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Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong

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Abstract

Vehicle emissions of VOCs were determined in summer and winter of 2003 at the Shing Mun Tunnel, Hong Kong. One hundred and ten VOCs were quantified in this study. The average concentration of the total measured VOCs at the inlet and outlet of the tunnel were 81 250 pptv and 117 850 pptv, respectively. Among the 110 compounds analyzed, ethene, ethyne and toluene were the most abundant species in the tunnel. The total measured VOC emission factors ranged from 67 mg veh^{-1} km^{-1} to 148 mg veh^{-1} km^{-1}, with an average of 115 mg veh^{-1} km^{-1}. The five most abundant VOCs observed in the tunnel were, in decreasing order, ethene, toluene, n-butane, propane and i-pentane. These five most abundant species contributed over 38% of the total measured VOCs emitted. The high propane and n-butane emissions were found to be associated with LPG-fueled taxi. And fair correlations were observed between marker species (ethene, i-pentane, n-nonane, BTEX) with fractions of gasoline-fueled or diesel-fueled vehicles. Moreover, ethene, ethyne, and propene are the key species that were abundant in the tunnel but not in gasoline vapors or LPG. In order to evaluate the ozone formation potential emissions in Hong Kong, the maximum increment reactivity is calculated. It was found that about 568 mg of O_3 is induced by per vehicle per kilometer traveled. Among them, ethene, propene and toluene contribute most to the ozone-formation reactivity.

1 Introduction

Vehicular emissions are a major source of volatile organic compounds (VOCs) in the urban areas throughout the Pearl River Delta Region. The VOCs emitted from vehicles directly influence human health due to their toxicity (e.g. benzene and 1,3-butadiene) as well as are precursors for the formation of ozone and other photo-oxidants in ambient air (Finlayson-Pitts and Pitts, 1986). Photochemical smog is now an everyday occurrence in many urban areas throughout the world. Smog is a mixture of sec-

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ondary pollutants such as ozone, nitrogen dioxide, nitric acid, aldehydes and other organic compounds, formed from photochemical reactions between nitrogen oxides and hydrocarbons.

In Hong Kong, diesel, gasoline, and LPG are the main fuels used by vehicles. In 2004, gasoline fueled vehicles accounted for 70.4% of the total licensed vehicles, while diesel and LPG fueled vehicles accounted for 24.5% and 3.5%, respectively (Transport Department, 2004). Vehicular performance affects fuel consumption and emissions in part because it would affect the combustion efficiency and evaporative emissions from the fuel system.

There are two widely used methods to determine vehicular emission profiles: chassis dynamometer tests and measurements in roadway tunnels. These two types of measurements strongly vary depending on many different factors, such as engine type (e.g., gasoline fueled and diesel fueled engines), engine operating conditions (e.g., cruising, idling, and transient modes), etc. (Kaiser et al., 1992; Heeb et al., 1999, 2000; Tsai et al., 2003). In the dynamometer approach, operating conditions and fuel composition can be controlled. Therefore, chassis dynamometer experiments have the ability to examine vehicular emissions under different driving/loading settings and to effectively evaluate exhaust control technologies (Ning et al., 2008). Moreover, it was used to better distinguish between exhaust and evaporative emissions (Liu et al., 2008). However, it is expensive and time consuming, and does not represent a composite of many on-road vehicles. Therefore, dynamometer tests may not be sufficient to reflect real world traffic emissions. The roadway tunnel method, the one which we chose in this study, has been widely used to determine in the past decade of vehicular emissions (Pierson et al., 1990; Haszpra and Szilagyi, 1994; Gertler et al., 1996; Duffy and Nelson, 1996; Mugica et al., 1998; Stemmler et al., 2005; Chiang et al., 2007). It provides a detailed determination of the overall vehicle fleet emissions. The profile from tunnel experiments represents the emissions of vehicles running on the road, including emissions from vehicle tailpipes, unconsumed gasoline, and vehicle evaporative emissions. It enables the estimation of the average emission of a large number of cars under real

world conditions. However, tunnel measurements have some limitations, they provide information that is specific to a particular tunnel under restricted conditions; such as no coldstart emissions, bias in fleet distributions, resistance caused by tunnel walls and speed limits inside the tunnels. The compositions of the VOCs in the tunnel air are believed to be representative of a large number of vehicles and fuel types used broadly in urban areas (Lonneman et al., 1986).

Schauer et al. (1999) quantified the vehicular emission rates of over 170 organic species including carbonyls, VOCs, and semi-volatile and particulate-phase organic compounds. The health and environmental impacts of all of these pollutants are not negligible; as a result, more research on the vehicular emissions is needed. This is an endless task as the emissions from motor vehicles change, i.e. synthesis and application of different types of fuels (Turrio-Baldassarri et al., 2004), modifications of engine designs, and improving emission control and catalytic technologies. All cause variations in emissions.

Many researchers (Guo et al., 2007; Chan et al., 2006; Barletta et al., 2005; Ho et al., 2004; Lee et al., 2002) have focused on the urban levels of VOCs in PRDR, due to the known and suspected carcinogenic nature of these species. On the other hand, VOCs play an important role in the formation of ground-level ozone and photochemical oxidants associated with urban smog (Monod et al., 2001). A previous study showed that toluene concentration in Hong Kong was relatively higher than that in other cities (Chan et al., 2002). This organic compound is mainly emitted from vehicular combustion, gasoline evaporation, and industrial use.

Hong Kong is a densely populated city. According to the Hong Kong Transportation Department, in December 2004 there were 532,872 licensed vehicles. Several ambient VOC studies have recently been completed indicating vehicular emissions are the most important source for these compounds in Hong Kong (Lee et al., 2001; Ho and Lee, 2002; Guo et al., 2004).

To our best knowledge, there are only limited measurement-based VOC emission profiles available in Hong Kong. This is a pilot study to determine local VOC emission

profiles from vehicular exhaust. Air samples were collected in the heavy usage tunnel during winter and summer in 2003. The project also developed a reliable monitoring program to determine the emission factors of VOCs. The emission factors were estimated by measuring the concentration differences between the tunnel inlet and outlet, the traffic rates, and the tunnel ventilation flux during sampling periods. The in-depth understanding provides important information for management of Hong Kong air quality.

2 Methodology

2.1 Sampling location – Shing Mun Tunnel

Shing Mun Tunnel composes of two sections, Smugglers Ridge side and Needle Hill side, and the monitoring stations are located at the Needle Hill sides of the Shing Mun Tunnel. The length of the section selected is approximately 1.6 km (Fig. 1). Shing Mun Tunnel is a two-bore tunnel (north bore and south bore) with two lanes of traffic per bore (without walkways), and is currently used on average by 53 300 vehicles per day (2004 Annual Traffic Census in Hong Kong). Two sampling stations were located in the south bore (Fig. 1), with vehicle flow from Shatin to Tsuen Wan. The length of the west side of the tunnel is approximately 1.6 km and there is an upgrade of 5.4% approaching the tunnel. The cross sectional area of the tunnel is 70.0 m^2. The vehicle speed limit is 80 $km\,h^{-1}$. There is no fresh air supply throughout the bores, therefore, the dilution factor of air pollutants was eliminated. The ventilation mode is longitudinal, which is achieved from the piston effect of the vehicles traversing it. There are 80 jet and 4 exhaust-air fans positioned along the ceiling throughout the tunnel but were all inactivated during sampling periods. The ventilation was thus induced by the flow of traffic through the tunnel and prevailing winds only. The average wind speeds in the tunnel were measured by the two sensors installed on the top roof of the tunnel near the sampling stations.

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2.2 Sampling and instruments

In total, 23 pairs of whole air samples were collected in the tunnel, including 5 and 18 in summer and winter of 2003, respectively. The sampling times were chosen to cover a wide variation of vehicle usages at different time periods. One pair of samples was collected simultaneously at the tunnel entrance and exit during each sampling. The inlet sampling station was located 686 m inside the entrance of the south bore of Shing Mun Tunnel and the outlet sampling station was located 350 m upwind of the exit (Fig. 1). Ambient volatile organic canister samplers (AVOCS) (Andersen Instruments Inc. Series 97-300) were used to collected whole air samples into pre-cleaned and pre-evacuated 2-l stainless steel canisters with a flow rate of 30 ml min^{-1} for 1 or 2 h.

The sampler was fixed on the ground level with an inlet at a height of ~1.5 m. The flow rates were checked in the field before and after each run using a calibrated flow meter. After sampling, the filled canisters were shipped to the laboratory of the University of California, Irvine for chemical analysis within two weeks of being collected.

2.3 Traffic count analysis

Vehicular composition and volume were determined by manual counts at the entrance of the tunnel tube at 15-min intervals during the sampling periods. Video-recording was also taken for data validation and review purposes. The vehicle types were classified into three major categories, namely gasoline-fueled vehicle (motor cycle and private car), LPG-fueled taxi and diesel-fueled vehicle (big bus, heavy goods vehicle, light goods vehicle and minibus). Traffic speed surveys were periodically conducted at Shing Mun Tunnel using the car chasing method. The instrumented vehicle equipped with a Darwin microwave speed sensor was driven and the tachometer sensor recorded vehicle speed on a second-by-second basis. The age and mileage distribution of vehicles were not obtained in this study.

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2.4 Chemical analyses

All canisters were shipped to the laboratory at the University of California, Irvine (UCI) and analyzed for carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), non-methane hydrocarbons (NMHCs), and halocarbons. Carbon monoxide analyses were carried out using a hydrogen gas methanizer upstream of a gas chromatograph (HP 5890) equipped with a flame ionization detector (FID) and a 3 m molecular sieve column. Methane was also analyzed using an HP 5890 GC equipped with an FID detector. The samples were injected into an 1/8″ stainless steel 0.9 m column packed with 80/100 mesh Spherocarb.

The analytical system used to analyze NMHCs, halocarbons and alkyl nitrates involved the cryogenic pre-concentration of 1520±1 cm^3 (STP) of air sample in a stainless steel tube filled with glass beads (1/8-inch diameter) and immersed in liquid nitrogen (−196°C). A mass flow controller with a maximum allowed flow of 500 mL min^{-1} controlled the trapping process. The trace gases were revolatilized using a hot water bath and then reproducibly split into five streams directed to different detector/column combinations.

Electron capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), flame ionization detectors (FID, sensitive to hydrocarbons), and quadrupole mass spectrometer detectors (MSD, for unambiguous compound identification, selected ion monitoring) were employed. The first column-detector combination (abbreviated as "DB5ms/MSD") was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 mm film thickness) output to a quadrupole MSD (HP-5973). The second combination ("DB1/FID") was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1 mm film thickness) output to a FID (HP-6890). The third combination ("PLOT-DB1/FID") was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5 mm film thickness) and output to an FID. The fourth combination ("Restek1701/ECD") was a RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50 mm film thickness) which was output to an ECD. The fifth combination ("DB5-Restek1701/ECD") was a DB-5 (J&W; 30 m,

0.25 mm I.D., 1 mm film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5 mm film thickness) and output to an ECD. The DB5ms/MS, DB1/FID, PLOT-DB1/FID, Restek1701/ECD, and DB5-Restek1701/ECD combinations received 10.1, 15.1, 60.8, 7.2, and 6.8% of the sample flow, respectively. Additional analytical details are given by Blake et al. (2001) and Colman et al. (2001). The measurement precision, detection limits and accuracy vary by compound and are quantified for each species in Colman et al. (2001). Briefly, the detection limit is 5 ppbv for CO, 3 pptv for NMHCs, 0.02 pptv for alkyl nitrates, and 0.01–10 pptv for halogenated species (CH_4 is always above its detection limit). The accuracy of our measurements is 1% for CH_4, 5% for CO, 5% for NMHCs, and 2–20% for halogenated species. The measurement precision is 2 ppbv for CH_4, 2 ppbv for CO, and ranges from 0.5–5% for NMHCs, and 1–5% for halogenated species.

2.5 Emission factor

The emission factors from tunnel measurements were calculated according to the method of Pierson (Pierson and Brachaczek, 1983; Pierson et al., 1996). The vehicular emission factor is the mass of specific pollutants produced in units of mg/kilometer, which can be determined from

$$EF_{veh} = \frac{(C_{out} - C_{in})AUt}{NL} \quad (1)$$

where EF_{veh} is the average vehicular emission factor in mg vehicle^{-1} km^{-1} traveled. C_{out} and C_{in} represent the mass concentrations of specific pollutants at the exit and entrance in mg m^{-3}. A is the area of tunnel cross-section in m^2, U is the wind speed in m s^{-1}, and t is the sampling duration (1 or 2 h in this study). N is the total traffic number during the sampling period. L is the distance between the two monitoring stations in km. The VOC concentrations at the entrance of the tunnel were subtracted from those in the tunnel. The difference was multiplied by the tunnel air flow to determine the mass emitted during the run. This value was divided by the total vehicle distance traveling

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during the run to obtain the fleet mean emission rate.

2.6 Photochemical reactivity

It is well known that VOC compounds are significant precursors of ozone formation (Guo et al., 2004). Individual VOCs have different photochemical reactivities. In order to calculate the ozone-forming potential of the vehicular emissions, the speciated emission factors for each vehicle type were multiplied by the maximum incremental reactivity (MIR) scale developed by Carter (1998). The MIR are in units of grams of ozone per gram of organic compound and therefore are simply multiplied by the emission factors (grams of organic compound per vehicle-km driven), to yield reactivity-adjusted emission rates in units of ozone per vehicle-km.

3 Results and discussion

3.1 Run description

The average number of vehicles traversed the tunnel per hour during this study was 1545, ranging from 786 to 2842. Table 1 shows the 1-h average traffic composition of Shing Mun Tunnel in summer and winter. On average, approximately 45% of the total vehicles were diesel-fueled, 45% gasoline, and the remaining were LPG vehicles. Diesel-fueled vehicles represented the highest proportion (more than 60%) during 11:00–13:00 and 14:00–16:00. The traffic speed for every run did not vary significantly, with most speeds recorded within the range of 60 to 70 $\mathrm{km\,h^{-1}}$. The average wind speed recorded in the tunnel during the sampling periods was about 4.7 $\mathrm{m\,s^{-1}}$.

3.2 Concentrations of VOCs

In this study, a total of 110 species were quantified in the samples collected at the inlet and outlet of Shing Mun Tunnel. These include carbon monoxide (CO), carbon

dioxide (CO_2), carbonyl sulfide (OCS), carbon disulfide (CS_2), methane (CH_4), 40 C_2-C_{10} saturated hydrocarbons, 32 C_2-C_{10} unsaturated hydrocarbons, 21 C_6-C_{10} aromatic hydrocarbons and 12 halogenated hydrocarbons.

The average concentrations and standard deviations of analyzed VOCs and their classes at the inlet and outlet of tunnel are given in Table 2. The average concentrations of the total measured VOCs (sum of all of measured species except CO, CO_2, CH_4, OCS and CS_2) at the inlet and outlet of the tunnel were 81 250 pptv and 117 850 pptv, respectively. Among the 107 compounds ethene was the most abundant VOC and ethyne was the next most abundant species, followed by toluene. Interestingly, propane is the fourth most abundant gas at the tunnel inlet while n-butane is the fourth most abundant species at the outlet. This is thought to be the result of emissions arising from LPG vehicles (see Sect. 3.3). It has been reported that concentrations of individual VOCs in tunnels were typically 10 times higher than those of the same species measured in fresh air at the ventilation intake (Kirchstetter et al., 1996) or outside the tunnel (Mugica et al., 1998). In this study, the individual VOCs in the tunnel were generally 5–10 times higher than those in Hong Kong ambient air (Guo et al., 2007). Although carbonyl sulfide (OCS) emissions make up only a small fraction of the total sulfur emitted into the atmosphere compared to sulfur dioxide, its relative inertness in the troposphere, OCS is transported to the stratosphere where it is photodissociated and oxidized to SO_2 and ultimately sulfate particles. Anthropogenic sources of COS arise from the combustion of biomass and fossil fuel. Emission of OCS from vehicles is one of such example (Fried et al., 1992). The average concentrations of OCS at the inlet and outlet of the tunnel were 970 pptv and 1200 pptv, respectively, which is higher than that of free troposphere (510 ppt) (Carroll, 1985) and similar to that in Beijing city (1340 ppt) (Mu et al., 2002).

For both sampling locations, unsaturated hydrocarbons were the most abundant hydrocarbon group (inlet: 43%±6%; outlet: 44%±5%) in the samples collected in the tunnel, followed by saturated (inlet: 37%±6%; outlet: 36%±5%) and aromatic hydrocarbons (inlet: 16%±2%; outlet: 17%±2%). The weight percentages between the two

locations showed no significant differences compared to their absolute concentrations. This is likely due to the fact that both of the locations were affected predominantly by vehicle exhaust.

Differences between concentrations measured at the tunnel outlet and those measured at the same time at the tunnel inlet are also shown in Table 2. The VOC composition in the tunnel air is influenced by ambient VOC concentrations. Therefore, the VOC composition obtained from the concentration difference between the two sites inside the tunnel better represents the VOC composition as compared to the results obtained from only one site. When looking at the net concentration, the five most abundant VOCs emitted by vehicles at the tunnel were, in decreasing order, ethene ethyne, n-butane, toluene and propane. This implies that ethene has the highest emission rate in vehicle exhaust. Ethene emissions in the tunnel contributed more than 20% of the total measured VOC emissions (except CO, CO_2, CH_4, and OCS and CS_2) during most of the measurement periods. And the five most abundant species contributed over 50% of the total measured VOCs. Based on the net concentration, unsaturated hydrocarbons (48%) are the most abundant, followed by saturated hydrocarbons (34%), and aromatics (17%).

3.3 VOC ratios

Using the ratio of a more reactive VOC to a less reactive VOC (photochemical lifetimes (or reactivities) against OH, a higher ratio indicates relatively little photochemical processing of the air mass and major impact from primary emissions. On the other hand, a lower ratio is reflective of more aged VOC mixes and thus presumably that the VOCs were emitted from more distant sources (Guo et al., 2007). Comparisons of the ratios can be used to estimate the relative ages of air parcels. In this study, the ratios of propane/ethane, ethene/ethane and m,p-xylene/ethylbenzene were used for comparison (Nelson and Quigley, 1983; Smyth et al., 1999; So and Wang, 2004). High ratios were determined in tunnel when compare with other ambient study in Hong Kong (Table 3). The average value of propane/ethane, ethene/ethane and

m,*p*-xylene/ethylbenzene in tunnel (1.42±0.36, 4.64±2.34, 2.61±0.30) are higher than the ratios measured at the urban/rural sites in Hong Kong (Guo et al., 2007), but are close to the value of other tunnel studies (Na et al., 2002; Vega et al., 2000).

Ethene and ethyne are typical tracers for combustion, and thus vehicle exhaust was the likely source of these two gases (Stoeckenius et al., 2006). Tsai et al. (2006) concluded that the ethyne/ethene ratios for Hong Kong, Macau, Guangzhou and Zhuhai were 0.53±0.03, 1.06±0.04, 1.26±0.04 and 1.01±0.21, respectively. And the ethene level in the Hong Kong roadside was a factor of two higher than ethyne, whereas ethene and ethyne were close in Guangzhou, Zhuhai and Macau. The average ethyne/ethene ratio in this study is 0.45±0.07 which is close to the previous roadside study in Hong Kong.

3.4 Correlation of VOCs

Correlation analysis of VOCs was carried out in order to measure the relationship between two variables. CO is generally emitted from incomplete combustion of fossil fuel. Determining the relationship between CO and VOCs can provide useful information on their sources and emission signatures (Wang et al., 2002, 2003; Guo et al., 2007). Among the VOCs measured, benzene was best correlated with CO (R^2=0.94), follow by ethyne, 2-methylheptane, propyne, i-butene (R=0.92) and m,p-xylenes (R=0.92) confirming a common source origin in tunnel. Generally, good and fair correlations (R=0.63–0.89) were observed between individual VOCs and CO, except halocarbons, isoprene and pinenes which are emitted from different sources. Some studies report the contribution of isoprene from vehicular exhaust (e.g., Borbon et al., 2001; Barletta et al., 2002). Here, the poor correlation between isoprene and CO suggests that vehicular emissions of isoprene are not significant.

Moreover, strong and fair correlations were determined from marker species of fuel vapor (gasoline, diesel and liquefied petroleum gas [LPG]). Propane, n-butane and i-butane are the major constituents of LPG in Hong Kong (Tsai et al., 2006) and strong correlations were found (R=0.95–0.98) among the species which indicated

that unburned LPG was emitted to the tunnel atmosphere. n-pentane, i-pentane, 2,3-dimethylbutane, 2-methylpentane and toluene are the most abundant VOCs in gasoline vapor in Hong Kong (Tsai et al., 2006). Strong correlations (R=0.82–0.96) of these species indicated the importance of running evaporative loss from gasoline-fueled vehicles. Moreover, good correlations (R=0.54–0.95) were observed among diesel-fueled species (n-noncan, n-decane and 1,2,4-trimethylbenzene) (Tsai et al., 2006).

3.5 Emission factors of VOCs for mixed vehicles

The average emission factors of VOCs are given in Table 2 (Zero emission factors for some VOCs results from C_{outlet} begins less than or the same as C_{inlet}). The total measured VOC emission factors ranged from 67.2 mg veh^{-1} km^{-1} to 148 mg veh^{-1} km^{-1}. The average emission factor was 115 mg veh^{-1} km^{-1}. The five most abundant VOC species in vehicle emissions were, in decreasing order, ethene (12.6±4.3 mg veh^{-1} km^{-1}), toluene (12.1±3.9 mg veh^{-1} km^{-1}), n-butane (8.7±3.1 mg veh^{-1} km^{-1}), propane (5.7±2.5 mg veh^{-1} km^{-1}) and i-pentane (5.6±2.1 mg veh^{-1} km^{-1}) (Table 2). The ethene emissions in tunnel contributed more than 11% of the total measured VOC emissions. And the five most abundant species contributed over 38% of the total measured VOC emissions. Emission factors measured in this study are for warm engine moving vehicles. Higher emissions of VOCs may be observed in an urban setting where more vehicles are in cold start and off-cycle conditions. The emission factor of OCS ranged from 0.05 mg veh^{-1} km^{-1} to 3.2 mg veh^{-1} km^{-1}. The average emission factor was 0.8 mg veh^{-1} km^{-1} which is higher than previous study done by chassis dynamometer (Fried et al., 1992).

Correlation analysis was carried out to determine the variations of EFs of individual VOC species with the change of the fractions of vehicle types (gasoline-fueled vehicle, LPG-fueled taxi and diesel-fueled vehicle) in tunnel. The equations of linear regression and correlation coefficient of selected VOCs (total emission factor >0.5 mg veh^{-1} km^{-1} and R>0.5) are presented in Table 3. High propane, i-butane and n-butane emissions

were found to be associated with a high proportion of LPG-fueled taxis. Fair correlations were observed between propane, i-butane and and n-butane with the fractions of LPG-fueled taxi. (R=0.54–0.58). Moreover, fair correlations were determined between marker species with fractions of gasoline-fueled and diesel-fueled vehicles (Table 3).

3.6 Effect of fuel evaporative loss in the tunnel atmosphere

Figure 2 shows the selected VOC distribution measured in Shing Mun Tunnel and was compared with the compositions of gasoline vapor and LPG collected in 2003 (in weight percent composition) (Tsai, 2007). The individual weight percentage was calculated by normalizing individual weight concentration (mg m^{-3}) to total weight concentration. As diesels samples consisted mainly of heavy (C_8-C_{10}) hydrocarbons (such as n-decane), these compounds have low vapor pressures and thus do not quickly evaporate into the atmosphere (Tsai et al., 2006), suggesting that evaporative loss from diesel to the tunnel atmosphere was insignificant compared with the light species from gasoline and LPG. It is clear that there are several VOC species that were abundant in the tunnel but not the gasoline vapors or LPG samples, namely ethene, ethyne, and propene. These species are typical tracers for fossil fuel combustion.

Propane, i-butane and n-butane are tracers for LPG, the propane/n- + i-butanes ratio of LPG was 0.30, and the ratio of tunnel sample ranged from 0.24 to 0.51. The similar propane/n- + i-butanes ratio obtained in Shing Mun Tunnel and the LPG samples indicates that the propane and butanes measured in the tunnel resulted from running evaporative losses of LPG. These findings are consistent with the previous study (Tsai et al., 2006). Moreover, the abundances of toluene and i-pentane were high in Shing Mun Tunnel. These two gases are tracers of gasoline evaporation and their enhanced concentrations indicated the importance of running evaporative loss from gasoline-fueled vehicles. Gasoline evaporation was found to contribute 14% of total VOC emission in Hong Kong in 2001–2002 (Guo et al., 2006).

3.7 Reactivity with respect to ozone formation

It is well known that VOCs are significant precursors of ozone formation. Individual VOCs have different photochemical reactivities. To assess the relative importance of VOCs from vehicular emissions found in Hong Kong, we use the maximum incremental reactivity (MIR) (Carter, 1994) to evaluate the contributions of individual VOCs to ozone production. In order to calculate the ozone-forming potential of the vehicular emissions, the speciated emission factors for each fuel types were multiplied by the maximum incremental reactivity (MIR) scale developed by Carter (1998). The MIRs are in units of grams of ozone per gram of organic compound and therefore are simply multiplied by the emission factors (grams of organic compound per vehicle-km driven), to yield reactivity-adjusted emission rates in units of ozone per vehicle-km.

The top ten reactivities with respect to ozone formation of emissions are presented in Table 4. The largest contributors to ozone production in Shing Mun Tunnel were ethene (126 mg O_3 veh^{-1} km^{-1}), propene (66 mg O_3 veh^{-1} km^{-1}), and toluene (51 mg O_3 veh^{-1} km^{-1}). Ethene emissions were responsible for 23% of the measured VOC reactivity for vehicular emissions, followed by propene and toluene at 12% and 9.0%. In the same tunnel, the emission factors of carbonyl compounds were determined (Ho et al., 2006). Using the same calculation method, the top ten ozone-forming potential of measured VOCs and carbonyl compounds are determined. Formaldehyde emissions have the highest ozone formation potential, followed by ethane and propene.

Individual species are grouped into saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons to determine the group lump-sum ozone formation potential. The unsaturated hydrocarbons contribute most to the potential ozone formation, at 56% but contribute to only 32% of ozone formation. The total ozone formation potential is 568 mg O_3 km^{-1} veh^{-1}. On the basis of 100 g VOCs emitted, ozone formation is 494 g (average emission rate of total VOCs is 115 mg km^{-1} veh^{-1}) which is similar to the results of Taipei tunnel, of 427 g (Hwa et al., 2002).

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3.8 Comparison of tunnel results with other studies

Of studies that identified VOCs from vehicular emissions in tunnels, few have included calculations of emission factors. A summary of literature data for selected VOCs are shown in Table 5. Generally, the emission factors from our study are similar or lower than other tunnel studies. The three largest abundant emission factors of VOCs in a Taipei Tunnel are toluene, ethene and 1,2,4-Trimethylbenzene (29.02±4.95, 26.23±4.89 and 14.28±2.94 mg km^{-1} veh^{-1}, respectively), which are 2 to 5 times higher than our study (Hwa et al., 2002). Characteristic VOCs emissions may directly reflect the specific formula of gasoline or diesel fuel used. The values of the BTX and i-pentane emission factors are about 20% lower than given in another tunnel studies as indicated in Table 5. This maybe due to the low fractions of gasoline-fueled vehicles in tunnels studied when compared to other studies. For propane and i-butane, the emission factors measured in our study are higher than previously measured in Taiwan and Switzerland. Due to the difference in fuel composition, i.e. 10% of LPG fueled vehicles in Hong Kong, significantly higher emission factors of propane and i-butane were anticipated and observed. This also demonstrates the need to establish local emission profiles.

4 Conclusions

Ethene, i-pentane and toluene were found to be the most abundant VOCs generated from the fueled vehicles. In this pilot vehicle source study, our observations are consistent with other studies done in Europe and Asian cities. But the average emission factor of OCS (0.8 mg veh^{-1} km^{-1}) was higher than previous study done by chassis dynamometer. These emission factors provide reliable estimations of VOCs introduced into the atmosphere from vehicular sources. On the basis of 100 g VOCs emitted, ozone formation is 494 g (average emission rate of total VOCs is 115 mg km^{-1} veh^{-1}) which is similar to the results of Taipei tunnel, of 427 g. This information will be useful

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in determining emission controls for different classes of vehicles. This will also allow for estimating the impact of VOC emissions from non mobile sources.

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Table 1. The 1-h average traffic composition of Shing Mun Tunnel in summer and winter.

Vehicle Type	Traffic composition (1-h average) %	
	Summer	Winter
Gasoline	39.9	45.6
LPG	9.9	10.7
Diesel	50.1	43.7

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Table 2. Average concentrations of VOCs and their emission factors in summer and winter.

VOCs	Concentrations (ppt)			Emission Factor (mg veh^{-1} km^{-1})	
	inlet	outlet	Outlet minus inlet	mean	range
CO_2 (ppmv)	580±50	710±80	130±30	310000±81000	180 000–480 000
CO (ppbv)	2800±720	4100±1000	1300±390	1900±380	1300–2600
Ethene	16000±4200	25000±7100	8500±3400	13±4.0	0.6–21
Toluene	6100±2000	8700±2800	2500±1200	12±3.9	6.9–23
n-Butane	5700±2500	8500±3700	2800±1300	8.7±3.1	3.9–17
CH_4 (ppmv)	1.91±0.1	1.92±0.1	0.01±0.01	7.2±4.8	0.0–17
Propane	5800±2800	8200±4000	2400±1300	5.7±2.5	1.6–13
i-Pentane	3200±1100	4600±1600	1500±660	5.6±2.1	3.1–11
i-Butane	3500±1800	5300±2600	1700±900	5.5±2.2	2.5–11
Propene	4500±1100	6900±1900	2400±900	5.3±1.5	3.2–8.3
Benzene	2500±620	3500±920	1100±380	4.5±0.9	2.5–6.0
Ethyne	7400±1800	10000±2600	3000±1300	4.0±1.3	1.6–7.0
1,2,4-Trimethylbenzene	720±400	1200±460	480±460	3.0±2.4	0.0–8.3
m-Xylene	1000±320	1500±500	470±230	2.6±0.9	1.3–4.6
i-Butene	1700±510	2600±850	840±560	2.5±1.3	0.0–4.7
1-Pentene	460±340	950±750	500±550	1.9±2.1	0.4–9.2
2-Methylpentane	940±330	1300±470	400±210	1.8±0.7	0.3–3.1
Ethane	4400±1500	5500±1800	1100±550	1.7±0.6	0.0+2.5
n-Pentane	980±310	1400±480	450±210	1.7±0.6	0.9–3.3
1-Butene	940±250	1500±380	530±210	1.6±0.6	0.4–2.6
o-Xylene	640±180	940±310	290±160	1.6±0.6	0.7–2.8
1,2,3-Trimethylbenzene	280±150	480±190	250±340	1.4±1.1	0.0–3.8
3-Ethyltoluene	320±130	530±200	210±180	1.4±0.9	0.0–3.7
n-Hexane	680±270	980±410	300±200	1.3±0.5	0.5–2.6
Ethylbenzene	590±210	820±270	240±110	1.3±0.4	0.7–2.0
3-Methylpentane	670±220	940±310	270±140	1.2±0.5	0.4–2.0
p-Xylene	450±140	660±210	200±96	1.1±0.4	0.6–2.0
2-Ethyltoluene	210±99	380±140	170±140	1.0±0.7	0.0–2.5
2,2,4-Trimethylpentane	350±280	490±330	140±250	1.0±0.7	0.0–2.3
Cylopentane	530±210	810±340	290±150	1.0±0.4	0.6–1.7
2-Methyl-1-pentene	260±150	460±280	200±130	0.9±0.5	0.1–1.9
n-Heptane	430±460	530±200	95±390	0.9±0.4	0.0–2.4
OCS	970±300	1200±450	200±440	0.8±1.3	0.0–5.0
n-Decane	140±100	245±120	103±71	0.8±0.6	0.0–2.4
1,3,5-Trimethylbenzene	180±70	300±92	120±72	0.8±0.4	0.3–1.8
3-Methylhexane	490±760	490±180	4±720	0.8±0.3	0.0–1.2
4-Ethyltoluene	130±61	270±230	130±210	0.7±0.8	0.0–2.8
n-Nonane	140±77	240±107	96±54	0.7±0.4	0.3–1.6
2-Methylhexane	390±340	480±180	90±290	0.7±0.3	0.0–1.1
Methylcyclopentane	320±110	470±170	150±65	0.7±0.2	0.4–0.9
2-Methyl-2-butene	260±180	400±240	140±130	0.6±0.4	0.0–1.7
1,4-Diethylbenzene	69±56	150±72	84±75	0.6±0.4	0.0–1.3
trans-2-Butene	400±130	620±210	220±87	0.6±0.2	0.5–1.1
trans-2-Pentene	270±100	440±170	160±71	0.6±0.2	0.3–1.0
2-Methyl-1-butene	210±82	330±130	120±53	0.5±0.2	0.2–0.9
n-Octane	150±54	230±76	84±36	0.5±0.2	0.1–0.9
n-Propylbenzene	120±41	200±63	74±43	0.5±0.2	0.2–0.9
cis-2-Butene	290±99	450±160	160±62	0.5±0.1	0.3–0.8
CS2	110±97	190±340	83±340	0.4±1.3	0.0–6.0
1-Hexene	130±56	210±110	86±72	0.4±0.3	0.0–1.3
cis-2-Pentene	200±74	320±120	120±54	0.4±0.2	0.2–0.7
Methylcyclohexane	220±170	280±110	62±130	0.4±0.2	0.0–0.8
2,5-Dimethylhexane	150±180	190±100	41±170	0.4±0.2	0.0–0.9
2,4-Dimethylhexane	180±220	220±110	37±220	0.4±0.2	0.0–0.9
1,3-Butadiene	410±390	360±340	−46±360	0.3±0.6	0.0–2.3
2,3-Dimethylbutane	140±64	200±85	61±46	0.3±0.2	0.0–0.7

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Table 2. Continued.

VOCs	Concentrations (ppt)			Emission Factor (mg veh^{-1} km^{-1})	
	inlet	outlet	Outlet minus inlet	mean	range
2,3-Dimethylhexane	74±40	120±72	46±39	0.3±0.2	0.0–0.6
Propyne	320±74	480±130	160±67	0.3±0.1	0.2–0.5
4-Methyl-1-pentene	93±31	170±57	73±38	0.3±0.1	0.2–0.6
Cyclohexane	180±93	240±99	62±39	0.3±0.1	0.0–0.6
2-Methylheptane	94±30	150±48	55±25	0.3±0.1	0.2–0.6
2-Methyl-2-pentene	78±43	120±60	43±37	0.2±0.2	0.0–0.7
2,3,4-Trimethylpentane	91±52	130±88	40±46	0.2±0.2	0.0–0.7
2,2-Dimethylbutane	98±36	130±49	28±45	0.2±0.2	0.0–0.6
1,3-Diethylbenzene	31±15	53±22	25±27	0.2±0.2	0.0–0.6
3-Methyl-1-butene	110±32	170±52	61±22	0.2±0.1	0.1–0.3
trans-2-Hexene	81±29	140±49	55±24	0.2±0.1	0.1–0.4
3-Methylheptane	99±31	140±44	39±21	0.2±0.1	0.0–0.4
cis-3-Methyl-2-pentene	67±37	100±51	38±31	0.2±0.1	0.0–0.6
2,4-Dimethylpentane	74±28	110±42	34±18	0.2±0.1	0.1–0.3
3-Methyl-1-pentene	69±31	99±31	30±32	0.2±0.1	0.0–0.3
2,6-Dimethylheptane	28±23	39±23	12±21	0.2±0.1	0.0–0.6
CH_3Br	50±120	72±190	22±78	0.1±0.5	0.0–2.3
2,4-Dimethylheptane	35±21	62±28	27±19	0.1±0.1	0.0–0.2
trans-3-Methyl-2-pentene	42±26	63±35	21±24	0.1±0.1	0.0–0.4
n-Butylbenzene	23±10	35±16	15±19	0.1±0.1	0.0–0.4
Isopropylbenzene	33±10	48±17	15±13	0.1±0.1	0.0–0.2
sec-Butylbenzene	20±11	31±15	14±11	0.1±0.1	0.0–0.3
1,2-Diethylbenzene	17±9	25±13	10±11	0.1±0.1	0.0–0.3
CH2Cl2	180±140	190±140	9.0±46	0.1±0.1	0.0–0.4
2,3-Dimethylpentane	57±71	64±51	7.0±68	0.1±0.1	0.0–0.4
cis-2-Hexene	44±17	74±29	30±14	0.1±0.0	0.1–0.2
trans-3-Hexene	34±14	54±23	20±11	0.1±0.0	0.0–0.2
2,2-Dimethylpentane	24±10	34±13	10±5.0	0.1±0.0	0.0–0.1
2,5-Dimethylheptane	14±6.0	25±10	10±5.0	0.1±0.0	0.0–0.1
3,3-Dimethylpentane	48±53	55±22	8.0±48	0.1±0.0	0.0–0.2
4-Methylheptane	10±6.0	17±10	8.0±5.0	0.1±0.0	0.0–0.1
3,3-Dimethylheptane	11±6.0	18±9.0	8.0±5.0	0.1±0.0	0.0–0.1
4,4-Dimethylheptane	15±7.0	23±10	8.0±4.0	0.1±0.0	0.0–0.1
limonene	9.0±5.0	11±9.0	5.0±11	0.0±0.1	0.0–0.4
2-Butyne	5.0±2.0	8.0±2.0	42±186	0.0±0.0	0.0–0.0
1-Butyne	12±5.0	21±7.0	9.0±4.0	0.0±0.0	0.0–0.1
cis-3-Hexene	21±6.0	27±10	6.0±12	0.0±0.0	0.0–0.1
Isobutylbenzene	7.0±3.0	10±5.0	5.0±4.0	0.0±0.0	0.0–0.1
2,2,3-Trimethylbutane	8.0±4.0	12±4.0	3.0±2.0	0.0±0.0	0.0–00
Isopropyltoluene	6.0±3.0	7.0±3.0	2.0±5.0	0.0±0.0	0.0–0.1
C_2HCl_3	50±78	51±81	2.0±9.0	0.0±0.0	0.0–0.2
1,2-dichloroethene	18±14	20±15	2.0±4.0	0.0±0.0	0.0–0.1
CH_3CCl_3	29±5.0	31±4.0	2.0±2.0	0.0±0.0	0.0–0.1
α−Pinene	12±7.0	10±7.0	1.0±5.0	0.0±0.0	0.0–0.1
$CHBr_3$	4.2±2.1	4.6±1.9	0.4±1.2	0.0±0.0	0.0–0.1
$CHCl_3$	28±19	28±13	0.0±4.0	0.0±0.0	0.0–0.1
CCl_4	99±4.0	100±3	0.0±3.0	0.0±0.0	0.0–0.1
β−Pinene	6.0±3.0	5.0±2.0	0.0±2.0	0.0±0.0	0.0–0.0
H-1211 ($CBrClF_2$)	7.0±4.0	8.0±5.0	0.0±1.0	0.0±0.0	0.0–0.1
CH_2Br_2	1.4±0.2	1.2±0.2	−0.1±0.1	0.0±0.0	0.0–0.0
3-Ethylpentane	55±100	53±23	−2±96	0.0±0.0	0.0–0.2
C_2Cl_4	96±91	95±85	−1±13	0.0±0.0	0.0–0.2
CH_3Cl	800±140	790±140	−11±87	0.0±0.0	0.0–0.7
Isoprene	160±340	56±63	−110±360	0.0±0.0	0.0–1.0
Saturated	**31 000±11 000**	**43 000±15 000**	**13 000±6400**	**44±12**	**23–66**
Unsaturated	**35 000±8400**	**52 000±14 000**	**17 000±6400**	**35±9.4**	**16–56**
Aromatics	**13 000±3800**	**20 000±6100**	**6400±3200**	**33±11**	**18–50**
Halocarbons	**1400±400**	**1400±380**	**26±130**	**0.5±0.5**	**0.0–2.4**
Total VOCs	**81 000±21 000**	**120 000±32 000**	**37 000±14 000**	**115±26**	**67–150**

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Table 3. Correlation of EFs of selected VOC species with the change of the fractions of vehicle types.

VOCs	Linear Regression[a]	*R*
Correlate with fractions of LPG-fueled vehicles		
propane	Propane=1.53+35.1 χ_L	0.58
i-butane	i-butane=1.87+32.2 χ_L	0.55
n-butane	n-butane=3.61+46.0 χ_L	0.54
Correlate with fractions of gasoline-fueled vehicles		
i-pentane	i-pentane=1.06+11.3 χ_g	0.53
n-pentane	n-pentane=0.185+3.45 χ_g	0.53
i-butene	i-butene=0.176+6.15 χ_g	0.60
cyclopentane	cyclopentane=0.067+2.27 χ_g	0.57
methylcyclopentane	methylcyclopentane=0.231+1.03 χ_g	0.60
2-methylpentane	2-methylpentane=0.269+3.70 χ_g	0.55
3-methylpentane	3-methylpentane=0.233+2.42 χ_g	0.55
2-methylhexane	2-methylhexane=0.061+1.63 χ_g	0.60
3-methylhexane	3-methylhexane=0.243+1.34 χ_g	0.58
2,2,4-trimethylpentane	2,2,4-trimethylpentane=−0.481+3.69 χ_g	0.61
toluene	toluene=0.59+27.8 χ_g	0.62
ethylbenzene	ethylbenzene=0.109+2.87 χ_g	0.60
m-xylene	m-xylene=0.137+5.58 χ_g	0.62
p-xylene	p-xylene=0.235+2.02 χ_g	0.57
o-xylene	o-xylene=0.247+3.07 χ_g	0.51
Correlate with fractions of diesel-fueled vehicles		
ethene	ethene=3.98+21.7 χ_d	0.74
1-pentene	1-pentene=−3.28+12.0 χ_d	0.59
n-octane	n-octane=0.236+0.675 χ_d	0.55
n-nonane	n-nonane=−0.321+2.20 χ_d	0.63

[a] χ_L=fractions of LPG-fueled vehicles; χ_g=fractions of gasoline-fueled vehicles; χ_d=fractions of diesel-fueled vehicles.

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Table 4. Top 10 VOCs for ozone-forming potential of vehicular emissions at Shing Mun Tunnel.

VOCs	Ozone-formation[a]
Ethene	125.9
Propene	65.9
Toluene	50.7
m-Xylene	28.7
1,2,4-Trimethylbenzene	22.6
1-Butene	17.5
i-Butene	17.2
1,2,3-Trimethylbenzene	16.4
n-Butane	12.6
o-Xylene	12.4

[a] Emission factor of VOCs×MIR coefficient (Emission factor unit, mg veh^{-1} km^{-1}; MIRunits, dimensionless, gram of ozone produced per additional gram of VOCs).

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Table 5. Comparison of emission factors of VOCs in mg/km-vehicle.

Unit: mg veh^{-1} km^{-1}	This Study	Chiang et al. (2007)	Hwa et al. (2002)	Staehelin et al. (1998)	Staehelin et al. (1998)
Tunnel, Location	Shing Mun Tunnel, Hong Kong	Chung-Liao Tunnel, Taiwan	Tai Pei Tunnel, Taiwan	Gubrist Tunnel, Switzerland	Gubrist Tunnel, Switzerland
Year of Experiment	2003	2005	2000	1993	1993
Type of Vehicle	All	All	All	GAV	DIV
Ethene	13	–	26	24	45
Toluene	12	29	29	16	21
n-Butane	8.7	5.1	6.6	9.7	27
Propane	5.7	0.2	2.4	0.15	5.7
i-Pentane	5.6	40	13	18	43
i-Butane	5.5	ND	4.6	1.7	5.2
Propene	5.3	10	12	14	22
Benzene	4.5	5.9	12	10	15
Ethyne	4.0	–	12	13	16
1,2,4-Trimethylbenzene	3.0	12	14	4.6	9.6
m-Xylene	2.6	8.4	9.0	11	27
p-Xylene	1.1				
i-Butene	2.5	–	–	8.0	11
1-Pentene	1.9	0.97	1.6	0.61	3.4
2-Methylpentane	1.8	13	5.3		
Ethane	1.7	–	4.3	4.3	3.2
n-Pentane	1.7	19	9.5	6.2	16
1-Butene	1.6	11	8.3	1.9	5.0
o-Xylene	1.6	6.4	7.9	4.8	6.3
1,2,3-Trimethylbenzene	1.4	2.0	–	0.97	2.4
n-Hexane	1.3	5.7	4.2	1.7	2.9
Ethylbenzene	1.3	5.3	5.9	3.6	7.2
3-Methylpentane	1.2	5.6	6.4		
2,2,4-Trimethylpentane	1.0	0.77	0.29		
Cylopentane	1.0	2.0	0.89		
n-Heptane	0.9	1.6	1.5	0.93	2.3
n-Decane	0.8	0.07	–	0.03	7.7
1,3,5-Trimethylbenzene	0.8	3.7	2.3	1.5	2.7
3-Methylhexane	0.8	2.8	2.9	–	–
n-Nonane	0.7	0.3	0.5	0.07	1.7
2-Methylhexane	0.7	2.5	–	–	–
trans-2-Butene	0.6	0.81	1.6	1.4	2.9
n-Octane	0.5	0.78	1.3	0.22	1.4
n-Propylbenzene	0.5	1.7	1.7	0.68	1.9
cis-2-Butene	0.5	1.6	1.8	1.3	2.5
1,3-Butadiene	0.3	3.8	2.6	1.6	-1.6
2,3-Dimethylbutane	0.3	13	1.3	–	–
Cyclohexane	0.3	0.4	0.98	4.5	6.1
2,4-Dimethylpentane	0.2	0.9	0.44	–	–
Isopropylbenzene	0.1	1.2	–	0.18	0.26
2,3-Dimethylpentane	0.1	0.72	–	8.6	16

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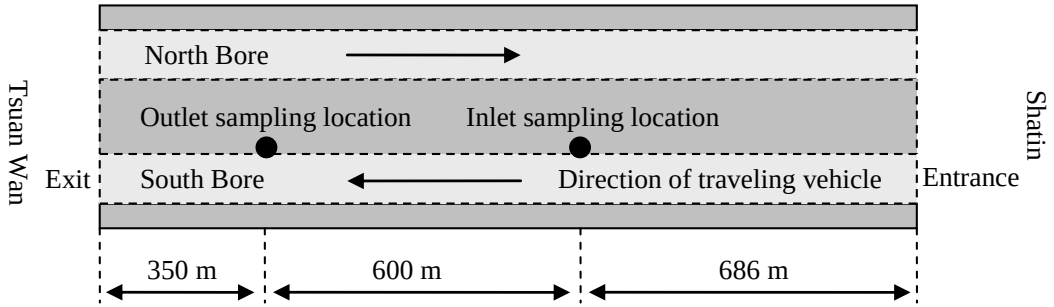

Fig. 1. Schematic diagram of the Shing Mun Tunnel.

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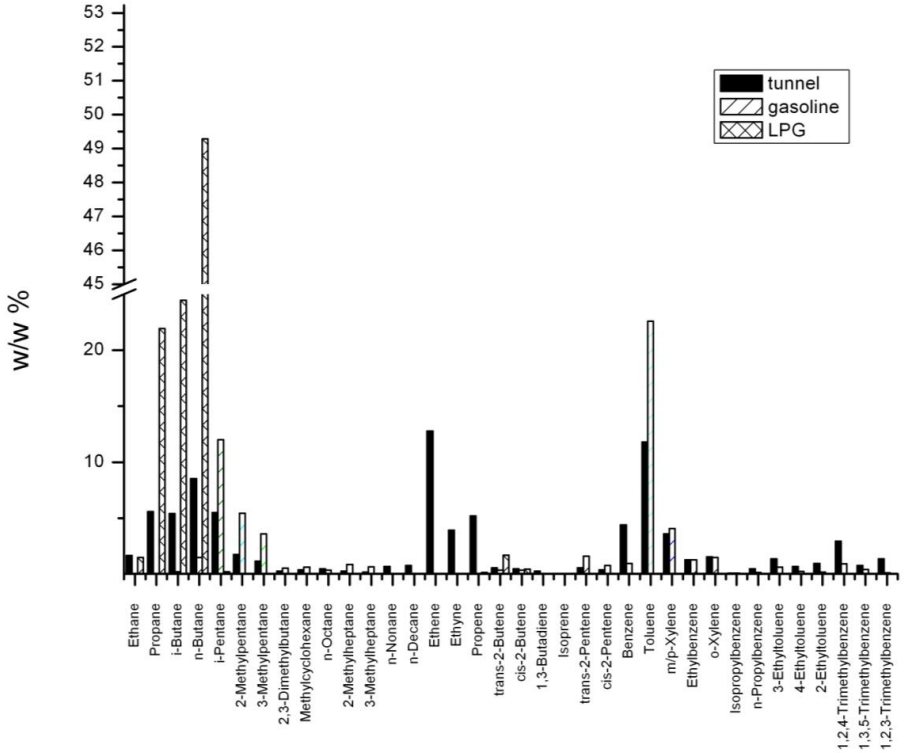

Fig. 2. Average VOC distributions (presented in w/w %) for gasoline vapor, LPG and Shing Mun Tunnel samples.

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