butane (3.41 ppb) were the most abundant

VOC at Central/Western and Tsuen Wan monitoring station respectively. Since year 1999, aromatic compounds are commonly added into unleaded gasoline due to fuel reformulation in Hong Kong. Referring to Chapter 6 in this study, high toluene concentrations were found in Hong Kong tunnels and at petrol refilling stations. Thus, the high toluene concentration may possibly come from gasoline evaporation from vehicles. Similarly, gasoline evaporation is the major source of n-butane regarding to previous studies. Due to the high average temperature in Hong Kong, gasoline is easier to evaporate into the atmosphere.

The total VOCs concentration at Tsuen Wan monitoring station (21.84 ppb) was higher than that of Central/Western monitoring station (17.87 ppb). The results indicate that the air quality is better in Central/Western area. It may be due to the fact that Tsuen Wan is a densely populated residential area with mixed commercial/industrial development. So, air pollutants may come from vehicle emissions and industrial emissions. On the other hand, there are no industrial premises in Central/Western area. Hence, the air pollutants are mainly from vehicle emissions.

Regarding to the results of correlation study of Central/Western and Tsuen Wan monitoring stations, the correlation coefficients of selected VOCs were from 0.4 $\{*P<0.01\}$ to 0.97 $\{**P<0.001\}$ and 0.34 $\{*P<0.01\}$ to 0.98 $\{**P<0.001\}$ respectively. High positive coefficients were found for pentane, butane and 2-methylbutane, which strongly indicate that the primary origin of these VOCs is from the same source. The result matches the PCA result that pentane, butane and 2-methylbutane were from the same source, which is gasoline evaporation. Moreover. concentrations of toluene, ethylbenzene and xylenes (denoted as TEX) were significant correlated, which indicate that they are from the same source. Similarly, the result matches the PCA result that TEX are from vehicle exhaust emission.

According to the PCA results, three factors were retained at Central/Western and Tsuen Wan monitoring stations, which account for 79.56% and 75.54% of the total variance respectively. VOCs at the two monitoring station in Hong Kong were mainly from three sources, which include vehicle exhaust emissions, gasoline evaporation and dry cleaning.

Table 7.1 Average Concentrations of Selected VOCs Measured at 2 Sites in Hong Kong

VOC	Site	Mean	SD	Range	VOC	Site	Mean	SD	Range
n-Butane	CW	2.14	1.03	0.46-5.40	Benzene	CW	0.60	0.41	0.09-1.78
	TW	3.41	2.26	0.85-15.04		TW	0.72	0.46	0.20-2.64
i-Butane	CW	1.06	0.58	0.01-3.86	Toluene	CW	3.27	2.12	0.27-11.19
	TW	1.40	0.85	0.46-6.17		TW	3.18	2.11	0.68-12.89
2-Methyl-butane	CW	0.95	0.48	0.27-2.61	CH_2Cl_2	CW	0.96	0.79	0.23-4.49
	TW	1.45	0.86	0.34-5.90		TW	1.03	0.74	0.19-3.96
Propane	CW	1.81	1.00	0.51-5.59	F-11	CW	0.53	0.25	0.20-1.30
	TW	2.47	1.73	0.66-10.16		TW	0.63	0.30	0.20-1.35
Pentane	CW	0.46	0.25	0.12-1.46	F-12	CW	0.97	0.39	0.43-1.85
	TW	0.67	0.43	0.13-2.85		TW	1.06	0.41	0.39-1.78
2-Methyl-pentane	CW	0.67	0.32	0.10-2.03	Total VOCs	CW	17.87	7.14	4.56-39.25
	TW	0.69	0.39	0.15-1.66		TW	21.84	10.87	7.75-68.59
Propene	CW	0.70	0.31	0.21-1.70	*Note:*	*CW*	– *Central/Western*		*(n=61)*
	TW	1.04	0.53	0.27-2.77		*TW*	– *Tsuen Wan*		*(n=59)*

Total VOCs : 38 species

Table 7.2 Emissions of Major Pollutants in Future Years in Hong Kong

Pollutant Emission (kilo tones per year)	1997	2000	2005	2010	2015
VOC	54	57	67	79	95
RSP	13	13	12	12	13
NO_x	114	122	127	132	146
SO_2	76	82	88	96	106

Source: Hong Kong Environment Department 2002

Table 7.3 Summary of Correlation Coefficients of Selected VOCs at Central/Western Monitoring Station (n=61)

Central/Western	1	2	3	4	5	6	7	8	9	10	11	12
1 Pentane	1	0.85 **	0.55 **	0.96 **	0.65 **	0.50 **	0.43 *	0.42 *	0.49 **	0.53 **	0.05	0.56 **
2 Butane		1	0.40 *	0.88 **	0.58 **	0.62 **	0.45 **	0.51 **	0.57 **	0.58 **	0.25	0.32
3 2,3-Dimethylbutane			1	0.47 **	0.13	0.10	0.03	0.12	0.17	0.17	0.16	0.47 **
4 2-Methylbutane				1	0.61 **	0.54 **	0.46 **	0.41 *	0.47 **	0.53 **	0.09	0.47 **
5 Benzene					1	0.59 **	0.49 **	0.44 **	0.48 **	0.48 **	-0.12	0.30
6 Toluene						1	0.83 **	0.80 **	0.81 **	0.61 **	0.22	0.09
7 Ethylbenzene							1	0.94 **	0.90 **	0.48 **	0.01	0.13
8 m,p-Xylene								1	0.97 **	0.60 **	0.24	0.03
9 o-Xylene									1	0.73 **	0.28	0.05
10 1,2,4-Trimethylbenzene										1	0.21	0.10
11 Tetrachloroethylene											1	-0.09
12 Methylene chloride												1

** *Correlation is significant at the 0.001 level (2-tailed), *Correlation is significant at the 0.01 level (2-tailed)*

Table 7.4 Summary of Correlation Coefficients of Selected VOCs at Tsuen Wan Monitoring Station (n=59)

Tsuen Wan	1	2	3	4	5	6	7	8	9	10	11	12
1 Pentane	1	0.95 **	0.67 **	0.98 **	0.79 **	0.56 **	0.43 *	0.42 *	0.45 **	0.40 *	0.05	0.64 **
2 Butane		1	0.53 **	0.95 **	0.76 **	0.61 **	0.44 **	0.43 *	0.45 **	0.43 *	0.01	0.63 **
3 2,3-Dimethylbutane			1	0.63 **	0.38 *	0.35 *	0.31	0.37 *	0.40 *	0.29	0.17	0.41 *
4 2-Methylbutane				1	0.74 **	0.53 **	0.37 *	0.36 *	0.39 *	0.34 *	0.02	0.69 **
5 Benzene					1	0.66 **	0.58 **	0.54 **	0.52 **	0.41 *	0.09	0.46 **
6 Toluene						1	0.74 **	0.81 **	0.78 **	0.65 **	0.39 *	0.40 *
7 Ethylbenzene							1	0.91 **	0.89 **	0.50 **	0.17	0.13
8 m,p-Xylene								1	0.97 **	0.70 **	0.21	0.07
9 o-Xylene									1	0.69 **	0.23	0.07
10 1,2,4-Trimethylbenzene										1	0.12	-0.06
11 Tetrachloroethylene											1	-0.04
12 Methylene chloride												1

** *Correlation is significant at the 0.001 level (2-tailed), *Correlation is significant at the 0.01 level (2-tailed)*

Table 7.5 The Results of PCA for Selected VOCs at Central/Western Monitoring Station[a]

VOCs	Factor 1	Factor 2	Factor 3	Communality
Pentane	0.43	0.87	-0.08	0.94
Butane	0.55	0.69	0.14	0.79
2,3-Dimethylbutane	-0.03	0.76	0.25	0.64
2-Methylbutane	0.44	0.83	-0.03	0.88
Benzene	0.56	0.45	-0.39	0.67
Toluene	0.87	0.19	0.10	0.80
Ethylbenzene	0.91	0.12	-0.13	0.85
m,p-Xylene	0.95	0.04	0.07	0.90
o-Xylene	0.95	0.11	0.12	0.94
1,2,4-Trimethylbenzene	0.72	0.25	0.22	0.63
Tetrachloroethene	0.18	0.05	0.92	0.88
Methylene chloride	-0.08	0.77	-0.14	0.62
% of variance	41.14	28.40	10.02	
Cumulative %	41.14	69.54	79.56	

[a] Extraction method: PCA; rotation method: varimax with Kaiser normalization

Table 7.6 The Results of PCA for Selected VOCs at Tsuen Wan Monitoring Station[a]

VOCs	Factor 1	Factor 2	Factor 3	Communality
Pentane	0.20	0.94	-0.02	0.93
Butane	0.27	0.85	-0.12	0.80
2,3-Dimethylbutane	0.14	0.72	0.25	0.59
2-Methylbutane	0.16	0.96	-0.06	0.94
Benzene	0.51	0.42	-0.03	0.44
Toluene	0.71	0.16	0.47	0.75
Ethylbenzene	0.92	0.01	0.09	0.86
m,p-Xylene	0.95	0.04	0.15	0.92
o-Xylene	0.94	0.11	0.14	0.92
1,2,4-Trimethylbenzene	0.58	0.18	-0.11	0.38
Tetrachloroethene	0.13	0.02	0.93	0.88
Methylene chloride	-0.11	0.72	0.08	0.53
% of variance	32.62	31.64	10.28	
Cumulative %	32.62	64.26	74.54	

[a] Extraction method: PCA; rotation method: varimax with Kaiser normalization

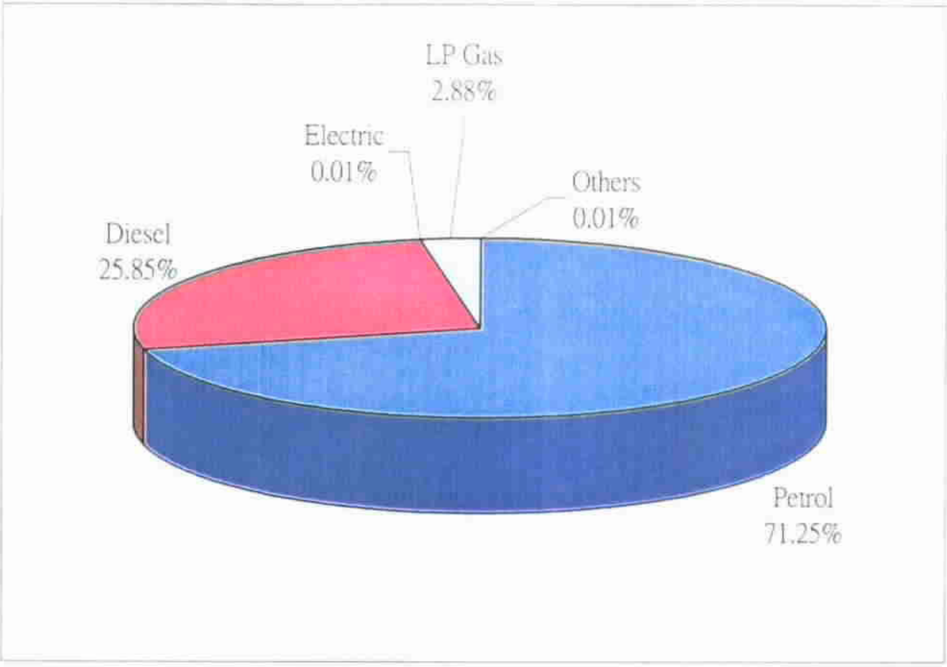
Figure 7.1 Air Quality Monitoring Network of Hong Kong

Figure 7.2 Photo Taken from the Central/Western Monitoring Station

Figure 7.3 Photo Taken from the Tsuen Wan Monitoring Station

Figure 7.4 Monitoring Instruments at the Stations

Figure 7.5 Vehicles by Fuel Type in Hong Kong – 2001



Source: Monthly Traffic and Transport Digest March 2002

CHAPTER 8 OVERALL CONCLUSION

In the past decades, air quality is deteriorating within the entire Pearl River Delta (PRD) Region due to the tremendous growth in economic and population in the region. In a recent study carried out by the Hong Kong Environmental Protection Department, it was found that both the local air pollution sources and the worsening regional air quality in the PRD cause the deteriorating air pollution in Hong Kong. Moreover, emission from transportation is the largest contributor to VOC emissions in the PRD Region.

In this study, volatile organic emissions from vehicular sources and contribution from vehicular VOC emissions to ambient volatile organic compound (VOC) levels were investigated. The VOC levels were quantified by using electropolished stainless steel canisters with GC/MS system in accordance with the USEPA Method TO-14. In order to obtain accurate and reliable results, a chain of quality assurance and quality control (QA/QC) procedures validated the accuracy of VOC analysis.

Tunnel Study

The study was aimed to obtain the characteristics of the VOC emissions in Hong Kong tunnel traffic. We also perform study of VOC emissions in vehicle tunnels for Hong Kong, Guangzhou and Shenzhen. Characteristics of VOC emissions in Hong Kong are high toluene concentration and relatively low BT ratio, which was 0.3 only. Generally, our results demonstrate that alkenes (i.e. ethene, ethyne) and alkanes (i.e. i-pentane, n-pentane, n-butane) are the most abundant hydrocarbon groups in all of the five tunnels and these two groups are mainly from vehicle exhaust. In all tunnels, ethene and ethyne were the predominant VOC species within the top 10 VOCs, which are recommended to be used as the tracer for vehicle exhaust. However, there are some differences, which are the higher EE ratios found in Guangzhou and Shenzhen. The higher EE ratios indicate a higher contribution from high emitting vehicles.

Vehicular Emissions in Hong Kong

This study measured the VOC concentrations of different vehicular sources in Hong Kong, which aimed to show the emission characteristics of each vehicular source. The most abundant hydrocarbon group in the exhaust of diesel-powered vehicles was alkenes, which include ethene. On the other hand, aromatic compound i.e. toluene was the most abundant VOC in the exhaust of gasoline-powered vehicles. Results also reflect that the composition of the gasoline in Hong Kong is rich in aromatic hydrocarbon. Thus, it contributes to high toluene concentrations in tunnels and the ambient air in Hong Kong. In the exhaust from LPG-powered vehicles, it was richer in saturated hydrocarbons, which include propane, ethane and butanes.

Contribution of Traffic-related Sources to VOC Level in Hong Kong

This study compared the VOC emissions at the two monitoring stations in Hong Kong, which include Central/Western and Tsuen Wan. The results show that toluene (3.27 ppb) and n-butane (3.41 ppb) were the most abundant VOCs at Central/Western and Tsuen Wan monitoring station respectively. The high toluene concentration may possibly be from gasoline evaporation from vehicles. Moreover, the air quality was found better in the Central/Western area. PCA results show that three factors were retained at both monitoring stations. The possible sources of the factors show that if may be from vehicle emissions, gasoline evaporation and solvent. Thus, traffic-related VOC emissions are among the major contributors to

VOCs in the ambient atmosphere of Hong Kong.

CHAPTER 9 RECOMMENDATION

In this study, the results only provide preliminary examination of VOCs emissions from traffic in Hong Kong. In order to improve the project and permit a more complete picture to be produced in the future, some refinement and improvement is necessary for future study.

In the present study, only three tunnels in Hong Kong were selected for VOC measurements. Totally, there are 11 tunnels in Hong Kong i.e. Eastern Harbour Crossing, Tate's Cairn Tunnel, Tseung Kwan O Tunnel etc. According to the Transport Department, the vehicular fleets are different in each tunnel. Therefore, a more comprehensive study including all the tunnels in Hong Kong would produce a more complete picture of the characteristics of vehicular emissions in Hong Kong. Also, the results of grab sampling can only reflect the VOC levels in a very short period of time in the tunnel e.g. 2-4 minutes. Therefore, longer sampling periods (e.g. 1-2 hours) should be adopted to produce more representative and accurate results. Moreover, traffic flow should be measured on site within the sampling period in tunnels in order to obtain the correlation between the real traffic conditions and the concentrations of VOC.

For the source sampling in Hong Kong, only limited number of vehicles were involved in the study, which provided limited data on the source emissions in Hong Kong. Thus, samples should be taken from a larger number of different types of vehicles to improve the accuracy of the measurements. In addition, LPG used as automobile fuel is new in Hong Kong. Thus, more samples should be taken to examine the characteristics of LPG exhaust emissions to produce more representative results.

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