Volatile Organic Compound Emissions from Light-Duty Vehicles in Monterrey, Mexico: a Tunnel Study

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ABSTRACT: A two-week tunnel study was conducted in Monterrey, Mexico during June 2009 to characterize volatile organic compound (VOC) emissions from the local vehicle fleet and estimate the corresponding emission factors (EFs). The Loma Larga Tunnel (LLT), a 532 meter-long structure that is mainly used by light-duty gasoline-powered vehicles was used as the experimental set-up. Ambient air samples (2-hour averages) were taken inside the LLT using 6 L SUMMA®-polished canisters. Samples collected in the canisters were analyzed for Total Non-Methane Hydrocarbons (TNMHC) and 53 individual VOCs using high-resolution GC-MS. Identified individual VOCs accounted for ~80% of the TNMHCs. The most abundant VOCs, on a molar basis, were ethene (13.8%), acetylene (9.0%), isopentane (7.1%), toluene (5.6%), and *n*-butane (5.5%). High correlations were obtained for known markers of vehicular emissions. Particularly, for the ethene/acetylene ratio values between 1.1 and 2.4 were obtained ($R^2 = 0.95$), indicating the presence of vehicles with a working catalytic converter. Estimated EFs were compared to values reported in similar studies elsewhere, including one in Mexico City. Results indicate that the vehicles in the LLT tend to emit lower molecular weight VOCs (in the C_2 to C_6 range). Reactivity of the emissions, expressed propylene-equivalent concentrations, was estimated resulting in an important contribution of the olefins (including isoprene) to the ozone-forming potential of the emitted mixtures.

Key words: Emission factor, Mobile sources, Air pollution, Air toxics, Ozone precursors

INTRODUCTION

In the Monterrey Metropolitan Area (MMA), the third largest urban center in the country (population-wise) and one of the Mexican cities with the worst air quality (Zuk *et al.*, 2007), the number of vehicles that make up the official vehicle fleet doubled from 1999 to 2005. As of 2010, the total fleet of the MMA consisted of more than 1'890,000 vehicles. This large number of mobile sources circulating in the MMA has important implications for the local environment. According to the 2005 official emissions inventory for the MMA (Barrios *et al.*, 2009), mobile sources contributed that year to 96.5% of the CO, 47.5% of the NOx (NOx = NO + NO_2), 47.2% of the volatile organic compounds (VOCs), and 1.5% of the SOx (SOx = SO_2 + SO_3) emitted. Overall, 69.7% of the gaseous emissions in the MMA came from mobile sources.

Of the compounds emitted by gasoline-powered vehicles, VOCs are of particular interest due to the environmental and health impacts associated with their release into the atmosphere. VOCs can cause serious health problems, including central nervous system depression (Maroni *et al.*, 1995) and irritation of the respiratory track (Mølhave, 1991) , while some are well-known carcinogens (Jones, 1999). In addition, VOCs and NOx, in the presence of sunlight, are precursors of ozone (O_3) and secondary organic aerosol (SOA) (Chameides *et al.*, 1992; Robinson *et al.*, 2007). Both O_3 and SOA have also been associated with respiratory and cardiovascular diseases (Syri *et al.*, 2001; Katsouyanni, 2003; Franklin *et al.*, 2007).

Even though VOCs have been identified as major contributors to air quality problems in Mexican urban centers (Velasco *et al.*, 2007), few studies outside Mexico City have been conducted to characterize in detail the emissions of local sources, including mobile sources. Emission inventories for the MMA are typically based on emission factors (EFs) proposed by the United States Environmental Protection Agency (US EPA), corrected with few field data to accommodate the differences between the two countries. Only recently, EFs based on remote sensing

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techniques were reported for the MMA vehicle fleet (Aguilar-Gómez *et al.*, 2009). However, no speciation information was derived for VOC emissions. This paper presents a field campaign conducted to characterize average fleet emissions from mobile sources in the MMA, and in particular the mixture of VOCs emitted, using a road tunnel as the experimental set-up.

Tunnel studies have proven to be a robust method when the objective is to obtain fleet-average EFs under real-world conditions, including those for VOC emissions (Pierson *et al.*, 1996; Fraser *et al.*, 1998; Hwa *et al.*, 2002; Stemmler *et al.*, 2005; Legreid *et al.*, 2007). The advantage of tunnel experiments is that the emissions measured come from vehicles that traverse the tunnel and that such emissions have not been subjected to photochemical degradation. In addition, tunnel studies deal with well-defined volumes of air. For these types of studies, variables related to the tunnel (geometry, slope and ventilation), vehicle fleet (technology, age, fuel, and engine) and driving conditions (traffic density, temperature, maintenance) need to be considered in the experimental set-up. Using this technique, EFs can be obtained by performing a mass balance over a control volume delimited by monitoring stations deployed inside the tunnel. These stations are usually located at the entrance and exit of a tunnel in which pollutant concentration, as well as other parameters such as vehicle speed, fleet count, wind speed, temperature and pressure are measured. Then, the difference in pollutant concentration between the "inlet" and "outlet" points is assumed to be the emitted mass from mobile sources that traversed the tunnel during each sampling period. Mancilla *et al.* (2012) reported the use of a tunnel experiment to derive

EFs for CO_2, CO, NOx and total non-methane hydrocarbons (TNMHC) for the MMA. Here we center our analysis on the speciation of the TNMHC samples obtained in the same study.

MATERIALS & METHODS

The Loma Larga Tunnel (LLT) is one of the main transit connections between the municipalities of Monterrey and San Pedro Garza Garcia, two of the 14 municipalities that comprise the MMA. The tunnel has an approximate length of 532 meters. It is composed of two independent bores, each one with a semicircular shape and a diameter of 17 meters (Fig. 1). Each bore has a four-lane configuration; however, the right-most lane in each bore is reserved for emergencies. In addition, each bore has a walking lane that traverses the full length of the tunnel. There is a small interconnection near the middle of the tunnel that connects both bores; this interconnection represents around 1% of the inner wall area of each bore. The Monterrey-San Pedro Garza Garcia bore (north to south direction) has a 3.5% positive slope, and thus the contrary flow is down-slope. Each bore has three ventilation ducts, which were not operational during the field campaign.

The field campaign was conducted in June 2009, following the sampling scheme shown in Table 1. Two sampling periods were selected for each day to account for high- and moderate-density traffic conditions. In each period, monitoring equipment was deployed at two points located over the bore's pedestrian lane. These two points, named "inlet" and "outlet", served as the limits of the control volume over which the mass balances were performed to estimate the corresponding
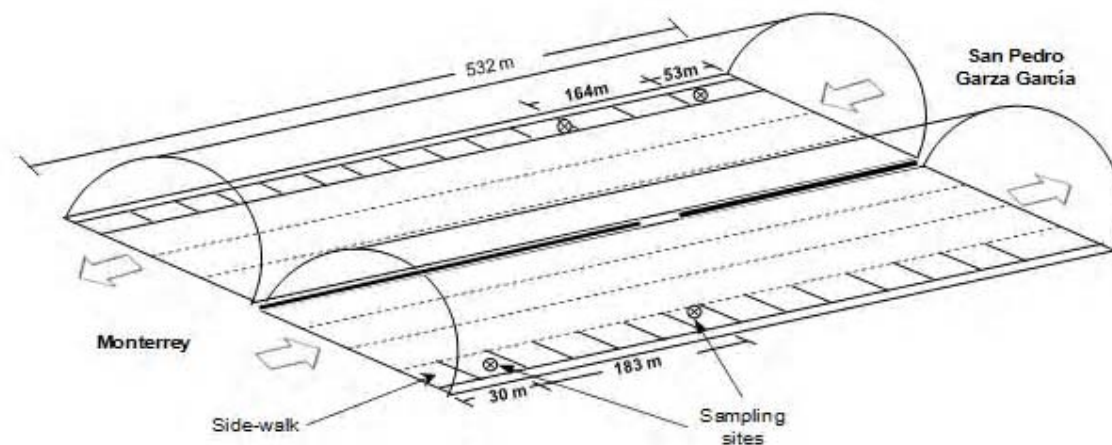

Fig. 1. Experimental set-up in the LLT

Table 1. Experimental design for the field campaign

Bore	Time period	Traffic density	Day 1 Monday 06/22/09	Day 2 Tuesday 06/23/09	Day 3 Wednesday 06/24/09	Day 4 Thursday 06/25/09	Day 5 Monday 06/29/09	Day 6 Tuesday 06/30/09
Monterrey – San Pedro (Bore 1)	7 to 9 hrs	High	√	√	√			
	11 to 13 hrs	Moderate	√	√	√			
San Pedro – Monterrey (Bore 2)	10 to 12 hrs	Moderate				√	√	√
	18 to 20 hrs	High				√	√	√

mobile emissions. The distance between sampling points, and between the "inlet" sampling point and the actual entrance to the tunnel (as shown in Fig. 1), were determined based on similar tunnel studies (Valiulis *et al.*, 2002; Cheng *et al.*, 2006). All sampling probes were located 1.5 m above the level of the side-walk, and at least 1.5 m from the tunnel wall.

At each sampling location, equipment was deployed to measure levels of ambient CO_2, temperature, pressure, and relative humidity using a Testo 435 device (Table 2). Values of the measured variables were recorded every minute during the 2.0 hours that each sampling period lasted. Simultaneously, air velocity at the same locations was measured using a thermal anemometer (Testo 425; measurement range: 0-20 m/s, accuracy ± (0.03 m/s + 5% mv), resolution 0.01 m/s).

TNMHC and speciated VOC concentrations were determined at each sampling location through whole air samples taken using 6 L SUMMA®-polished stainless-steel canisters (24 samples in total). The sampling train included a canister and a pre-calibrated mass-flow controller to obtain two-hourly integrated samples. In addition, the sampling inlet was connected to a Teflon sampling line to elevate the sampling point to the level of the rest of the monitoring devices. The sampling train was subject to vacuum tests before each run to identify possible leaks. Chemical analysis was performed for 54 target species (Table 3) using US EPA's method TO-12 for TNMHC (flame ionization detection) and TO-15 for the individual VOCs (high resolution GC-MS). These chemical species have been identified in vehicle emissions and are included in the Photochemical Assessment Monitoring Stations list of the US EPA (ERG, 1997). Chemical analysis of canister samples was conducted by TestAmerica Laboratories (Austin, TX).

EFs can be estimated from measurements taken in the interior of a tunnel by performing a mass balance over each pollutant (Pierson *et al.*, 1996). Here, the main assumption is that the difference in concentrations between the exit and inlet points of the control volume set inside the tunnel corresponds exclusively to the emissions from mobile sources that went through the tunnel. Thus, the mass emitted per unit time of species k from the vehicles (M_k) can be expressed as:

$$M_k = \left(C_{k,e} V_e - C_{k,i} V_i \right) \qquad (1)$$

where V is the air volumetric flow and C_k is the concentration of pollutant k (e.g., mg/m³). Subindices e and i represent the exit and inlet sampling points, respectively, set inside the tunnel. Thus, the average EF for species k (E_k) in terms of mass emitted per distance traveled per vehicle can be obtained from:

$$E_k = \frac{M_k}{L \cdot N} \qquad (2)$$

where N is the number of vehicles that passed through the sampling points during the experimental period and L is the distance between sampling points.

EFs for species k can also be estimated in terms of mass emitted per volume of fuel burned (E'_k) through a carbon mass balance (Martins *et al.*, 2006):

$$E'_k = \left(\frac{\Delta C_k}{\Delta C_{CO_2} + \Delta C_{CO} + \Delta C_{TNMHC}} \right) \rho_g w_c \quad (3)$$

where ΔC_k is the concentration difference of species k between the sampling points (i.e., $C_{k,e} - C_{k,i}$), ΔC_{CO_2}, ΔC_{CO} and ΔC_{TNMHC} are the concentration differences of CO_2, CO and TNMHC, respectively, ρ_g is the gasoline density (740 g/L; Schifter *et al.*, 2000) and w_c is the mass fraction of carbon in the gasoline (0.84, assuming C_8H_{18} as the average molecular composition of gasoline). The average molecular weight of TNMHC

Table 2. Technical specifications of the TESTO 435 device

Parameter	Range	Precision	Resolution
CO_2	0 to 9,999 ppm	± (50 ppm CO_2 ± 2% of mv) (from 0 to 5,000 ppm CO_2); ±(100 ppm CO_2 ±3% of mv) (from 5,001 to 10,000 ppm CO_2)	1 ppm
Relative Humidity (RH)	0 to 100%	±2 %RH (+2 to +98 %RH)	0.1%
Temperature	0 to 50°C	± 0.3°C	0.1°C
Pressure	600 to 1150 hPa	± 5 hPa	0.1 hPa

Table 3. List of target VOCs selected for chemical analysis from the canister samples

No.	Compound	No.	Compound	No.	Compound
1	TNMHC	19	2,2-dimethylbutane	37	3-metihyheptane
2	Ethane	20	2,3-dimetihybutane	38	*n*-Octane
3	Ethene	21	Isoprene	39	Ethylbenzene
4	Propane	22	2-methylpentane	40	*m,p*-xylene
5	Propylene	23	3-methylpentane	41	Styrene
6	Isobutane	24	1-hexene	42	*o*-xylene
7	Acetylene	25	*n*-Hexane	43	*n*-Nonane
8	*n*-Butane	26	Methylcyclopentane/2,4-Dimethylpentane	44	Cumene
9	*t*-2-butane	27	Benzene	45	Propylbenzene
10	1-butene	28	Cyclohexane	46	2,4-ethyltoluene
11	*cis*-2-butene	29	2,3-dimethylpentane	47	1,3,5-trimethylbenzene
12	Cyclopentane	30	3-methylhexane	48	2-ethyltoluene
13	Isopentane	31	2,2,4-trimethylpentane	49	1,2,4-trimethylbenzene
14	*n*-Pentane	32	*n*-Heptane	50	*n*-Decane
15	1,3-butadiene	33	Methylcyclohexane	51	1,2,3-trimethylbenzene
16	*t*-2-pentene	34	2,3,4-trimethylpentane	52	1,3-diethylbenzene
17	1-pentene	35	Toluene	53	1,4-diethylbenzene
18	*cis*-2-pentene	36	2-methylheptane	54	*n*-Undecane

was assumed at 92 g/gmol. Finally, ΔC_{CO2}, ΔC_{CO} and ΔC_{TNMHC} were obtained from values reported in a complementary paper (Mancilla *et al*., 2011).

RESULTS & DISCUSSION

Average micrometeorological conditions inside the LLT during the field campaign were: 22.5°C, 715.4 mm Hg, and 43.3% relative humidity. Overall, 87,393 vehicles were sampled during the whole field campaign. Two-hour average vehicle velocities were as low as 41.9 ± 7.2 km/h (Monterrey-San Pedro bore; June 24, 11-13 hrs), and as high as 75.9 ± 9.5 km/hr (San Pedro-Monterrey bore; June 25, 10-12 hrs). However, the global average vehicle speeds up-slope and down-slope were quite similar (50 km/hr vs. 57 km/hr, respectively). Approximately, 97% of the vehicles sampled were gasoline-powered vehicles: 56.8% light-duty vehicles, 8.4% taxis, 20.2% SUVs, and 11.7% pick-up trucks (gasoline). The remaining 3% were diesel buses and trucks (2.4%), and motorcycles (0.6%). The

vehicle mix was very similar between bores and remained practically constant regardless of the sampling period. The number of vehicles, their velocity and classification were determined using a video recording system positioned synchronously at the "inlet" and "outlet" sampling sites of each bore. A very similar vehicular mix was obtained in a study conducted in June of 2007 by the Council for Transportation and Highways Administration of the State of Nuevo León (Araizaga Esquivel, 2009).

Mancilla *et al*. (2011) reported for the same study average TNMHC EFs of 1.54 g/km-veh and 0.78 g/km-veh for up-slope and down-slope conditions, respectively. Higher emissions during up-slope movement can be attributed to the fuel enrichment of the mixture fed to the vehicles' engines during those conditions. However, an analysis of variance indicated that there was no difference in emissions ($p < 0.001$) between traffic moving upslope or downslope, or between different traffic conditions. Average TNMHC

EFs values obtained by Mancilla *et al*. (2012) are higher than those reported by other tunnel studies. In particular, TNMHC EFs were twice the value with respect to a remote sensing study conducted in the MMA in 2008 (Aguilar *et al*., 2009).

Tables 4 and 5 list EFs for the 53 individual VOCs that were characterized and Fig. 2 presents an average chemical profile of the main emitted VOCs. The identified individual species represent approximately 80% of the measured TNMHC. The species that contribute the most to the total VOCs (on a molar basis) were: ethene (13.8%), acetylene (9.0%), isopentane (7.1%), toluene (5.6%), and butane (5.5%)(Fig.2). The average EFs (mg/km-veh) of the main emitted species were: isopentane 47.5±9.5, toluene 42.9±3.9, ethene 32.4±1.5, *n*-pentane 25.8±3.4, acetylene 19.5±0.5, propane 17.5±1.8, benzene 15.9±2.0, *m*, *p*-xylene 14.5±3.5, 2,2,4-trimethyl pentane 13.4±5.0, and isobutane 10.3±5.4. Benzene concentrations inside the tunnel were highly correlated with the main aromatic species: with toluene $R^2 = 0.7$, with *m,p* xylene $R^2 = 0.90$, with *o*-xylene $R^2 = 0.96$, with ethyl benzene $R^2 = 0.96$, and with 1,2,4 trimethyl benzene $R^2 = 0.81$. This is relevant since vehicle exhaust gases typically contain aromatic compounds; however toluene and xylenes are also found in solvent emissions while benzene is not. Thus, the high correlation between benzene and the other aromatic species provides evidence that no other major VOC emission source is influencing the ambient air concentrations inside the tunnel. Among aliphatic species, the best correlations (expressed as R^2) were between isopentane and the following species: *n*-butane (0.88), *n*-pentane (0.94), 2,2 dimethyl butane (0.87), 2-methyl pentane (0.92), 3-methyl pentane (0.93), and 2-methyl hexane (0.80). Other highly-correlated pairs of aliphatic species were: ethene-propylene (0.90), ethene-acetylene (0.95), acetylene-propylene (0.94), 1,3 butadiene-propylene (0.76), and acetylene-propylene (0.94). The best correlations between aliphatic and aromatic species (above 0.8) were those that involved the xylenes with isobutane, *n*-butane, isopentane, 2-methyl pentane, 3-methyl pentane, 2-methyl hexane, and 3-methyl hexane. The results indicate high contribution and correlation among species that are well-known tracers of mobile emissions (Barletta *et al*., 2002; Chan *et al*., 2002).

While correlation analyses between emitted species provide valuable information on the emission source, i.e. highly correlated species would indicate a high probability that the emission source is the same, ratios between particular species have also proven to be good indicators of emission sources. Of these, the ethene/acetylene ratio is a good indicator of mobile source emissions, and the value of its ratio can give additional information of the vehicles being characterized, particularly of the presence of a working catalytic converter (Duffy and Nelson, 1996; Sagebiel *et al*., 1996; Barletta *et al*., 2002). A value of this ratio between 1 and 3 indicates the presence of a working catalytic converter, while lower values indicate the contrary. Here we obtained values of this ratio that ranged from 1.1 to 2.4 (Table 6; $R^2 = 0.95$). Statistically,
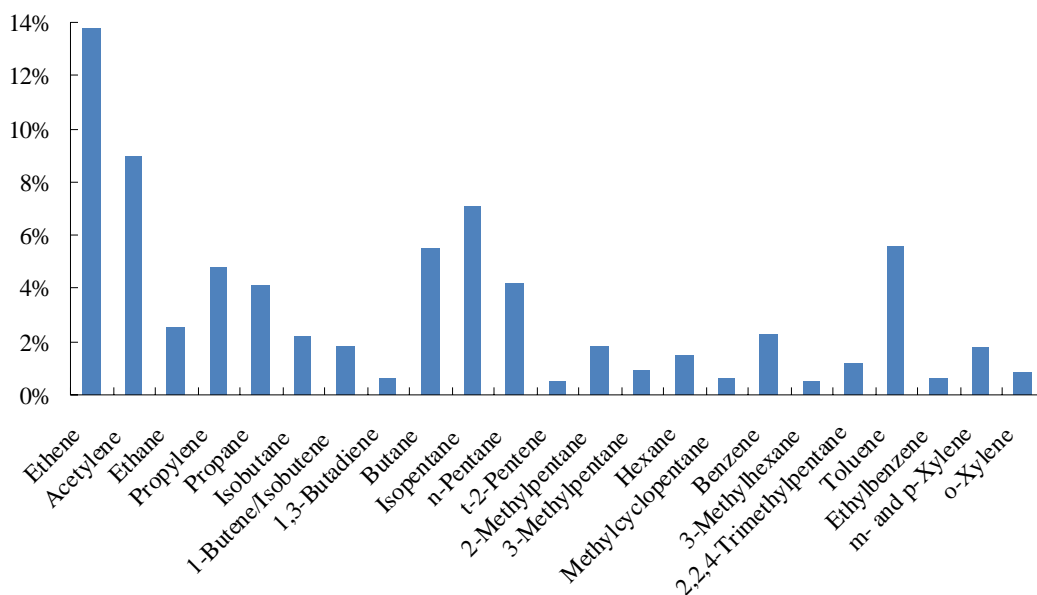

Fig. 2. Share of Compounds Contributing to Over-all Voc$_s$

Table 4. EFs for individual VOCs (mg/km-veh)

Species	Bore 1		Bore 2	
	Traffic density		Traffic density	
	High	Moderate	High	Moderate
Ethene	40.23 ± 1.66	29.88 ± 2.31	41.59 ± 1.15	17.79 ± 1.02
Acetylene	29.56 ± 0.41	13.95 ± 0.58	27.89 ± 0.58	6.79 ± 0.52
Ethane	6.71 ± 3.35	7.23 ± 4.66	9.32 ± 7.78	4.99 ± 6.92
Propylene	31.04 ± 1.50	13.66 ± 2.09	8.60 ± 2.88	6.63 ± 2.56
Propane	21.55 ± 1.65	15.27 ± 2.29	25.28 ± 1.77	4.31 ± 1.57
Isobutane	19.78 ± 4.26	7.16 ± 5.92	11.95 ± 6.05	2.49 ± 5.38
1,3-Butadiene	6.07 ± 4.11	1.70 ± 5.71	1.07 ± 5.64	0.35 ± 5.02
n-Butane	39.29 ± 20	17.67 ± 2.78	41.69 ± 4.14	8.69 ± 3.68
trans-2-Butene	3.08 ± 0.38	1.75 ± 0.53	1.04 ± 1.25	1.21 ± 1.11
cis-2-Butene	1.74 ± 1.18	1.69 ± 1.64	1.33 ± 3.27	0.83 ± 2.91
Isopentane	49.28 ± 6.04	36.12 ± 8.39	83.63 ± 12.57	19.39 ± 11.17
1-Pentene	1.57 ± 0.19	0.58 ± 0.26	0.84 ± 2.17	0.36 ± 1.93
n-Pentane	28.88 ± 1.59	20.56 ± 2.21	42.43 ± 5.21	14.01 ± 4.63
Isoprene	1.52 ± 0.07	1.63 ± 0.10	1.02 ± 1.12	1.10 ± 0.99
trans-2-Pentene	3.89 ± 0.10	2.43 ± 0.13	2.71 ± 0.66	1.47 ± 0.58
cis-2-Pentene	1.59 ± 0.03	1.96 ± 0.05	2.26 ± 0.66	1.18 ± 0.58
2,2-Dimethyl butane	2.23 ± 0.20	1.60 ± 0.28	2.28 ± 2.08	0.71 ± 1.85
Cyclopentane	2.57 ± 0.11	2.35 ± 0.15	1.28 ± 0.33	1.52 ± 0.29
2,3-Dimethyl butane	4.22 ± 0.06	2.68 ± 0.08	3.15 ± 0.40	2.16 ± 0.36
2-Methyl pentane	18.88 ± 0.1	10.03 ± 0.14	20.98 ± 2.56	6.37 ± 2.28
3-Methyl pentane	9.98 ± 0.10	4.84 ± 0.14	8.03 ± 1.82	3.87 ± 1.61
1-Hexene	0.91 ± 0.01	2.23 ± 0.02	1.63 ± 2.46	2.57 ± 2.19
Hexane	14.19 ± 2.75	5.60 ± 3.83	9.61 ± 7.21	10.59 ± 6.41
Mehtyl cyclopentane	7.91 ± 0.15	3.47 ± 0.21	3.52 ± 3.35	2.01 ± 2.98
2,4-Dimehtyl pentane	1.57 ± 0.15	1.90 ± 0.21	0.93 ± 0.23	0.94 ± 0.21
Benzene	22.9 ± 2.15	12.98 ± 2.99	19.74 ± 1.49	7.07 ± 1.32
Cyclohexane	2.04 ± 2.43	1.60 ± 3.38	1.12 ± 6.92	1.00 ± 6.15
2-Mehtyl hexane	5.94 ± 0.11	3.22 ± 0.16	4.60 ± 5.04	1.15 ± 4.48
2,3-Dimehtyl pentane	2.33 ± 0.09	2.65 ± 0.12	2.83 ± 6.69	1.70 ± 5.94
3-Mehtyl hexane	7.16 ± 0.09	3.15 ± 0.13	3.24 ± 3.99	2.34 ± 3.55
2,2,4-Trimehtyl pentane	19.03 ± 2.53	8.96 ± 3.52	17.81 ± 7.35	4.71 ± 6.54
n-Heptane	5.46 ± 4.59	1.94 ± 6.38	3.02 ± 3.45	1.91 ± 3.06
Mehtyl cyclohexane	1.43 ± 0.01	1.86 ± 0.02	1.27 ± 1.38	1.03 ± 1.23
2,3,4-Trimehtyl pentane	5.57 ± 0.11	2.76 ± 0.15	2.83 ± 3.59	1.04 ± 3.19
Toluene	54.34 ± 4.84	29.46 ± 6.72	61.91 ± 2.25	31.79 ± 2.00

Table 4. EFs for individual VOCs (mg/km-veh)

2-Mehtylheptane	1.30 ± 0.09	2.07 ± 0.12	1.48 ± 3.16	1.20 ± 2.81
3-Mehtylheptane	1.14 ± 0.36	2.25 ± 0.50	2.92 ± 2.67	1.20 ± 2.38
n-Octane	0.93 ± 2.03	2.21 ± 2.83	3.75 ± 0.68	1.54 ± 1.45
Ehtyl benzene	9.83 ± 1.50	3.77 ± 2.08	4.63 ± 1.82	2.88 ± 3.87
m- and *p*-Xylene	31.99 ± 2.63	10.34 ± 3.65	7.36 ± 2.42	8.96 ± 5.13
Styrene	1.67 ± 2.29	3.72 ± 3.18	0.32 ± 2.74	2.16 ± 5.80
o-Xylene	12.28 ± 1.29	4.71 ± 1.80	3.54 ± 1.10	3.40 ± 2.34
n-Nonane	0.39 ± 0.88	0.28 ± 1.23	0.80 ± 5.47	0.27 ± 4.87
Cumene	1.73 ± 10.00	1.77 ± 13.91	0.67 ± 10.03	0.31 ± 12.13
n-Propyl benzene	0.98 ± 1.67	1.79 ± 2.32	0.60 ± 1.78	0.38 ± 3.77
3- Ehtyl toluene	5.17 ± 0.20	1.90 ± 0.27	2.61 ± 0.96	1.09 ± 2.03
4- Ehtyl toluene	2.2 ± 2.20	1.25 ± 3.06	0.56 ± 2.19	1.11 ± 4.65
1,3,5-Trimehtyl benzene	1.24 ± 2.39	2.30 ± 3.32	7.00 ± 2.67	2.77 ± 5.66
2-Ehtyl toluene	1.68 ± 0.05	2.29 ± 0.07	7.11 ± 0.87	0.44 ± 1.86
1,2,4-Trimehtyl benzene	8.09 ± 2.33	1.80 ± 3.24	2.61 ± 2.34	1.78 ± 4.97
n-Decane	0.48 ± 1.28	0.80 ± 1.78	0.26 ± 0.99	0.28 ± 2.10
1,2,3-Trimehtyl benzene	1.31 ± 0.08	1.81 ± 0.11	0.66 ± 6.20	0.41 ± 5.52
1,3-Diehtyl benzene	0.12 ± NA	2.36 ± NA	1.24 ± 6.60	0.54 ± 5.87
1,4-Diehtyl benzene	0.84 ± 0.24	0.99 ± 0.33	0.19 ± 0.69	0.20 ± 1.47
n-Undecane	0.08 ± 2.81	1.17 ± 3.90	1.44 ± 2.05	0.29 ± 4.36

NA: Not available.

Table 5. EFs for individual VOCs (mg/L)

Species	Bore 1		Bore 2	
	Traffic density		Traffic density	
	High	Moderate	High	Moderate
Ethene	560.2 ± 24.9	319.6 ± 28.3	263.1 ± 25.3	1026.9 ± 19.1
Acetylene	406.9 ± 6.2	149.9 ± 7.1	100.4 ± 12.8	743.1 ± 9.7
Ethane	92.6 ± 50.2	76.2 ± 57.2	189.2 ± 17.2	216.5 ± 13.0
Propylene	426.6 ± 22.5	147.7 ± 25.6	98.0 ± 63.6	174.2 ± 48.1
Propane	290.8 ± 24.6	162.6 ± 28.0	87.9 ± 39.1	637.7 ± 29.5
Isobutane	269.5 ± 63.8	79.6 ± 72.6	110.1 ± 13.3	302.0 ± 10.1
1-Butene / Isobutene	291.2 ± 43.4	62.7 ± 49.4	53.7 ± 10.2	33.3 ± 7.7
1,3-Butadiene	83.8 ± 61.4	18.6 ± 70.0	10.6 ± 12.4	13.6 ± 9.4
n-Butane	536.8 ± 30.0	193.0 ± 34.1	518.2±9.1	1116.6 ±6.9
trans-2-Butene	42.5 ± 5.7	19.0 ± 6.5	43.1 ± 27.5	21.5 ± 20.8
cis-2-Butene	23.9 ± 17.7	18.0 ± 20.1	20.6 ± 72.2	29.2 ± 54.6
Isopentane	683.0 ± 90.3	388.3 ± 102.9	796.8 ± 27.7	2126.1 ± 21.0
1-Pentene	22.3 ± 2.8	14.9 ± 3.2	18.5 ± 47.8	18.0 ± 36.2
n-Pentane	404.5 ± 23.8	222.5 ± 27.1	685.3 ± 11.5	947.7 ± 8.7
Isoprene	20.9 ± 1.1	17.3 ± 1.2	29.1 ± 24.7	30.0 ± 18.7
trans-2-Pentene	54.2 ± 1.4	26.1 ± 1.6	92.8 ± 14.5	63.5 ± 11.0

Table 5. EFs for individual VOCs (mg/L)

cis-2-Pentene	22.0 ± 0.5	20.9 ± 0.6	39.2 ± 14.5	45.9 ± 11.0
2,2-Dimethyl butane	31.6 ± 3.0	17.1 ± 3.4	30.9 ± 45.8	58.1 ± 34.7
Cyclopentane	36.1 ± 1.6	25.5 ± 1.8	47.9 ± 7.3	25.9 ± 5.5
2,3-Dimethyl butane	60.0 ± 0.9	29.1 ± 1.0	58.0 ± 8.9	68.9 ± 6.7
2-Methyl pentane	266.8 ± 1.5	108.9 ± 1.7	277.2 ± 56.5	517.0 ± 42.7
3-Methyl pentane	141.0 ± 1.5	52.9 ± 1.7	163.7 ± 40.1	173.5 ± 30.3
1-Hexene	12.8 ± 0.2	23.5 ± 0.2	51.3 ± 54.3	30.5 ± 41.1
Hexane	202.3 ± 41.2	62.0 ± 46.9	626.9 ± 15.9	201.3 ± 12.0
Mehtyl cyclopentane	113.1 ± 2.3	37.9 ± 2.6	100.3 ± 73.9	67.2 ± 55.9
2,4-Dimehtyl pentane	22.2 ± 2.2	20.4 ± 2.5	20.3 ± 5.2	14.7 ± 3.9
Benzene	316.9 ± 32.1	139.7 ± 36.6	272.0 ± 32.8	480.6 ± 24.8
Cyclohexane	29.2 ± 36.4	17.3 ± 41.4	31.5 ± 15.3	19.7 ± 11.5
2-Mehtyl hexane	85.2 ± 1.7	34.7 ± 1.9	62.7 ± 11.1	103.0 ± 8.4
2,3-Dimehtyl pentane	33.3 ± 1.3	28.5 ± 1.5	36.5 ± 14.7	68.0 ± 11.2
3-Mehtyl hexane	101.9 ± 1.4	34.6 ± 1.5	75.7 ± 8.8	65.5 ± 6.7
2,2,4-Trimehtyl	268.2 ± 37.9	98.4 ± 43.1	118.0 ± 16.2	431.3 ± 12.3
n-Heptane	78.0 ± 68.7	21.5 ± 78.3	68.3 ± 76.0	38.4 ± 57.5
Mehtyl cyclohexane	20.5 ± 0.2	19.8 ± 0.2	27.3 ± 30.4	16.1 ± 23.0
2,3,4-Trimehtyl	78.6 ± 1.6	30.2 ± 1.9	25.8 ± 79.1	36.0 ± 59.8
Toluene	771.2 ± 72.4	317.1 ± 82.4	1539.9 ± 49.6	1388.9 ± 37.5
2-Mehtylheptane	18.1 ± 1.3	22.0 ± 1.5	31.8 ± 69.6	19.1 ± 52.6
3-Mehtylheptane	16.2 ± 5.4	23.9 ± 6.2	31.8 ± 59.0	37.0 ± 44.6
n-Octane	12.8 ± 30.4	23.8 ± 34.7	40.9 ± 15.1	47.6 ± 11.4
Ehtyl benzene	138.2 ± 22.4	41.2 ± 25.5	115 ± 40.2	58.8 ± 30.4
m- and *p*-Xylene	450.9 ± 39.3	115.3 ± 44.8	405.81 ± 53.4	106.1 ± 40.3
Styrene	21.9 ± 34.3	39.6 ± 39.0	57.28 ± 60.3	6.8 ± 45.6
o-Xylene	172.7 ± 19.4	51.5 ± 22.1	152.15 ± 24.3	94.8 ± 18.4
n-Nonane	5.3 ± 13.2	2.9 ± 15.1	12.73 ± 12.1	21.3 ± 9.1
Cumene	23.6 ± 149.7	19.0 ± 170.5	14.49 ± 221.3	17.1 ± 167.3
n-Propyl benzene	13.7 ± 24.9	18.8 ± 28.4	17.26 ± 39.2	14.6 ± 29.6
3- Ehtyl toluene	72.1 ± 2.9	20.4 ± 3.4	38.35 ± 21.1	33.1 ± 16.0
4- Ehtyl toluene	30.2 ± 33.0	13.2 ± 37.6	29.87 ± 48.3	7.1 ± 36.5
1,3,5-Trimehtyl	16.7 ± 35.7	24.4 ± 40.7	54.11 ± 58.8	88.9 ± 44.5
2-Ehtyl toluene	23.4 ± 0.7	24.2 ± 0.8	19.55 ± 19.3	90.2 ± 14.6
1,2,4-Trimehtyl	112.2 ± 34.9	20.1 ± 39.8	71.08 ± 51.7	33.2 ± 39.1
n-Decane	6.8 ± 19.2	8.8 ± 21.8	12.79 ± 21.8	3.4 ± 16.5
1,2,3-Trimehtyl	18.0 ± 1.1	18.9 ± 1.3	19.48 ± 13.7	15.9 ± 10.3
1,3-Diehtyl benzene	1.7 ± NA	24.6 ± NA	25.13 ± 14.6	32.0 ± 11.0
1,4-Diehtyl benzene	10.7 ± 3.6	10.4 ± 4.1	9.43 ± 15.3	2.4 ± 11.5
n-Undecane	1.2 ± 42.0	12.2 ± 47.8	13.54 ± 45.3	40.0 ± 34.2

NA: Not available.

we found no difference in the ethene/acetylene ratio with respect to the bore being sampled or the traffic density. In a recent study conducted in another northern Mexican city (Mexicali), in an area heavily influenced by mobile sources, the values obtained for this ratio were less than one (Mendoza *et al.*, 2009). This indicates that the vehicle fleet sampled in this study was rather new and well maintained compared, at least, to the Mexicali fleet. In the same way, the BTEX species (benzene, toluene, ethyl benzene and xylenes) are also of interest in characterizing mobile emissions. Table 7 presents a comparison between the average ratios obtained here and a sample of values reported by others for cities around the world. The average value found for the T:B ratio in the LLT falls well within the range reported by others. Moreover, its value is quite close to what Barletta *et al.* (2002) and Chan *et al.* (2002) report as an indicator for mobile source emissions (ratio of ~2.5). The E:B and X:B ratios fall in the lower end of the range of values reported by others. These differences can be attributed to many factors, including fuel composition, vehicle technology and age, local driving conditions, etc.

Table 8 presents a comparison of the EFs (mg/km-veh) obtained here with respect to the ones obtained by others in tunnels elsewhere, while Table 8 presents a comparison of the EFs on a basis of mass emitted per volume of fuel burned between a study conducted in Los Angeles, California, and our study. EF data from tunnel studies in Mexico is scarce. We found only one study reported (Vega *et al.,* 2000), which is discussed later on. Even though we acknowledge that many factors will make EF values different between tunnel studies (e.g., vehicle technology, fuel composition and quality, existence of inspection and maintenance programs, ambient conditions, etc.), the comparison is still valuable in that the order of magnitude differences can provide qualitative information between the sampled vehicle fleets. From Table 8, the overall emission profile of the vehicles in the LLT seems to match the one from the Fort McHenry Tunnel (FMT) more closely. However, there is a tendency toward higher emissions of smaller VOCs (C_2-C_6) in the LLT than in the FMT, while in the FMT the larger VOCs ($>C_6$) tend to be emitted more than in the LLT. This same behavior also occurs when comparing the data in Table 9.

Table 6. Ethene/Acetylene ratio for the different sampling periods

Day	Group[a]	Time period	Ethene/Acetylene Ratio
Monday, June 22	B1H	7:00-9:00	1.12
Tuesday, June 23	B1H	7:00-9:00	1.17
Wednesday, June 24	B1H	7:00-9:00	1.53
Monday, June 22	B1M	11:00-13:00	2.01
Tuesday, June 23	B1M	11:00-13:00	1.71
Wednesday, June 24	B1M	11:00-13:00	2.22
Thursday, June 25	B2M	10:00-12:00	2.43
Tuesday, June 30	B2M	10:00-12:00	1.32
Thursday, June 25	B2H	18:00-20:00	1.19
Tuesday, June 30	B2H	17:00-19:00	2.38

[a] B1H: Bore 1, high traffic density; B1M: Bore 1, moderate traffic density; B2H: Bore 2, high traffic density; B2M: Bore 2, moderate traffic density

Table 7. BTEX ratios comparison

Ratio	Values reported by others[a]		LLT
	Minimum	**Maximum[b]**	
Toluene/Benzene	1.75	4.0	2.57 ± 1.19
Ethylbenzene/Benzene	0.3	0.6	0.3 ± 0.06
Xylenes/Benzene	1.6	3.4	1.29 ± 0.32

[a] According to values reported by: Sweet *et al*. (1992), Scheff *et al*. (1993), Kenski *et al*. (1995), Zielinska *et al*. (1996), Gee *et al*. (1998), Mujica *et al*. (1998), Doskey *et al*. (1999), Singer *et al*. (1999), Chan *et al*. (2002), Na *et al*. (2004, 2005). [b] Maximum values correspond to Singer *et al*. (1999) and represent cold-start emissions.

Table 8. EF comparison among several tunnel studies (EF in g/km-veh)

Species	Tunnels				
	Tuscarora[a]	Fort McHenry[b]	Taipei[c]	Gubrist[d]	LLT
Ethene	14.5 ± 1.1	22.1 ± 2.1	26.2 ± 4.9	24.1 ± 6.1	34.6 ± 1.8
Acetylene	3.9 ± 1.5	7.6 ± 1.3	11.6 ± 3.0	12.8 ± 3.2	21.5 ± 0.6
Ethane	1.0 ± 1.0	5.5 ± 0.5	4.3 ± 1.0	4.3 ± 0.9	7.4 ± 5.7
Propane			2.4 ± 0.8	0.2 ± 1.2	18.8 ± 2.0
Isobutane			4.6 ± 0.9	1.7 ± 1.0	11.9 ± 5.7
1-Butene/Isobutene	5.3 ± 0.8	5.6 ± 0.6	8.3 ± 1.6	1.9 ± 0.6	9.7 ± 4.1
1,3-Butadiene			2.6 ± 0.4	1.6 ± 0.2	3.1 ± 5.6
n-Butane	5.1 ± 1.1	6.5 ± 1.1	6.6 ± 2.0	9.7 ± 5.3	28.7 ± 3.2
trans-2-Butene			1.6 ± 0.4	1.4 ± 0.6	2.0 ± 0.8
Isopentane	14.5 ± 3.6	32.1 ± 2.5	12.5 ± 4.1	18.2 ± 7.3	49.4 ± 9.7
n-Pentane	5.4 ± 1.4	9.7 ± 0.9	9.5 ± 3.1	6.2 ± 4.5	27.2 ± 3.3
trans-2-Pentene			2.8 ± 0.8	1.2 ± 0.8	2.8 ± 0.3
2,3-Dimethyl butane	1.4 ± 0.4	3.8 ± 0.4	1.3 ± 0.7		3.4 ± 0.2
2-Methyl pentane	4.8 ± 1.4	10.4 ± 0.8	5.3 ± 1.7		15.0 ± 1.1
3-Methyl pentane	3.0 ± 0.9	5.8 ± 0.5	6.4 ± 1.5		7.2 ± 0.8
n-Hexane	2.4 ± 0.7	4.8 ± 0.4	4.2 ± 1.6	1.7 ± 0.6	9.3 ± 5.0
Methyl cyclopentane	0.0 ± 0.1	3.6 ± 0.4	0.4 ± 0.1		4.7 ± 1.4
Benzene	9.3 ± 0.9	14.9 ± 1.1	12.2 ± 3.3	10.4 ± 2.3	17.3 ± 2.3
2-Methyl hexane	1.8 ± 0.6	3.6 ± 0.4			4.2 ± 2.1
3-Methyl hexane	1.5 ± 0.4	4.9 ± 0.9	2.9 ± 0.4		4.5 ± 1.6
2,2,4-Trimethyl pentane	3.4 ± 0.7	11.6 ± 0.9	0.3 ± 0.2		14.1 ± 4.9
n-Heptane			1.5 ± 0.2	0.9 ± 0.4	3.5 ± 5.3
2,3,4-Trimethyl pentane	1.3 ± 0.3	4.2 ± 0.3			3.7 ± 1.3
Toluene	14.3 ± 2.3	28.7 ± 2.6	29.0 ± 5.0	16.0 ± 4.8	44.6 ± 4.7
Ethyl benzene	2.8 ± 0.6	7.1 ± 1.4	5.9 ± 1.6	3.6 ± 0.9	6.1 ± 2.0
m- and *p*-Xylene	10.6 ± 2.2	24.0 ± 4.9	9.0 ± 2.4	10.8 ± 3.0	16.7 ± 3.0
o-Xylene	4.1 ± 0.9	8.8 ± 1.6	7.9 ± 2.1	4.8 ± 0.6	7.7 ± 1.5
3-Ethyl toluene	3.2 ± 0.7	9.3 ± 2.1			3.2 ± 0.5
1,2,4-Trimethyl benzene	5.3 ± 1.3	15.2 ± 3.4			4.3 ± 2.9

[a] Pierson et al., 1996; [b] Pierson et al., 1996; [c] Hwa et al., 2002; [d] Legreid et al., 2007.

In 1996, a tunnel study was conducted in the Chapultepec Tunnel, located in Mexico City, to estimate VOC EFs (Vega *et al.,* 2000). Given the difference in years between the studies, differences in the results are expected due to changes in vehicle technology, fuel composition, ambient conditions (particularly the height of Mexico City with respect to sea level), etc., as mentioned for studies conducted elsewhere. The comparison is still valuable because the Chapultepec Tunnel Study (CTS) is the only additional tunnel study reported for the country. In addition, the composition of the vehicle fleet reported in the CTS is comparable to the one found in the LLT: 1.4% diesel vehicles (mainly trucks) and 87% gasoline light-duty vehicles. Fig. 3 illustrates the chemical profiles found for both studies. In the LLT study, three- and four-carbon species had higher contribution values than in the CTS (propylene, propane, *i*-butane, *i*-butene, *n*-butane). Isopentane, benzene, toluene, and 2,2,4-trimethylpentane also presented this behavior. Five and six carbon species showed, on average, similar contribution values. Seven or more carbon species had higher contribution values in the CTS than in the LLT. These results could indicate the relative presence of more reactive species in the emissions from the vehicles in the LLT, as a clear sign of differences in fuel composition.

This last comparison highlights the importance of assessing the relative reactivity or ozone-forming potential of the mixture of COVs being emitted by the

Table 9. EF (g/L) comparison between the LLT and values from a Los Angeles, CA tunnel

Species	Los Angeles (Fraser *et al.*, 1998)	LLT
Ethene	637	637
Acetylene	486	436
Ethane	119	172
Propane	47	379
n-Butane	146	748
trans-2-Butene	37	34
n-Pentane	230	680
trans-2-Pentene	40	68
2,3-Dimethyl butane	68	62
2-Methyl pentane	242	361
3-Methyl pentane	153	154
n-Hexane	135	300
Methyl cyclopentane	9	87
2,4-Dimethyl pentane	70	20
Benzene	382	365
2-Methyl hexane	111	84
2,3-Dimethyl pentane	122	51
3-Methyl hexane	119	77
2,2,4-Trimethyl pentane	208	284
n-Heptane	8	45
2,3,4-Trimethyl pentane	76	37
Toluene	748	1,179
3-Methyl heptane	60	22
Ethyl benzene	143	90
m- and *p*-Xylene	557	278
o-Xylene	200	106
n-Propyl benzene	34	18
3- Ethyl toluene	67	42
1,3,5-Trimethyl benzene	77	33
2-Ethyl toluene	56	26
1,2,4-Trimethyl benzene	219	60
1,2,3-Trimethyl benzene	84	20

sampled vehicle fleet. A volume of air that is emitted from a given source can have a large concentration of VOC species, but if most of those VOC species are rather unreactive, the ozone-forming potential of the emission as a whole would be limited. Conversely, an emission source can emit limited amounts of VOCs, but if these are highly reactive then the emitted gases will be major contributors to ozone formation. A simple method to perform such analysis is the propylene-equivalent method (Chameides *et al.*, 1992). Here, a propylene-equivalent concentration of each emitted VOC is corrected based on its reaction rate with the •OH radical:

$$C_{p-eq,j} = C_j \frac{k_{OH,j}}{k_{OH,C_3H_6}} \qquad (4)$$

where $C_{p-eq,j}$ is the propylene-equivalent concentration of species *j*, C_j is its original concentration of species

j, $k_{OH,j}$ is the reaction rate constant between species *j* and •OH, and $k_{OH,C3H6}$ is the reaction rate constant between propylene and •OH. To perform this analysis, we used the average concentrations obtained in the canister samples. The corresponding reaction rate constants were obtained from Carter (2009).

The compounds with a higher propylene-equivalent concentration (*t*-2-butene, isoprene, styrene and other olefins) were not the ones with a higher concentration in the canister samples (ethene, toluene, isopentane) (Table 10). Even though isoprene has been recognized as being emitted mainly from biogenic sources, it is also known that mobile sources emit this compound (McLaren *et al.*, 1996). When biogenic isoprene emissions are negligible, it has been found that ambient air isoprene tends to be well related to 1,3-butadiene, a well-known marker of mobile source emissions (Borbon *et al.*, 2001). In ambient air samples that were evidently influenced mainly by vehicle
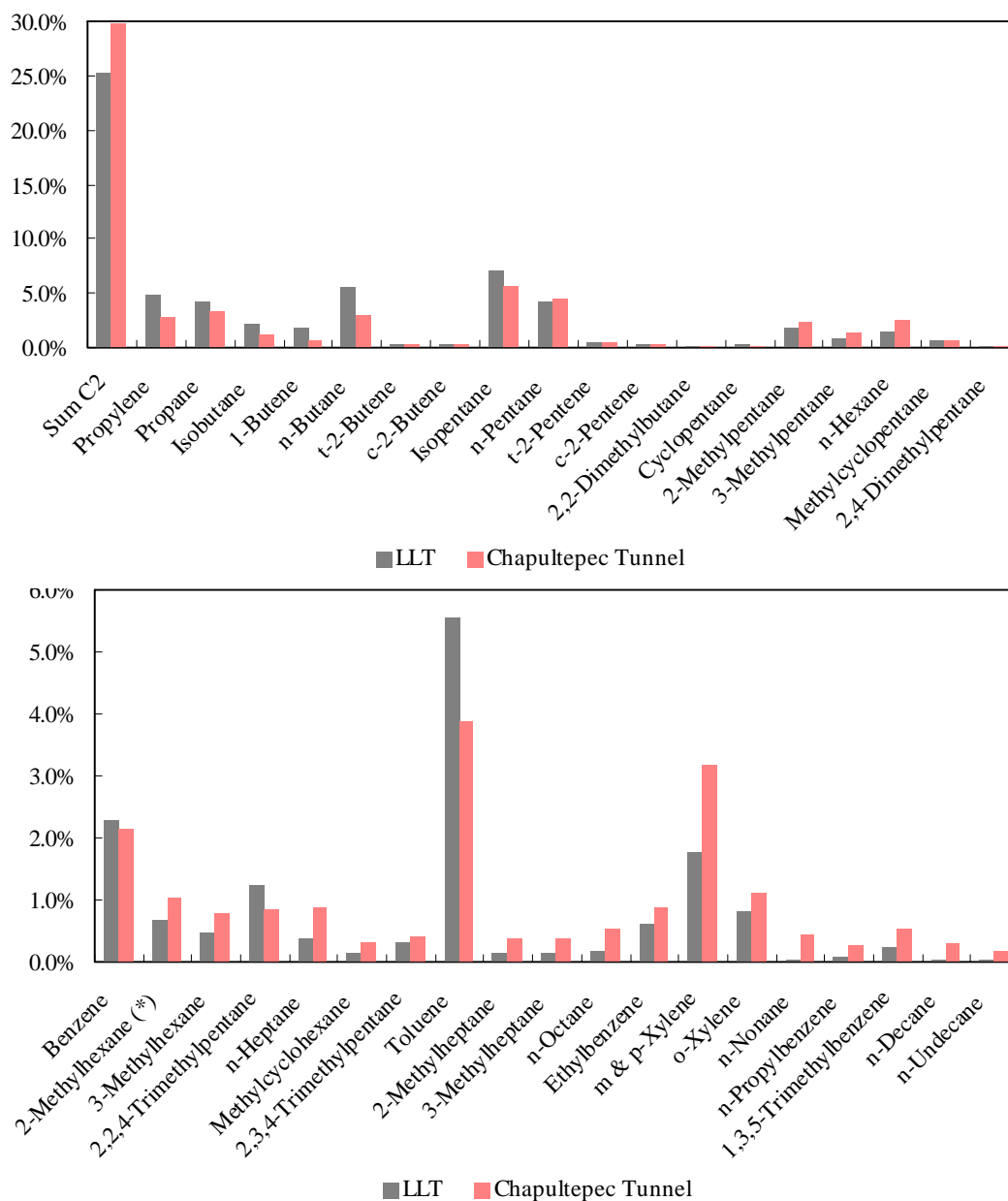
Fig. 3. Chemical Profile for LLT & CT

emissions, McLaren *et al.* (1996) obtained a linear regression line with a slope of 0.38 ($R^2 = 0.96$) between isoprene and 1,3-butadiene concentrations (in ppbv terms), whilst Borbon *et al.* (2001) obtained a regression line with a slope of 0.304 ($R^2 = 0.96$). In a similar way, we regressed $\Delta C_{isoprene}$ against $\Delta C_{1,3-butadiene}$ (following the nomenclature of equation 3), obtaining a slope of 0.24 ($R^2 = 0.98$) and a near-zero intercept, thus providing evidence that the isoprene observed came preferentially from the vehicles in the tunnel. Furthermore, Borbon *et al.* (2001) reported isoprene

EFs that ranged from 0.29 ± 0.12 mg/km-veh to 3.80 ± 2.50 mg/km-veh, corresponding to catalyst and non-catalyst petrol vehicles, respectively. The EFs found in the LLT were as low as 1.02 ± 1.12 mg/km-veh and as high as 1.63 ± 0.10 mg/km-veh, which fall well in the range of values reported by Borbon *et al.* (2001) as would be expected from sampling a fleet with vehicles in different conditions. Thus, when using the speciation data presented here in further air quality modeling exercises, it is important to consider the range of species found to account for the most abundant as well as the most reactive species.

Table 10. Average concentrations and propylene-equivalent concentrations of VOC species inside the LLT

Species	C_j (ppbC)	Species	$C_{p\text{-}eq,j}$ (ppbC)
Ethene	92.78	*trans*-2-Butene	35.01
Toluene	47.54	Isoprene	34.43
Isopentane	37.53	Styrene	23.17
n-Pentane	24.58	1,3-Butadiene	21.08
m- and *p*-Xylene	22.64	Propylene	20.64
Propane	22.10	*m*- and *p*-Xylene	20.11
n-Butane	20.89	1-Penteno	18.46
Propylene	20.64	Ethene	11.24
Isobutane	18.78	Toluene	10.20
2- Methyl heptane	17.68	Propane	9.43
Benzene	16.98	1,3,5-Trimethyl benzene	7.90
1-Pentene	15.29	*trans*-2-Pentene	7.85
2,2,4-Trimethyl pentane	14.47	*cis*-2-Pentene	7.27
trans-2-Butene	14.40	1-Hexene	6.43
Ethane	14.36	1,2,4-Trimethyl benzene	6.24
2-Methyl pentane	14.25	2- Methyl heptane	5.65
3-Methyl pentane	11.75	Isopentane	5.20
Styrene	10.39	*cis*-2-Butene	5.08
n-Hexane	9.84	*o*-Xylene	4.86
o-Xylene	9.29	*n*-Pentane	3.29
Isoprene	8.99	2-Methyl pentane	2.85
Cyclohexane	8.69	3-Methyl pentane	2.35
Methyl cyclopentane	8.68	Cyclohexane	2.35
1,3-Butadiene	8.32	2-Ethyl toluene	2.34
n-Heptane	7.94	*n*-Heptane	2.08
Ethyl benzene	7.03	*n*-Hexane	1.99
3-Methyl hexane	5.42	1,2,3-Trimethyl benzene	1.97
1,2,4-Trimethyl benzene	5.00	*n*-Butane	1.91
2-Methyl hexane	4.82	Methyl cyclopentane	1.90
1-Hexene	4.52	Ethyl benzene	1.89
2,3-Dimethyl butane	4.11	2,2,4-Trimethyl pentane	1.88
2,3,4-Trimethyl pentane	4.06	3- Ethyl toluene	1.68
2,3-Dimethyl pentane	3.80	Isobutane	1.55
2,4-Dimethyl pentane	3.78	3-Methyl hexane	1.49
n-Nonane	3.70	*n*-Nonane	1.39
3- Ethyl toluene	3.67	4- Ethyl toluene	1.31
1,3,5-Trimethyl benzene	3.62	2-Methyl hexane	1.28
2-Ethyl toluene	3.28	*n*-Decane	1.15
trans-2-Pentene	3.05	Methyl cyclohexane	1.07
cis-2-Pentene	2.91	2,3-Dimethyl pentane	1.04
Methyl cyclohexane	2.89	2,3,4-Trimethyl pentane	1.03
4- Ethyl toluene	2.88	2,3- Dimethyl butane	0.92
Cyclopentane	2.84	Benzene	0.80
n-Decane	2.73	3-Methyl heptane	0.76
cis-2-Butene	2.37	*n*-Octane	0.72
3-Methyl heptane	2.29	2,4-Dimethyl pentane	0.69
n-Octane	2.28	Cyclopentane	0.55

CONCLUSION

In order to create a confident emission inventory for any given region, it is important to use appropriate data for that particular region. In this sense, inventories based on experimental data are typically superior to those generated exclusively from model data. Here we conducted a tunnel study to derive EF and speciated VOC profiles for emissions from mobile sources for the MMA. This is the first study that reports this type of data for the region. Given the characteristics of the tunnel used as the experimental set-up, the results obtained are a good estimate for gasoline-powered light-duty vehicles of the MMA. Speciation results are in line with what would be expected to be the highest emitted individual VOCs from mobile sources. Results indicate a high correlation between typical vehicle emission tracer species, including benzene with other aromatic species and isopentane with other aliphatic species. Of particular interest is the ethene/acetylene ratio since it indicates that the sampled fleet tends to be composed of vehicles with a functioning catalytic converter. Compared to other tunnel studies, the emissions from the vehicle fleet sampled had a higher relative contribution of C_2 to C_6 species, which indicates clear differences in the gasoline composition being used at the different sites. Furthermore, this has implications on the reactivity of the emitted mixtures as olefins, including isoprene, were found to control the ozone-forming potential (expressed as propylene-equivalent concentrations) of the emissions.

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