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Emissions of C_2 – C_{12} hydrocarbons in the Hsuehshan tunnel, Taiwan

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Abstract

The concentrations of 56 hydrocarbons from C_2 to C_{12} were measured simultaneously in the southbound bore, the northbound bore and the exhaust air shafts of the Hsuehshan tunnel near Yilan, Taiwan for 12 days during 2007 and 2008. A total of 60 integrated air samples were collected using stainless steel canisters and analyzed using GC/FID and GC/MS. The five most abundant species in all samples were ethylene, acetylene, isopentane, propylene and toluene. The exit/entrance ratios of total non-methane hydrocarbons (NMHC) concentration were 7.8 and 4.8 for the southbound and northbound bores, respectively. Furthermore, the exhaust from the vertical shafts affects air quality in the neighborhood. The most abundant species of emission rate (ER) was toluene (21.93–42.89 mg/sec), followed by isopentane, ethylene, propylene and 1-butene, with ER ranging from 2.50 to 9.31 mg/sec. The species in the three exhaust air shafts showed that the reactivities of these emissions are similar to those of vehicle emissions. Notably, the control of emissions in the vertical shafts of the vehicle tunnel will be important in the future.

Key words: tunnel; non-methane hydrocarbons; vehicle emissions; shaft; rate

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Introduction

Efforts to support the present road transportation system and to find space for a rapidly growing fleet of vehicles have led to extensive plans for new road tunnels throughout the world. Presently, the 24.5 km-long of Lærdal tunnel in Norway is the longest road tunnel in the world. It is followed by the Zhongnanshan tunnel (18.04 km) in China, the St. Gotthard Tunnel (16.9 km) in Switzerland, and the Arlberg tunnel (13.97 km) in Austria. The Hsuehshan tunnel in Taiwan is the fifth longest road tunnel in the world.

The transport path of pollutants and the effects on human health of the long tunnel differ from those on typical roads. The pollutants are difficult to disperse in the three dimensions within in a semi-closed tunnel, and the ventilation systems are not as effective as anticipation. The pollutants were transported in the driving direction, and accumulated at the two extremities of tunnel. The problem of air pollution is particularly serious in long tunnels, because pollution levels are higher and exposure time is longer. Exposure in tunnels also contributes to long-term health effects, of which cancer and other genotoxic effects are regarded as particularly important. Reported concentrations of hydrocarbons in a 3 km-long road tunnel in Brussels were approximately double those in the 0.5 km-long Tingstad tunnel. Estimates suggest 14 cases of cancer per year among one million individuals who drive regularly through the 13 km-long tunnel in Stockholm (Barrefors, 1996).

Various tunnel studies have focused on the composition of volatile organic compounds (Gertler et al., 1996; Zielinska et al., 1996; Barrefors, 1996; Pierson et al., 1996; Fraser et al., 1998; Touaty and Bonsang, 2000; Hwa, 2002; Na et al., 2002; Na, 2006). In Taiwan, such studies of long tunnels are few, but related studies of fine particle and ultrafine particle levels, as well as their size distributions, in the Hsuehshan tunnel in Taiwan, have been published (Cheng et al., 2010; Zhu et al., 2010). However, those studies have not been able to capture variations in real-world vehicle emissions in a long tunnel. Moreover, they ignore the fact that pollutants from vehicles are emitted into the ambient air near the tunnel by the ventilation system in the vertical shafts. Volatile organic compounds (VOCs) are emitted by vehicles and exhausted from vertical shafts and estimating their effect on ozone levels is important.

The study presents measurements of the concentrations of 56 VOC species in the Hsuehshan tunnel. The characteristics and concentration of the vertical ventilation system (shaft) exhaust were investigated. Variations of VOC levels in the long traffic tunnel were also considered.

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1 Methodology

1.1 Description of tunnel, shafts and vehicles

The measurements were made in the Hsuehshan tunnel, which carries a freeway under the Hsuehshan Mountain in northern Taiwan. The tunnel extends southeastward from metropolitan Taipei to Yilan County. The tunnel has two bores, with two unidirectional lanes per bore. The dimensions of the tunnel are 12.9 km long, 7.6 m wide and 4.6 m high. The tunnel descends steadily from an elevation of 208 m at Pingling at the northern end at a downhill grade of 1.25% to an elevation of 44 m at Toucheng at the southern end. The cross-sectional area of the tunnel is 56.6 m^2, and its internal volume is 730,140 m^3. Vehicles were divided into two types-light-duty vehicles (about 99% of which use gasoline fuel) and heavy-duty diesel buses.

The tunnel is equipped with a ventilation system to maintain air quality. It includes three air exchange stations and three air interchange stations. The tunnel has three exhaust air shafts that comprise a forced ventilation system. The altitudes of No. 1, No. 2, and No. 3 shafts are 512.3, 260.1, and 470.3 m, respectively. The internal diameter of No.2 shaft is 6.5 m, and that of the others is 6.0 m. No. 1, 2 and 3 exhaust air shafts are 2.28, 5.97, and 9.69 km, respectively, from the entrance of the southbound bore. Fifty-six jet fans on the ceiling in each bore of the tunnel are also used as auxiliaries. The polluted air in each bore is exchanged with fresh air at the exchange station, using separated fresh and exhaust air shafts. The fresh air shaft comprises four sets of fans. Two sets of fans are used to supply fresh, cold air from the shaft to the southbound bore and the other two sets of fans are used northbound bore. The polluted, hot air is discharged to the exhaust shafts using four sets of fans. Two sets of fans are used to discharge polluted air from the southbound bore into the shaft and the other two are used to discharge polluted air from the northbound bore. Fans in the exchange stations trigger individually at a temperature of > 40°C or a CO level of > 75 ppm in the tunnel. The air in one bore at interchange between the two bores permits using one bore at an auxiliary.

1.2 Sample and analysis

Measurements were made in the tunnel and shafts simultaneously on 27–28 December 2007 and 19–20 January, 13–16 march, 20–21 April in 2008 (on six working days and six weekend days). On each day the sampling periods were 2 hr in the morning (08:00–10:00), around midday (12:00–14:00) and in the evening (16:00–18:00). The meteorological parameters in the tunnel were measured every hour. Grab sampling of C_2–C_{12} hydrocarbons was conducted using 6 L polished stainless steel canisters with a high vacuum of 10^{-4} Torr, certified according to the US EPA Method TO-14 (1988). The unit organic concentration used in this study of as ppb is volume fraction, complying with the US EPA Method TO-14. The VOCs in ambient air using specially prepared canisters with subsequent analysis by gas chromatography. These compounds have been successfully stored in canisters and measured at the parts per billion by volume (ppb) level.

As indicated in Fig. 1, the entry site sampler in this study was located 1.7 km from the tunnel entrance, and 1.45 km from the tunnel exit. The entrance and exit sampling sites within the tunnel were the No. 1 and No. 8 temporary parking areas for vehicles, respectively. The samples were positioned 1.5 m above the ground and 2.0 m horizontally from the passing vehicles. A total of 60 VOC samples (24 inside the tunnel and 36 at the exits of the shafts) were obtained. Moreover, a Teflon tube, extending to within 3 m of the shaft exit, was used to extract the samples and avoid any effect of ambient pollution thereon.

The canisters were cleaned in the laboratory, pressurized with humidified zero air at ca. 100°C prior to sampling, and pre-concentrated in a purge-and-trap system (Entech

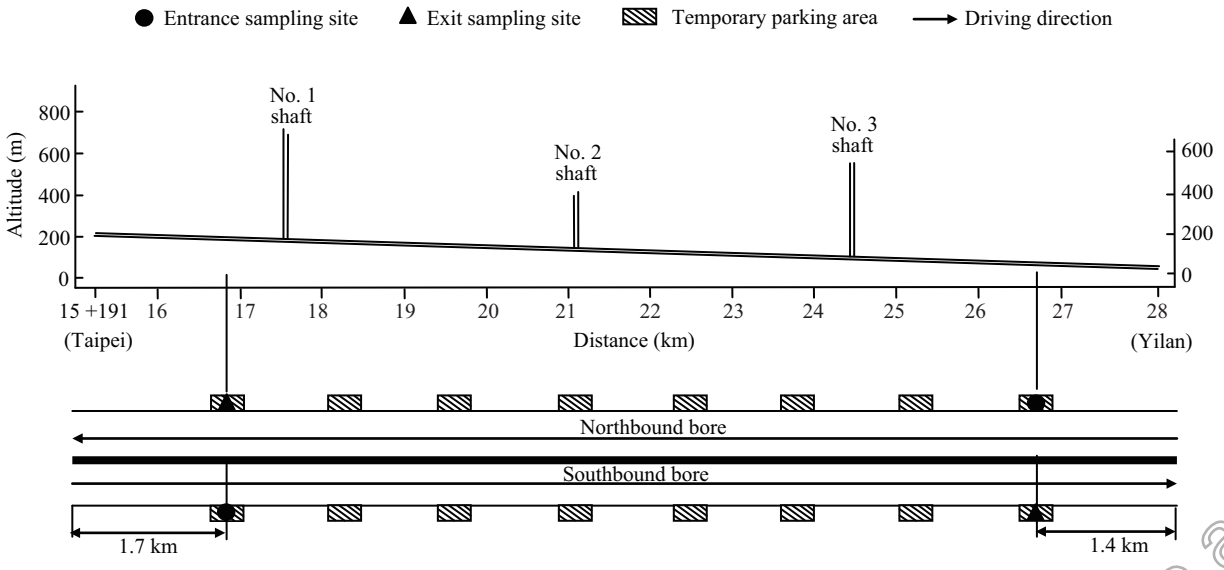

Fig. 1 Diagram of sampling sites and ventilation system in the Hsuehshan tunnel.

7100 instrument). They were subsequently analyzed using a GC/FID (HP-6890, Agilent Technologies, USA) and GC/MS (HP-5973 N Mass Spectrometer, USA). A GC/FID was used to quantify C_2 hydrocarbons. Separation was achieved using a capillary column (60 m × 0.32 mm I.D. × 3.0 μm film thickness RTX-1 column). A GC/MS was used to identify and quantify C_2–C_{12} hydrocarbons. These hydrocarbons were separated using DB-1 fused silica column (60 m × 0.32 mm I.D. × 1.0 μm thick film of polydimethylsiloxane (J&W Scientific, USA). Quality control and assurance required establishing GC retention times, the calibration R^2, the method detection limit (MLD) and the studying the reproducibility of all analyses of compounds. The relative standard deviation (RSD) was 5%–15%, which was within the acceptable range of ±20%. Precision, as determined from five replicate analyses of the standards and samples, was less than 15% for the compounds at concentrations above 5 ppb, and the detection limit (DL) is shown in Table 2. The organic concentration as carbon (ppb C) of a compound is the carbon number of the compound times its volume fraction (ppb), complying with the US EPA Method 25A. Then, the concentration of total non-methane hydrocabons (NMHC) (ppb C) was obtained by summing all individual organic concentrations as carbon. A Davis Weather Wizard III (Model 7425) was used to measure the meteorological conditions (including wind speed, temperature and relative humidity) at 1 sec intervals at the entrance and exit sampling sites within the tunnel during the sampling periods. Hourly traffic data were obtained from the Pinglin Traffic Control Center, which maintains hourly records of the total number and speeds of vehicles that pass through the Hsuehshan tunnel.

2 Results and discussion

2.1 Meteorological conditions and vehicle volume in the tunnel

Table 1 shows the temperatures of 22.4–26.6°C and 28.0–31.0°C at the entrance and exit of the sampling sites, respectively. The temperature difference between the exit and entrance of the southbound and northbound bores were +5.3°C (+4.6°C) and +5.4°C (+5.7°C) on weekends (weekdays), respectively. The difference between the relative humidity (RH) at the exit and entrance of the southbound bore and northbound bore were –10% (–6.8%) and –13% (–13.2%) on weekends (weekdays), respectively. The temperature increased with downwind distance from the tunnel entrance, while the RH declined. The highest temperature and lowest RH were observed at the exit of the tunnel, because of the accumulation in the tunnel of waste heat that was exhausted from the vehicles. Additionally, the temperature and RH in the northbound bore were significantly higher and lower, respectively, than those in the southbound bore. Some studies reported in the literature (Charron and Harrison, 2003; Rönkkö et al., 2006) suggest that low ambient temperature and high humidity could enhance condensation and nucleation. Therefore, meteorological conditions could have caused the difference in VOC concentrations. Moreover, the driving state of the vehicles could be realized by the wind speed datum in the tunnel. Stemmler et al. (2005) indicated the wind speed is strongly dependent on traffic density in the tunnel. Furthermore, meteorological conditions in this study could provide useful information for designing the long tunnels in the future.

Table 1 also shows the volume of vehicles that passed

Table 1 Meteorological conditions and vehicle volume during sampling periods in the Hsuehshan tunnel

		Time	Wind speed (m/sec)	Temperature (°C)	RH (%)	Vehicle volume (vehicles/hr)
Southbound bore						
Weekday	Entrance	08:00–10:00	2.4 ± 0.8	23.5 ± 1.5	67.2 ± 5.1	2108
		12:00–14:00	2.0 ± 1.1	25.2 ± 0.5	63.8 ± 2.5	2196
		16:00–18:00	2.3 ± 0.8	24.1 ± 0.7	68.2 ± 1.8	2227
	Exit	08:00–10:00		28.0 ± 0.8	60.2 ± 1.8	
		12:00–14:00		29.5 ± 0.6	58.4 ± 3.1	
		16:00–18:00		29.3 ± 0.2	60.1 ± 1.1	
Weekend	Entrance	08:00–10:00	3.3 ± 1.2	22.5 ± 1.9	69.4 ± 4.9	3888
		12:00–14:00	2.4 ± 0.7	25.0 ± 0.5	61.8 ± 0.8	3426
		16:00–18:00	3.6 ± 1.2	23.8 ± 0.4	65.4 ± 1.9	3112
	Exit	08:00–10:00		29.0 ± 0.9	56.4 ± 2.3	
		12:00–14:00		29.2 ± 0.5	53.0 ± 1.2	
		16:00–18:00		29.2 ± 0.5	57.2 ± 1.5	
Northbound bore						
Weekday	Entrance	08:00–10:00	2.9 ± 1.1	23.3 ± 1.4	70.6 ± 5.4	1668
		12:00–14:00	2.5 ± 0.9	24.7 ± 2.2	64.5 ± 1.7	1755
		16:00–18:00	2.4 ± 0.9	24.5 ± 0.6	66.1 ± 2.1	2666
	Exit	08:00–10:00		29.8 ± 0.6	54.3 ± 1.5	
		12:00–14:00		29.8 ± 0.4	53.6 ± 1.4	
		16:00–18:00		30.2 ± 0.1	53.9 ± 1.8	
Weekend	Entrance	08:00–10:00	3.4 ± 1.0	22.4 ± 1.8	70.1 ± 7.4	1855
		12:00–14:00	3.0 ± 1.0	25.5 ± 0.7	61.1 ± 1.9	3207
		16:00–18:00	1.8 ± 0.7	26.6 ± 0.4	60.5 ± 1.1	4023
	Exit	08:00–10:00		29.5 ± 1.6	52.9 ± 4.2	
		12:00–14:00		31.0 ± 0.5	49.9 ± 0.7	
		16:00–18:00		30.2 ± 0.2	49.8 ± 0.3	

RH: relative humidity.

through the southbound and northbound bores of the Hsuehshan tunnel on weekdays and weekends during the sampling periods. The volumes were 1668–2666 vehicles/hr on weekdays and 1855–4023 vehicles/hr on weekends, respectively. The traffic volumes in the southbound and northbound bores were 1.6 and 1.5 times higher on weekends than that on weekdays, respectively. Buses comprised 1.33%–5.76% (average 2.6%) of vehicles. The wind speed declined as the vehicle volume increased. On weekends, vehicle volumes peaked at 8:00–10:00, with 3888 vehicles' passing through the southbound bore, and at 16:00–18:00, with 4023 vehicles' passing through the northbound bore. On the weekend, traffic volumes are high in the morning in the southbound bore of the Hsuehahan tunnel as people travel to Yilan from Taipei and high in the afternoon in the northbound bore as people return to Taipei. Vehicle speeds in the tunnel are limited to 50–80 km/hr and 50–70 km/hr for passenger cars and buses, respectively, and the distance between two vehicles is maintained at around 50 m. Vehicle speeds in the tunnel slow to < 60 km/hr when hourly traffic volumes exceed 2000 vehicles/hr (Chang, 2007). A 1–2 km-long traffic jam commonly occurs at the entrance of the northbound bore on weekend afternoons.

2.2 Average concentrations of individual VOCs

Table 2 summarizes the means and standard deviations (SD) of 56 VOC species obtained from all of the entrances and exits of the Hsuehshan tunnel during the sampling periods. The total concentrations of 56 VOCs were 331.26 ± 32.87 ppb C (466.40 ± 87.22 ppb C) at the entrance and 1992.2 ± 220.4 ppb C (2246.6 ± 317.5 ppb C) at the exit of the southbound (northbound) bore. The exit/entrance ratios of the total VOCs concentrations were 7.8 and 4.8 for the southbound bore and the northbound bore, respectively. On average, the weight composition was 37.1%–38.2% alkanes, 34.2%–35.4% aromatics, and 21.8%–22.9% alkenes. The light alkanes and alkenes constituted by far the highest proportions of VOCs from catalyst-equipped gasoline-driven passenger cars (Stemmler et al., 2005).

The most abundant species at all sampling sites was ethylene (9.08–204 ppb). The next most abundant species were acetylene, isopentane, propylene and toluene, with concentrations ranging from 1.76 to 98.2 ppb. These results are in some ways similar to those obtained for others tunnels. Gertler et al. (1996) found that light duty (LD) vehicles in the Cassiar tunnel (Canada) emitted predominantly isopentane and acetylene, and Touaty and Bonsang (2000) found that in the Thiais tunnel (Paris), *iso*-propentane, ethylene, acetylene, propylene and *n*-butane were the most abundant VOC emissions. A study based on European driving cycles of vehicles running on dynamometers reported the same compounds (Ahlvik et al., 1997). Isopentane and *n*-butane were emitted from both combustion and evaporation processes, with the highest emission from gasoline evaporation. In contrast, the other major compounds, ethylene, propylene, and acetylene, were emitted only from combustion (Ahlvik et al., 1997; Touaty and Bonsang, 2000). Large amounts of *iso*, *n*-butane and *iso*, *n*-pentane are also emitted by evaporation (Touaty and Bonsang, 2000). Generally, engine-out emissions, or emissions from non-catalyst vehicles, of ethylene and acetylene are in a ratio of approximately 1:1, while catalyst-equipped cars have FTP-weighted emissions ratios of approximately 2.8:1 to 6.4:1 (Hoekman, 1992). Mole ratios for LD vehicles of 3.4:1 at Tuscarora tunnel and 2.7:1 at Fort McHenry tunnel have been measured. However, the weighted emissions ratio of ethylene/acetylene at the entrance of the northbound (southbound) both was 2.3:1 (2.4:1) and at the exit was 2.9:1 (2.8:1) (Table 3). Therefore, the major species in the long tunnel did not differ significantly from those in other tunnels, although the levels of VOCs did.

2.3 Effect of roadway grade on emission and source profile

Figure 2 shows that the mass composition percentage of most compounds in the southbound bore (downhill) and the northbound bore (uphill). The differences in the weight percentages of 1-butene, isopentane, *n*-pentane, benzene, 2,2,4-trimethylpentane, toluene, styrene and m-ethyltoluene between the two bores were statistically significant ($p < 0.05$) using the *t*-test (with an "asterisk"), and concentrations of 2,2,4-trimethylpentane and *m*-ethyltoluene were higher in the southbound bore than in the northbound bore. In general, variations in the source profile in the southbound bore (downhill) were similar to those in the northbound bore (uphill). The effects of roadway grade on the composition of NMHC emissions were generally weak, and the results are similar to those in the Fort McHenry tunnel (Pierson et al., 1996).

Table 3 shows the effect of roadway grade on mass ratio. In the Fort McHenry tunnel, the downgrade reaches –3.76% (with an average of –1.8%) and the upgrade reaches +3.76% (with an average of +3.3%). The posted speed is 50 mile/hr (80.5 km/hr). Although the gradient of Hsuehshan tunnel is similar to that of the Gubrist tunnel, the LD ethylene/acetylene mass ratio is slightly higher in the Hsuehshan tunnel than in the Gubrist tunnel. The LD ethylene/acetylene mass ratio in the Fort McHenry tunnel changed greatly from 2.1 ± 0.4 (downhill) to 5.8 ± 3.5 (uphill) (Pierson et al., 1996). However, the LD ethylene/acetylene ratios did not differ significantly between the uphill bore and the downhill bore in this study, without respect to the entrance sampling site or the exit sampling site.

The mass ratio (aliphatic and alicyclic)/(unsaturated)/(aromatic)/total NMHC was approximately (0.39–0.4)/(0.26–0.27)/(0.34–0.35)/1 in this study, without respect to the entrance sampling site or the exit sampling site. The mass ratio (aliphatic and alicyclic)/(unsaturated)/(aromatic)/total NMHC at the uphill bore differed slightly between the Hsuehshan tunnel and the Gubrist tunnel. The largest difference was in the heavy duty (HD) unsaturated and aromatic compounds: the mass ratio (aliphatic and alicyclic)/(unsaturated)/(aromatic)/total NMHC went from 0.47/0.16/0.37/1 at the downhill bore of the Fort McHenry

Table 2 Concentrations (mean ± SD) of 56 VOC species at entrance and exit of tunnel (unit: ppb)

		Southbound bore				Northbound bore				
		Entrance		Exit		Entrance		Exit		
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	DL[a]
***n*-Alkanes**	Ethane	4.7	1.0	21.1	7.5	5.6	2.5	18. 7	5.0	0.30
	Propane	4.0	4.0	16.3	12.9	2.8	1.5	10.0	3.9	0.30
	n-Butane	2.5	1.3	17.3	8.7	3.3	3.4	16.0	6.5	0.40
	n-Pentane	1.7	0.8	16.6	7.8	3.2	3.7	18.4	7.3	0.13
	n-Hexane	1.0	0.5	7.3	2.5	1.4	1.0	6.3	2.3	0.13
	n-Heptane	0.7	0.5	3.7	1.2	0.8	0.7	3.3	1.1	0.43
	n-Octane	–[c]	–	1.3	0.3	0.2	0.4	1.1	0.3	0.13
	n-Nonane	–	–	1.0	0.3	–	–	1.0	0.2	0.13
	n-Decane	–	–	1.0	0.2	–	–	0.9	0.4	0.13
	n-Uecane	–	–	1.0	0.2	–	–	0.8	0.4	0.13
	n-Dodecane	–	–	0.9	0.3	–	–	0.5	0.5	0.13
***i*-Alkanes**	Isobutene	2.0	0.8	10.9	5.4	2.2	2.2	10.0	4.4	0.13
	Isopentane	5.9	2.4	46.7	21.8	10.1	11.2	50.2	20.0	0.13
	2,2-Dimethylbutane	–	–	2.0	0.7	0.2	0.5	2.2	0.9	0.13
	2,3-Dimethylbutane	0.1	0.3	–	–	–	–	–	–	0.10
	2-Methylpentane	1.4	0.6	12.0	4.9	2.1	2.0	10.9	4.0	0.13
	3-Methylpentane	0.9	0.4	7.3	2.7	1.3	1.2	6.5	2.5	0.13
	2,3-Dimethylpentane	0.1	0.3	1.6	0.5	0.2	0.4	1.4	0.5	0.10
	2,4-Dimethylpentane	–	–	1.7	0.6	0.2	0.4	1.3	0.5	0.13
	2-Methylhexane	1.2	0.2	9.9	15.4	1.3	0.6	4.5	1.4	0.13
	3-Methylhexane	1.0	0.4	5.1	1.7	1.2	0.6	4.4	1.5	0.13
	2,2,4-Trimethylpentane	0.6	0.5	4.1	1.5	0.6	0.6	2.3	1.0	0.13
	2,3,4-Trimethylpentane	0.1	0.2	1.8	0.6	0.2	0.4	1.1	0.3	0.13
	2-Methylheptane	0.1	0.2	1.3	0.3	0.2	0.4	1.1	0.3	0.13
	3-Methylheptane	–	–	1.5	0.4	0.2	0.4	1.2	0.4	0.13
Alkenes	Ethylene	15.2	4.6	118.3	46.3	20.8	12.9	97.2	29.9	0.30
	Propylene	5.5	2.5	44.2	11.6	7.7	4.3	41.4	12.8	0.15
	1-Butene	3.6	1.7	28.0	9.3	5.7	4.1	25.3	7.2	0.18
	trans-2-Butene	0.9	0.4	5.9	2.8	1.3	1.3	5.3	2.7	0.28
	cis-2-Butene	0.7	0.1	4.3	2.1	0.9	1.1	3.8	2.0	0.23
	1-Pentene	0.2	0.4	2.0	0.7	0.3	0.6	1.9	0.8	0.13
	Isoprene	0.2	0.4	1.5	0.8	0.4	0.5	1.0	0.8	0.35
	trans-2-Pentene	0.4	0.5	4.9	2.3	0.8	1.1	4.9	2.3	0.13
	cis-2-Pentene	0.1	0.2	2.1	0.9	0.3	0.5	2.1	1.0	0.13
	1-Hexene	0.1	0.2	1.6	0.4	0.2	0.4	1.3	0.5	0.13
Alkynes	Acetylene	7.1	2.5	46.4	13.3	10.3	8.7	38.2	10.9	2.38
Naphthenes	Cyclopentane	0.1	0.2	–	–	–	–	–	–	0.10
	Methylcyclopentane	0.5	0.5	3.7	1.2	0.6	0.7	3.2	1.2	0.13
	Cyclohexane	–	–	0.1	0.6	–	–	0.1	0.4	0.13
	Methylcyclohexane	–	–	1.2	0.2	0.2	0.4	1.1	0.3	0.13
Aromatics	Benzene	2.4	0.8	19.8	5.1	4.0	2.6	17.5	5.5	0.80
	Toluene	6.1	2.3	35.8	6.9	6.5	4.4	30.3	9.1	0.68
	Ethylbenzene	1.0	0.1	5.6	1.3	1.2	0.6	4.8	1.5	0.13
	m,p-Xylene	2.4	1.0	19.4	4.8	3.6	2.5	16.8	4.9	0.13
	o-Xylene	1.1	0.2	7.9	1.9	0.3	0.5	1.7	0.6	0.13
	i-Propylenebenzene	–	–	0.7	0.4	1.5	1.0	7.0	2.0	0.13
	n-Propylbenzene	–	–	1.3	0.3	–	–	0.5	0.5	0.13
	m-Ethyltoluene	1.0	0.3	5.4	1.4	0.2	0.4	1.1	0.3	0.13
	p-Ethyltoluene	0.2	0.4	2.3	0.6	0.9	0.7	4.2	1.4	0.13
	o-Ethyltoluene	0.2	0.4	2.2	0.5	0.3	0.5	1.4	0.5	0.13
	1,2,4-Trimethylbenzene	1.1	0.5	9.3	2.5	0.3	0.5	1.8	0.6	0.13
	1,2,3-Trimethylbenzene	0.2	0.4	2.4	0.6	1.6	1.1	7.9	2.3	0.13
	1,3,5-Trimethylbenzene	0.1	0.2	1.8	0.4	0.4	0.5	1.9	0.6	0.13
	m-Diethylbenzene	–	–	1.0	0.2	0.4	0.5	2.1	0.7	0.13
	p-Diethylbenzene	–	–	1.5	0.5	–	–	0.9	0.3	0.13
	Alkanes (ppb C)	124.3	20.4	964.3	173. 6	172.8	64.5	857.4	118.3	
	Alkenes (ppb C)	72.1	14.5	583. 6	107.5	106.5	34.7	513.5	79.1	
	Alkynes (ppb C)	14.3	4.9	92.7	26.6	20.5	17.5	76.4	21.8	
	Naphthenes (ppb C)	3.5	3.8	35.0	9.0	5.7	5.6	30.4	9.3	
	Aromatics (ppb C)	117.1	20.8	900.2	77.3	160.9	44.0	768.9	89.0	
	Total NMHC (ppb C)	331.3	64.4[b]	2575.8	220.4[b]	466.4	166.3[b]	2246.6	317.5[b]	

[a] DL is the detection limit; [b] TSD = $(\Sigma SD_i^2)^{1/2}$, where SD_i is the standard deviation of the compound i; [c] below detection limit.

tunnel to 0.39/0.06/0.55/1 at the uphill bore. The aromatic portion of total NMHC at the uphill bore of Fort McHenry tunnel exceeded those in Hsuehshan tunnel and Gubrist tunnel. The vehicle type was different, but the main factor that affected the levels of aromatic compounds was roadway grade. The emission factor (mg/km) for benzene, toluene, and group of the xylene from LD vehicles were very sensitive to the roadway grade. As the roadway grade

Table 3 Effect of roadway grade on mass ratio

	Hsuehshan tunnel	Fort McHenry tunnel[c]	Gubrist tunnel[d]
Length (km)	13.9	2.174	9
Roadway grade	1.25%	Downgrade reaches –3.76% Upgrade reaches +3.76%	1.3%
Vehicle speed (km/hr)	50–80	ca. 80.5	ca. 93
Average fraction of heavy duty vehicles	2.6%	0	0
Mass ratio (light duty, LD)			
Ethylene/acetylene			
Uphill	Entrance (2.3) Exit (2.9)	5.8 ± 3.5	1.88
Downhill	Entrance (2.4) Exit (2.8)	2.1 ± 0.4	–[a]
Aliphatic and alicyclic/unsaturated/aromatic/total NMHC			
Uphill	Entrance (0.39/0.27/0.34/1) Exit (0.40/0.26/0.34/1)	0.39/0.06/0.55/1[b]	0.36/0.34/0.29/1
Downhill	Entrance (0.39/0.26/0.35/1) Exit (0.39/0.26/0.35/1)	0.47/0.16/0.37/1[b]	–[a]

[a] not reported; [b] the mass ratio for heavy duty (HD); [c] Pierson et al., 1996; [d] Staehelin et al., 1998.

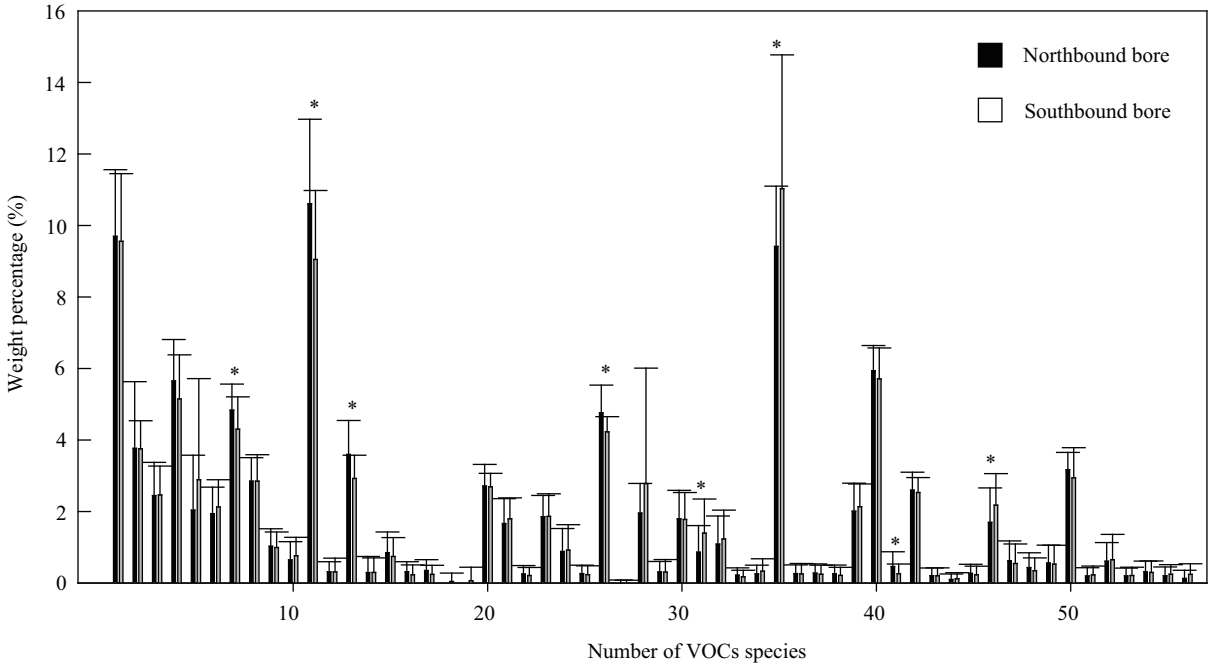

Fig. 2 VOC source profiles of exhaust from vehicles in the southbound bore (downhill) and the northbound bore (uphill). The numbers correspond with the number per compound as given in Table 4. Species are marked with an "asterisk" were statistically significant ($p < 0.05$), according to the *t*-test.

increased from 0 to 1%, the levels of aromatic compounds increased significantly, given an average speed of 87 km/hr under real-world driving conditions according to dynamometric tests (UBA, 1999).

2.4 Emission rate of VOCs from vertical shaft

Few recent studies have discussed the emissions from vertical ventilation systems (shafts). Table 4 presents the mean emission rate (ER) and standard deviation (SD) during the periods of sampling for the three shafts. The most abundant species of ER is toluene (21.93–42.89 mg/sec), followed by isopentane, ethylene, propylene and 1-butene, with ER ranging from 2.50 to 9.31 mg/sec. The total NMHC follows the order No. 2 shaft > No. 3 shaft > No. 1 shaft. The total NMHC in No. 2 shaft was 1.5 times and double those in No. 3 shaft and No. 1 shaft, respectively. Since the exhaust systems in the No. 1 shaft and the No. 3 shaft were set close to the entrance and exit of the two bores in the tunnel, the pollution from vehicle exhausts significantly accumulated closed to the No. 2 shaft inside the middle tunnel during periods without traffic jams.

Figure 3 shows that the average VOC composition on weekdays was very similar to that on weekends in this tunnel. The percentages of all species except toluene were higher on weekends than on weekdays. The weight percentage of the 21 species that are marked with an "asterisk" were statistically significant ($p < 0.05$), according to the *t*-test. The differences between weekdays and weekends are attributable only to differences in vehicle type, vehicle speed and vehicle volume. The exhaust from the vertical shafts affects air quality in the neighborhood. Therefore, the emission data herein are provide information about hydrocarbon compositions for future source apportionment analysis, using either a chemical mass balance (CMB) or a multivariate principal component/factor.

Table 4 Emission rate of vertical shaft (unit: mg/sec)

Number	Species	No. 1 shaft		No. 2 shaft		No. 3 shaft	
		Mean	S.D.	Mean	S.D.	Mean	S.D.
1	Ethylene	4.96	3.99	8.34	11.05	4.05	2.49
2	Acetylene	1.93	1.56	2.86	3.33	1.62	0.99
3	Ethane	1.20	0.95	1.63	1.82	0.94	0.57
4	Propylene	3.23	2.67	4.97	5.70	2.50	1.62
5	Propane	1.23	1.27	2.00	2.74	1.09	0.68
6	Isobutane	1.27	1.23	2.08	2.78	1.09	0.65
7	1-Butene	3.10	2.59	5.91	6.22	3.55	2.36
8	*n*-Butane	2.00	2.04	3.12	4.68	1.38	0.91
9	trans-2-Butene	0.62	0.62	0.94	1.45	0.40	0.28
10	cis-2-Butene	0.44	0.44	0.66	0.99	0.27	0.22
11	Isopentane	7.33	8.19	9.31	12.64	4.30	2.97
12	1-Pentene	0.27	0.25	0.50	0.57	0.27	0.15
13	*n*-Pentane	2.60	2.70	3.60	4.98	1.59	1.09
14	Isoprene	0.14	0.15	0.26	0.28	0.21	0.12
15	*trans*-2-Pentene	0.62	0.71	1.01	1.57	0.40	0.27
16	*cis*-2-Pentene	0.28	0.30	0.46	0.64	0.23	0.13
17	2,2-Dimethylbutane	0.34	0.30	0.51	0.68	0.27	0.18
18	Cyclopentane	–[a]	–	–	–	–	–
19	2,3-Dimethylbutane	0.01	0.01	0.01	0.03	0.01	0.02
20	2-Methylpentane	1.77	1.80	2.86	3.98	1.26	0.89
21	3-Methylpentane	1.09	1.09	1.81	2.40	0.83	0.54
22	1-Hexene	0.29	0.23	0.46	0.46	0.26	0.15
23	*n*-Hexane	1.66	2.28	1.77	2.25	0.84	0.52
24	Methylcyclopentane	0.58	0.56	0.98	1.30	0.46	0.31
25	2,4-Dimethylpentane	0.28	0.30	0.51	0.56	0.27	0.21
26	Benzene	2.33	1.92	3.61	4.45	1.80	1.15
27	Cyclohexane	–	–	–	–	–	–
28	2-Methylhexane	1.55	1.27	1.81	1.95	1.17	0.75
29	2,3-Dimethylpentane	0.39	0.30	0.54	0.56	0.33	0.19
30	3-Methylhexane	1.50	1.50	2.07	2.18	1.28	0.82
31	2,2,4-Trimethylpentane	0.68	0.67	1.14	1.42	0.62	0.41
32	*n*-Heptane	1.48	1.73	1.62	1.85	1.01	1.05
33	Methylcyclohexane	0.24	0.24	0.39	0.36	0.30	0.18
34	2,3,4-Trimethylpentane	0.30	0.31	0.48	0.57	0.33	0.22
35	Toluene	27.61	28.97	42.89	27.37	21.93	22.26
36	2-Methylheptane	0.36	0.26	0.48	0.44	0.32	0.22
37	3-Methylheptane	0.31	0.28	0.52	0.48	0.35	0.21
38	*n*-Octane	0.53	0.44	0.73	0.50	0.62	0.55
39	Ethylbenzene	0.70	0.57	1.14	1.42	0.39	0.23
40	*m,p*-Xylene	2.39	1.94	3.83	4.89	1.11	0.67
41	Styrene	0.31	0.23	0.41	0.37	0.19	0.20
42	*o*-Xylene	0.90	0.73	1.48	1.90	0.41	0.25
43	*n*-Nonane	0.03	0.14	0.23	0.42	0.05	0.15
44	Isopropylenebenzene	–	–	0.07	0.26	–	–
45	*n*-Propylbenzene	0.33	0.27	0.41	0.38	0.12	0.22
46	*m*-Ethyltoluene	0.64	0.52	0.99	1.24	0.37	0.22
47	*p*-Ethyltoluene	0.38	0.28	0.53	0.51	0.15	0.22
48	1,3,5- Trimethyl benzene	0.38	0.27	0.49	0.42	0.16	0.24
49	*o*-Ethyltoluene	0.37	0.27	0.51	0.49	0.15	0.21
50	1,2,4-Trimethyl benzene	1.09	0.88	1.53	1.97	0.42	0.26
51	*n*-Decane	0.23	0.32	0.50	0.43	0.43	0.26
52	1,2,3- Trimethyl benzene	0.38	0.28	0.51	0.49	0.17	0.23
53	*m*-Diethylbenzene	0.07	0.19	0.24	0.54	–	–
54	*p*-Diethylbenzene	0.33	0.33	0.43	0.43	0.13	0.25
55	*n*-Undecane	0.20	0.33	0.54	0.49	0.23	0.27
56	*n*-Dodecane	0.13	0.29	0.33	0.47	0.19	0.34
	Total NMHC	83.38[b]	31.37[c]	127.01[b]	35.87[c]	62.82[b]	23.03[c]

[a] Below detection limit; [b] total NMHC (total 56 VOCs measured in this study); [c] $TSD = (\sum SD_i^2)^{1/2}$.

3 Conclusions

The characteristics of 56 hydrocarbons from C_2 to C_{12} were investigated in the southbound bore, the northbound bore and exhaust air shafts of the Hsuehshan tunnel. The most abundant species in the tunnel was ethylene (9.08–204 ppb), followed by acetylene, isopentane, propylene and toluene, with concentrations ranging from 1.76 to 98.2 ppb. On average, the composition by weight 37.1%–38.2% alkanes, followed by 34.2%–35.4% aromatics and 21.8%–22.9% alkenes. The variations of the source profile in the southbound bore (downhill) were similar to those in the northbound bore (uphill).

The total NMHC in the exhaust air shafts followed the order No. 2 shaft > No. 3 shaft > No. 1 shaft. The total NMHC in No. 2 shaft was 1.5 times and double

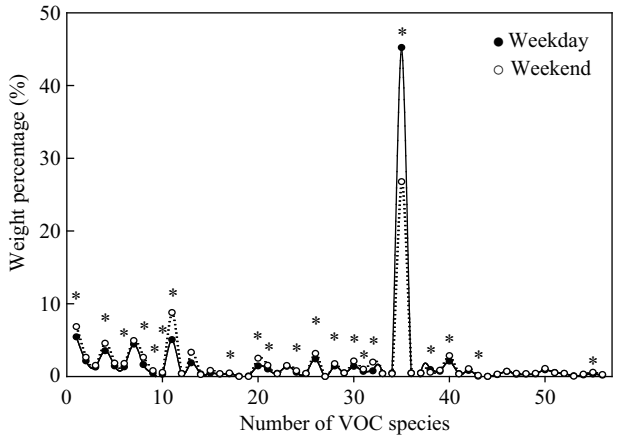

Fig. 3 VOC source profiles of exhaust from the three vertical ventilation shafts during weekdays and weekends. The numbers correspond with the number per compound as given in Table 4. Species are marked with an "asterisk" were statistically significant ($p < 0.05$), according to the *t*-test.

those in No. 3 and No. 1 shafts, respectively. The ozone formation potential in the three shafts also shows that the reactivities of the emissions therein are similar to those of vehicle emissions. Emission controls in shafts from the traffic tunnel are possible solutions, with could prevent deterioration of air quality in the future.

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