Characterization of VOC Emissions from Light-Duty Vehicles in Monterrey, Mexico: Tunnel Study

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ABSTRACT

A two-week tunnel study was conducted in Monterrey, Mexico during the month of June of 2009 to characterize volatile organic compound (VOC) emissions from the local vehicular fleet. The Loma Larga Tunnel (LLT), a 532 meters-long structure that is mainly used by light-duty gasoline-powered vehicles was used as experimental set-up. Ambient air samples (2-hour averages) were taken inside the LLT using 6 L SUMMA®-polished canisters. In addition, CO_2 levels, temperature, pressure, and wind intensity at the same sampling points were recorded and registered on 2-minutes intervals. Samples collected in the canisters were analyzed for Total Non-Methane Organic Compounds (TNMOC) and 53 individual VOCs. During the campaign, 87,393 vehicles went across the sampling points with average velocities, on 2-hour intervals, as low as 41.9±7.2 km/hr and up to 75.9±9.5 km/hr. Estimated emission factors for TNMOC and CO_2 were 1.16 g/km-veh and 182 g/km-veh, respectively. The emission factors for both species tended to be higher for traffic moving upslope. However, an analysis of variance indicated that no statistical difference could be identified between traffic moving upslope or downslope, and between different traffic conditions. The average vehicle mileage estimated from the field data gave 12.3 km/L. With respect to individual VOC species, the most abundant ones were Ethene (10.6%), Isopentane (7.6%), Acetylene (7.3%), Toluene (5.9%) and *n*-Butane (5.6%). High correlations were obtained for known markers of vehicular emissions. Particularly, for Ethene-Acetylene (R^2 = 0.95) a ratio between 1.1 and 2.4 was obtained, which indicates the presence of vehicles with a working catalytic converter.

INTRODUCTION

The use of vehicles with internal combustion engines has increased significantly in Mexico during the last years, particularly in urban areas. For example, in the Monterrey Metropolitan Area (MMA), the third largest urban center in the county, the amount of vehicles that compose the official vehicular fleet doubled from 1999 to 2005. This has important environmental implications. On average, mobile sources represent the largest contribution of pollutants emitted to the atmosphere by anthropogenic sources in the country. According to the 1999 official emissions inventory for the MMA,[1] mobile sources contributed that year to 92% of the CO, 60% of the NOx (NOx = NO + NO_2), 39% of the VOCs, 12% of the NH_3 and 3% of the SOx (SOx = SO_2 + SO_3) emitted. Overall, 69% of the gaseous emissions in the MMA came from mobile sources.

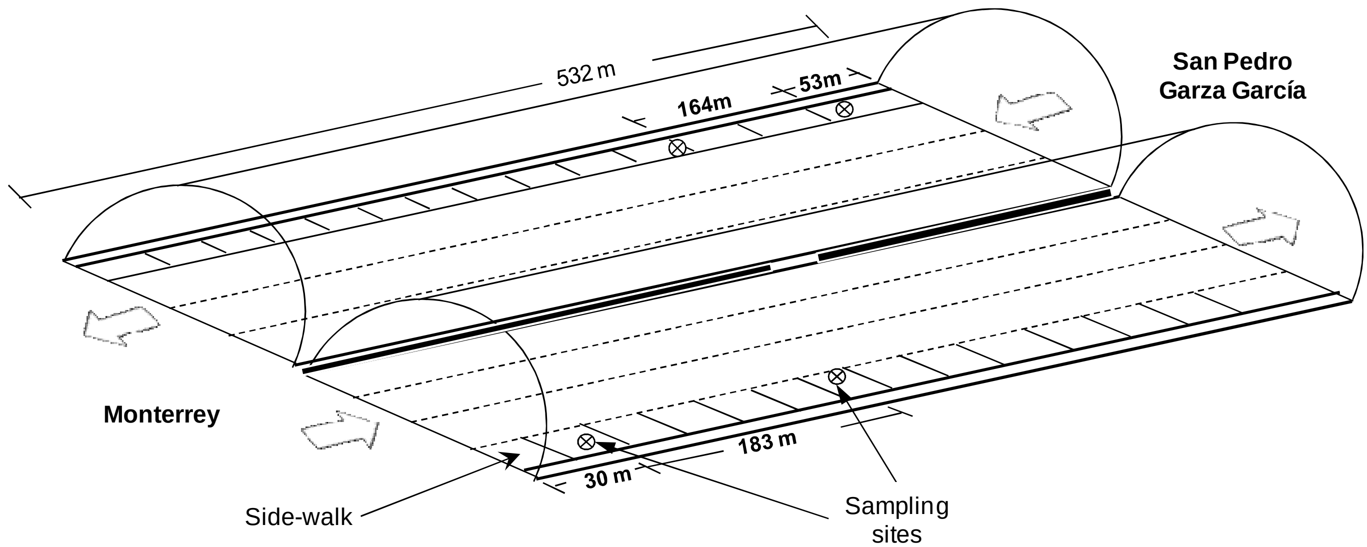
Of the compounds emitted by gasoline-powered vehicles, VOCs are of particular interest due to the environmental and health impacts associated with their release to the atmosphere. VOCs can provoke serious health problems, including memory loss and irritation of the respiratory track, while some are well-known cancerigens.[2] In addition, VOCs and NOx, in the presence of sunlight, are precursors of ozone and secondary organic aerosol. Even though VOCs have been identified as major contributors to air quality problems in Mexican urban centers,[3] few studies outside Mexico City have been conducted to characterize in detail the emissions of local sources, including mobile sources.

Emissions inventories for the MMA are based on US emission factors (EFs) corrected with very few field data to accommodate the differences between the two countries. Only recently, EF based on remote sensing techniques were reported for the MMA vehicular fleet.[4] However, no VOCs speciation information was derived. This study presents a field campaign conducted to characterize the emissions from mobile sources in the MMA, and in particular the mixture of VOCs emitted, using as experimental set-up a road tunnel.

METHODS

Experimental Site and Measurement Description. The Loma Larga Tunnel (LLT) is one of the main transit connections between the municipalities of Monterrey and San Pedro Garza García, which are part of 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 (Figure 1). Each bore has a four-lanes 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. The Monterrey-San Pedro Garza García 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.

Figure 1. Experimental set-up in the LLT.



The field campaign was conducted in June of 2009, following the sampling scheme shown in Table 1. Two sampling periods were selected for each day trying to account for high- and moderate-density traffic conditions. In each period, monitoring equipment was deployed at two points located over the walking lane of the bore. These two points, named "inlet" and "outlet", served as the limits over which the mass balances were performed to estimate the corresponding mobile emissions. The distance between sampling points, and between the "inlet" sampling point and the actual entrance to the tunnel (as shown in Figure 1), were determined based on what others have done in similar tunnel studies.[5,6] 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 CO_2, temperature, pressure, and relative humidity using a Testo 435 device. Simultaneously, air velocity at the same locations was measured using a thermal anemometer (Testo 425). NOx levels at the "outlet" point were measured using a Shimadzu NOA-7000 device. Due to resources constraints, NO_x levels could not be measured at the "inlet" point. Instead, the NO_x inlet condition was estimated using the concentration reported by the Obispado air quality station from the routine air quality monitoring system of the MMA, located less than 3 km (linear distance) from the experimental site. The Obispado station is located in downtown Monterrey and is influenced mainly by mobile source emissions. In the same way, equipment malfunction during the field campaign limited the collection of valid samples to measure levels of CO. Instead, NO_x levels were used as surrogate for CO concentrations, as confirmed by the relationship observed in the air quality reports from the Obispado station (Figure 2):

Equation (1) $$\left(\frac{CO}{NO_x}\right)_{Obispado} = \left(\frac{CO}{NO_x}\right)_{LLT}$$

where

$(CO/NO_x)_{Obispado}$ = CO/NO_x concentration ratio at the Obispado site, and

$(CO/NO_x)_{LLT}$ = CO/NO_x concentration ratio in the "outlet" point inside the LLT

Finally, Total Non-Methane Organic Compounds (TNMOC) and speciated VOC concentrations where obtained at each sampling location through whole air samples obtained using 6 L SUMMA®-polished stainless-steel canisters. Pre-calibrated mass-flow controllers where used to obtain two-hour integrated samples with these devices. Chemical analysis was performed for 54 target species (including TNMOC, Table 2) using US EPA's method TO-12 for TNMOC (flame ionization detection) and TO-15 for the individual VOCs (high resolution GC-MS). Chemical analysis of canister samples was conducted by TestAmerica labs (Austin, TX).

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 Wednes. 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 a 9 hrs	High	√	√	√			
	11 a 13 hrs	Moderate	√	√	√			
San Pedro – Monterrey (Bore 2)	10 a 12 hrs	Moderate				√	√	√
	18 a 20 hrs	High				√	√	√

EFs Estimation. EFs can be estimated from measurements taken in the interior of a tunnel and then conducting a mass balance over each pollutant.[7] Here, the main assumption is that the difference in concentrations between in 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:

Equation (2) $$M_k = \left(C_{k,e}V_e - C_{i,k}V_i\right)$$

where

V = air volumetric flow

C_k = concentration of pollutant k (e.g., mg/m^3)

Figure 2. NOx-CO correlation based on observations from the Obispado station.

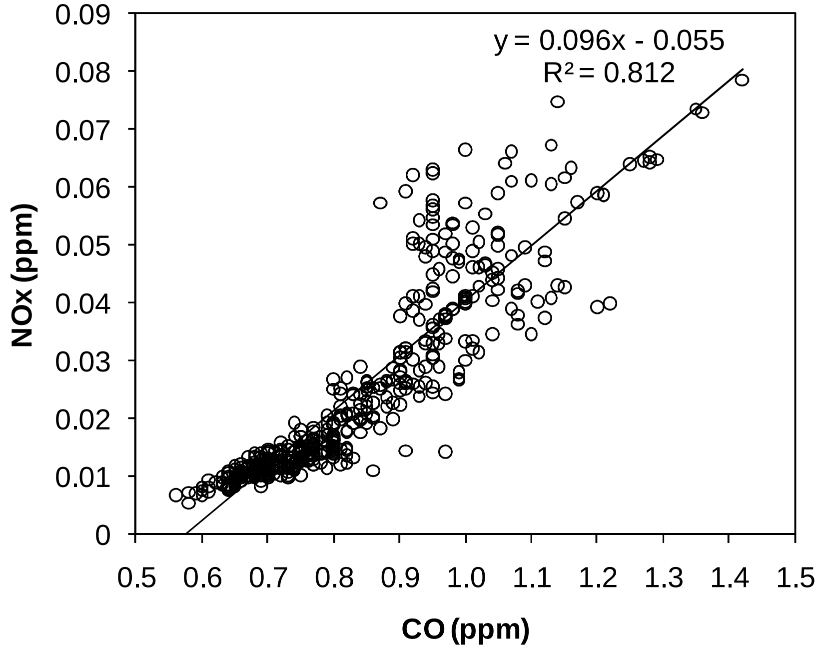


Table 2. List of target VOCs selected for chemical analysis from the canister samples.

No.	Compound	No.	Compound	No.	Compound
1	TNMOC	**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-penteno	**36**	2-methylheptane	**54**	*n*-Undecane

Subindices *e* and *i* in the concentration terms 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:

Equation (3) $$E_k = \frac{M_k}{L \cdot N}$$

where

N = number of vehicles that passed through the sampling points during the experimental period

L = 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:[8]

Equation (4) $$E'_k = \left(\frac{\Delta C_k}{\Delta C_{CO_2} + \Delta C_{CO} + \Delta C_{TNMOC}} \right) \rho_g w_c$$

where

ΔC_k = concentration difference of species k between the sampling points (i.e., $C_{k,e} - C_{k,i}$)

ΔC_{CO2} = concentration difference for CO_2

ΔC_{CO} = concentration difference for CO

ΔC_{TNMOC} = carbon-equivalent concentration difference for TNMOC

ρ_g = gasoline density (740 g/L)[9]

w_c = 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 TNMOC was assumed at 92 g/gmol.

RESULTS

Main Species EFs. Overall, 87,393 vehicles were sampled during the whole field campaign. Two-hour average vehicle velocities were as low as 41.9 ± 7.18 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). Approximately, 97% of the vehicles sampled where 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.

Figure 3 illustrates typical CO_2 time series from the sampled points inside the LLT. It can be observed that the "outlet" data tracks well the "intet" data. However, in some sampling periods concentration cross-over was observed due to traffic jams. When this occurred, the data was discarded for further analysis. Average EFs obtained for CO_2, CO, NOx, and TNMOC are shown in tables 3 and 4. When compared by bore, EFs tended to be higher in the Monterrey-San Pedro bore, which has a positive slope: 190±52 g/km-veh vs. 175±36 g/km-veh for CO_2, and 1.5 g/km-veh vs. 0.8 g/km-veh for TNMOC. However, an ANOVA demonstrated that the estimated EFs were independent of the bore and the sampling period. With the values obtained for CO_2, an average fuel consumption of 12.3±2.3 km/L was calculated.

Tables 3 and 4 also show a comparison between the EFs obtained in this study against values reported for other tunnel studies. EF estimated for CO_2, CO and TNMOC based on the LLT data are higher than in the other tunnels, while NOx is lower (on a mass per distance traveled basis). CO and NO_x EFs have to be used with caution due to the uncertainty associated with the assumptions made to obtain the value that is being reported.

Figure 3. Examples of CO_2 time series: a) Bore 1, June 23, 2009; b) Bore 2, June 25, 2009.

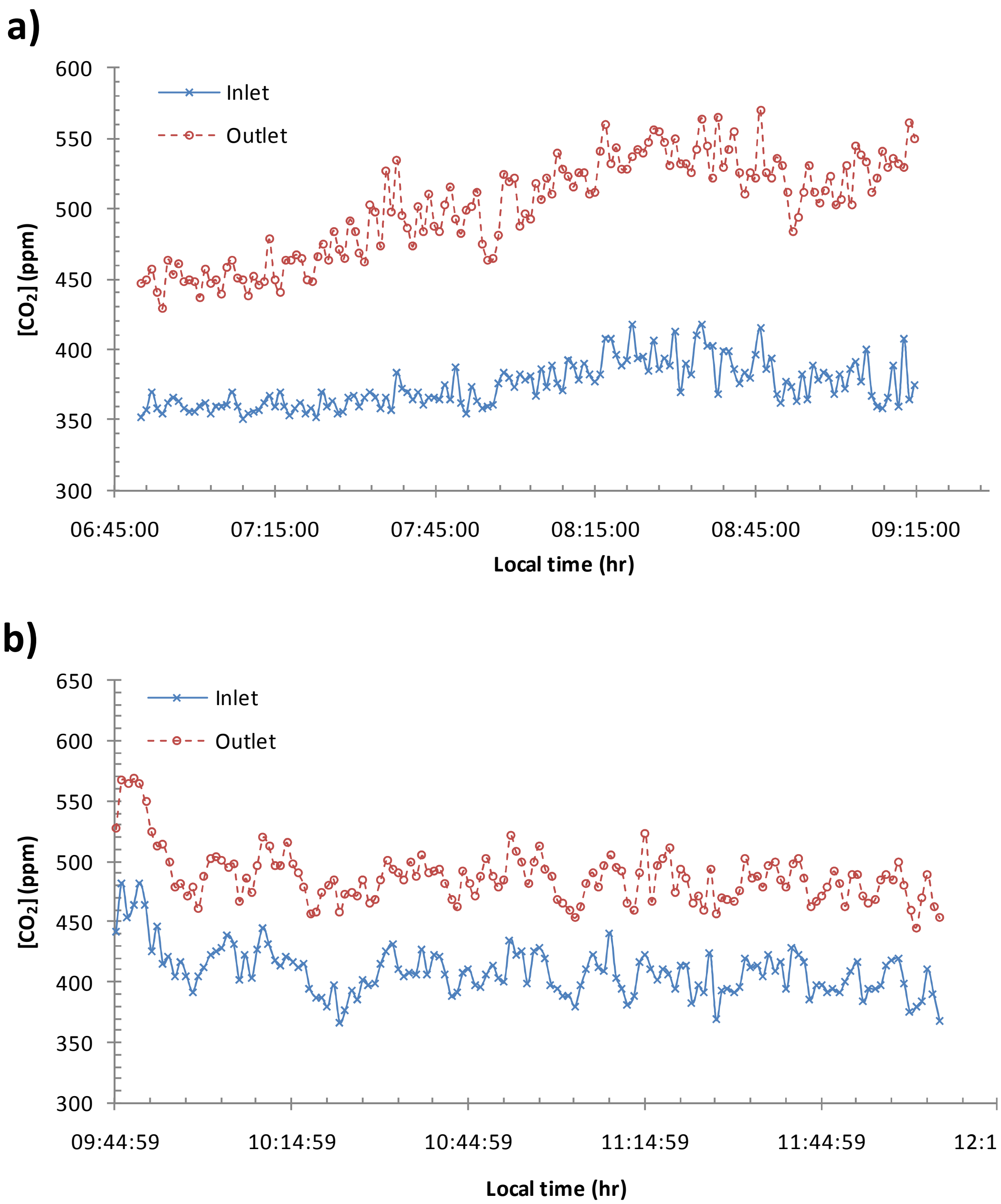


Table 3. Comparison of EFs (g/km-veh) obtained in this study with other tunnel studies.

Species	Tunnel					
	LLT	Taipei[10]	Chung-Cheng[10]	Gubrist[11]	Fort McHenry[7]	Tuscarora[7]
CO_2	182.7 ± 44.0				175.6 ± 0.9	145.0 ± 7.5
CO	4.83 ± 2.90	3.64 ± 0.26	6.25	4.18 ± 0.38	3.95 ± 0.34	3.04 ± 0.30
NOx	0.11 ± 0.07	0.9 ± 0.18	1.02	1.05 ± 0.09	0.50 ± 0.06	0.24 ± 0.16
TNMOC	1.16 ± 0.05	0.44 ± 0.06	1.51	0.46 ± 0.04	0.39 ± 0.06	0.18 ± 0.04

Table 4. Comparison of EFs (g/L) obtained in this study with other tunnel studies.

Species	Tunnel						
	LLT	Callahan (Boston)[12]	Lincoln (NY)[12]	Deck Park (Phoenix)[12]	Sepulveda (LA)[12]	Fort McHenry[7]	Tuscarora[7]
CO_2	2,159 ± 57					2,263	2,269
CO	111.3 ± 29	45	39	45	56	56	48
NOx	4.7 ± 2.1	9.2	10	8.4	7.3	4.9	3.9
TNMOC	19.8 ± 13.8	4.5	5.2	6.1	5.3	7.8	2.9

As indicated previously, Aguilar *et al*.[4] report composite EFs for the MMA vehicular fleet based on remote sensing data obtained in a June 2008 field campaign. In that study, vehicle speeds were mainly between 20 km/h and 35 km/h, with most of the vehicles driven in acceleration mode. Table 5 presents a comparison between the EFs obtained by Aguilar *et al*.[4] and our study. In this comparison, we only consider data reported, in the remote sensing study, for vehicles 1999 and newer, which are the type of vehicles that typically are found in the LLT. CO EF derived from the LLT is well within the range of values reported in the remote sensing study, while NOx EF is half the value and hydrocarbons EF is twice the value with respect to what Aguilar *et al*.[4] report.

Table 5. Comparison of EFs for the MMA obtained through two different techniques.

Species	**LLT**	**Remote sensing[4,a]**		
		Automobiles	**Pick-ups**	**SUVs**
CO	4.83 ± 2.90	3.5	7.7	1.9
NO_x	0.11 ± 0.07	0.46	0.77	0.21
HC[b]	1.16 ± 0.05	0.5	0.9	0.2

[a] Values reported are estimates based on readings from Figures 12, 13 and, 14. [b] Remote sensing data is reported as HC, while in this study TMNOC values were obtained, which are not necessarily fully comparable.

Chemical Profiles. Tables 6 and 7 list EFs for the 53 individual VOCs that were characterized and Figure 4 presents an average chemical profile of the emitted VOCs. The identified individual species represent approximately 80% of the measured TNMOC. The species that contribute the most to the total VOCs (on a molar basis) were: ethene (10.6%), isopentane (7.6%), acetylene (7.3%), toluene (5.9%), and butane (5.6%). 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*- and *p*-xylene 14.5±3.5, 2,2,4-trimethylpentane 13.4±5.0, and isobutane 10.3±5.4. Given that ethene, acetylene, butane, benzene and Isopentane are tracers for mobile emissions, results give a validation that what is being observed are in fact emissions from mobile sources.

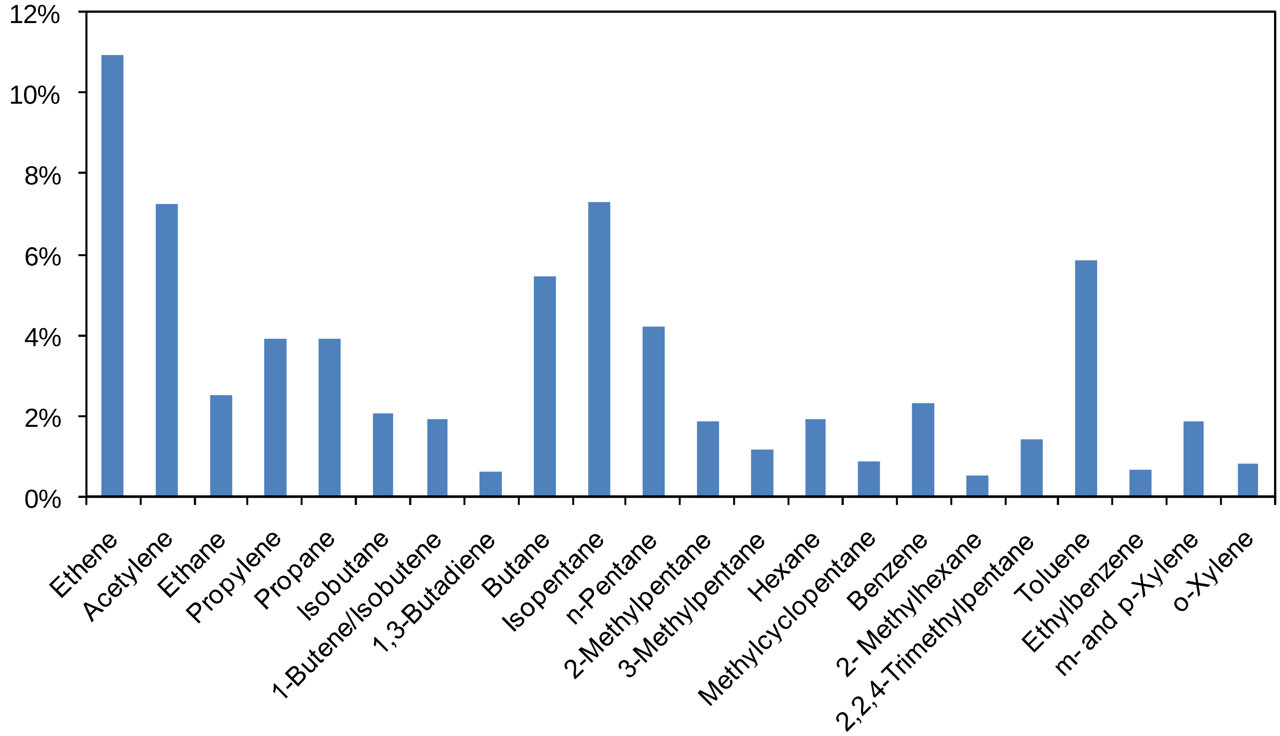
Table 6. EFs for individual VOCs (mg/km-veh).

Species	Bore 1 (high traffic density)	Bore 1 (moderate traffic density)	Bore 2 (high traffic density)	Bore 2 (moderate traffic density)
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 ± 2.00	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 ± 0.10	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	4.6 ± 5.04	1.15 ± 4.48
2,3-Dimehtyl pentane	2.33 ± 0.09	2.65 ± 0.12	2.83 ± 6.69	1.7 ± 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
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 ± 10.0	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	2.20 ± 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 ± ND	2.36 ± ND	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

Table 7. EFs for individual VOCs (mg/L).

Species	Bore 1 (high traffic density)	Bore 1 (moderate traffic density)	Bore 2 (high traffic density)	Bore 2 (moderate traffic density)
Ethene	560.2 ± 24.9	319.63 ± 28.3	263.08 ± 25.3	1026.90 ± 19.1
Acetylene	406.88 ± 6.2	149.94 ± 7.1	100.43 ± 12.8	743.11 ± 9.7
Ethane	92.57 ± 50.2	76.20 ± 57.2	189.17 ± 17.2	216.48 ± 13.0
Propylene	426.59 ± 22.5	147.66 ± 25.6	98.01 ± 63.6	174.23 ± 48.1
Propane	290.75 ± 24.6	162.63 ± 28.0	87.87 ± 39.1	637.71 ± 29.5
Isobutane	269.50 ± 63.8	79.58 ± 72.6	110.06 ± 13.3	301.95 ± 10.1
1-Butene / Isobutene	291.22 ± 43.4	62.70 ± 49.4	53.72 ± 10.2	33.30 ± 7.7
1,3-Butadiene	83.81 ± 61.4	18.56 ± 70.0	10.63 ± 12.4	13.58 ± 9.4
n-Butane	536.81 ± 30.0	193.02 ± 34.1	518.17 ± 9.1	1116.59 ± 6.9
trans-2-Butene	42.47 ± 5.7	18.98 ± 6.5	43.10 ± 27.5	21.49 ± 20.8
cis-2-Butene	23.89 ± 17.7	18.04 ± 20.1	20.60 ± 72.2	29.16 ± 54.6
Isopentane	682.98 ± 90.3	388.26 ± 102.9	796.83 ± 27.7	2126.14 ± 21.0
1-Pentene	22.27 ± 2.8	14.94 ± 3.2	18.49 ± 47.8	17.98 ± 36.2
n-Pentane	404.52 ± 23.8	222.49 ± 27.1	685.28 ± 11.5	947.7 ± 8.7
Isoprene	20.85 ± 1.1	17.29 ± 1.2	29.13 ± 24.7	29.99 ± 18.7
trans-2-Pentene	54.22 ± 1.4	26.13 ± 1.6	92.80 ± 14.5	63.51 ± 11.0
cis-2-Pentene	21.96 ± 0.5	20.93 ± 0.6	39.23 ± 14.5	45.92 ± 11.0
2,2-Dimethyl butane	31.55 ± 3.0	17.11 ± 3.4	30.85 ± 45.8	58.06 ± 34.7
Cyclopentane	36.05 ± 1.6	25.47 ± 1.8	47.88 ± 7.3	25.85 ± 5.5
2,3-Dimethyl butane	59.99 ± 0.9	29.05 ± 1.0	58.00 ± 8.9	68.90 ± 6.7
2-Methyl pentane	266.80 ± 1.5	108.88 ± 1.7	277.20 ± 56.5	516.99 ± 42.7
3-Methyl pentane	141.03 ± 1.5	52.88 ± 1.7	163.73 ± 40.1	173.49 ± 30.3
1-Hexene	12.82 ± 0.2	23.48 ± 0.2	51.30 ± 54.3	30.50 ± 41.1
Hexane	202.25 ± 41.2	62.00 ± 46.9	626.92 ± 15.9	201.29 ± 12.0
Mehtyl cyclopentane	113.05 ± 2.3	37.91 ± 2.6	100.30 ± 73.9	67.20 ± 55.9
2,4-Dimehtyl pentane	22.23 ± 2.2	20.41 ± 2.5	20.25 ± 5.2	14.72 ± 3.9
Benzene	316.88 ± 32.1	139.67 ± 36.6	271.97 ± 32.8	480.57 ± 24.8
Cyclohexane	29.19 ± 36.4	17.34 ± 41.4	31.53 ± 15.3	19.67 ± 11.5
2-Mehtyl hexane	85.22 ± 1.7	34.70 ± 1.9	62.70 ± 11.1	102.98 ± 8.4
2,3-Dimehtyl pentane	33.28 ± 1.3	28.51 ± 1.5	36.50 ± 14.7	68.01 ± 11.2
3-Mehtyl hexane	101.86 ± 1.4	34.64 ± 1.5	75.68 ± 8.8	65.48 ± 6.7
2,2,4-Trimehtyl pentane	268.16 ± 37.9	98.35 ± 43.1	118.04 ± 16.2	431.27 ± 12.3
n-Heptane	77.96 ± 68.7	21.48 ± 78.3	68.28 ± 76.0	38.36 ± 57.5
Mehtyl cyclohexane	20.49 ± 0.2	19.80 ± 0.2	27.33 ± 30.4	16.12 ± 23.0
2,3,4-Trimehtyl pentane	78.58 ± 1.6	30.22 ± 1.9	25.82 ± 79.1	35.97 ± 59.8
Toluene	771.20 ± 72.4	317.07 ± 82.4	1539.9 ± 49.6	1388.88 ± 37.5
2-Mehtylheptane	18.10 ± 1.3	21.98 ± 1.5	31.79 ± 69.6	19.12 ± 52.6
3-Mehtylheptane	16.20 ± 5.4	23.92 ± 6.2	31.79 ± 59.0	37.04 ± 44.6
n-Octane	12.79 ± 30.4	23.76 ± 34.7	40.86 ± 15.1	47.55 ± 11.4
Ehtyl benzene	138.15 ± 22.4	41.17 ± 25.5	115.00 ± 40.2	58.75 ± 30.4
m- and *p*-Xylene	450.94 ± 39.3	115.27 ± 44.8	405.81 ± 53.4	106.05 ± 40.3
Styrene	21.91 ± 34.3	39.62 ± 39.0	57.28 ± 60.3	6.84 ± 45.6
o-Xylene	172.70 ± 19.4	51.52 ± 22.1	152.15 ± 24.3	94.75 ± 18.4
n-Nonane	5.29 ± 13.2	2.92 ± 15.1	12.73 ± 12.1	21.33 ± 9.1
Cumene	23.62 ± 149.7	19.03 ± 170.5	14.49 ± 221.3	17.06 ± 167.3
n-Propyl benzene	13.71 ± 24.9	18.81 ± 28.4	17.26 ± 39.2	14.60 ± 29.6
3- Ehtyl toluene	72.08 ± 2.9	20.36 ± 3.4	38.35 ± 21.1	33.07 ± 16.0
4- Ehtyl toluene	30.18 ± 33.0	13.24 ± 37.6	29.87 ± 48.3	7.09 ± 36.5
1,3,5-Trimehtyl benzene	16.65 ± 35.7	24.35 ± 40.7	54.11 ± 58.8	88.88 ± 44.5
2-Ehtyl toluene	23.35 ± 0.7	24.22 ± 0.8	19.55 ± 19.3	90.21 ± 14.6
1,2,4-Trimehtyl benzene	112.16 ± 34.9	20.07 ± 39.8	71.08 ± 51.7	33.16 ± 39.1
n-Decane	6.84 ± 19.2	8.76 ± 21.8	12.79 ± 21.8	3.35 ± 16.5
1,2,3-Trimehtyl benzene	18.00 ± 1.1	18.87 ± 1.3	19.48 ± 13.7	15.91 ± 10.3
1,3-Diehtyl benzene	1.74 ± ND	24.56 ± ND	25.13 ± 14.6	32.01 ± 11.0
1,4-Diehtyl benzene	10.66 ± 3.6	10.39 ± 4.1	9.43 ± 15.3	2.44 ± 11.5
n-Undecane	1.22 ± 42	12.15 ± 47.8	13.54 ± 45.3	39.97 ± 34.2

Figure 4. Average chemical speciation profile (molar) of VOCs emitted inside the LLT.



The ethene/acetylene correlation is also a particularly good indicator of mobile source emission, and the value of its ratio can give information of the vehicles measured, particularly of the presence of a working catalytic converter.[13] A value of this ratio between 1 and 3 indicates the presence of a working catalytic converter, less indicates the contrary. Here we obtained values of this ratio that ranged from 1.1 to 2.4 (Table 8; R^2 = 0.95). 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.[14] This indicates that the vehicular fleet sampled in this study was rather new and well maintained compared, at least, to the Mexicali fleet.

Table 8. 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.

EF Comparison with tunnel studies outside Mexico. Table 9 presents a comparison of EFs on a mass emitted per distance traveled per vehicle basis from other studies with respect to the ones obtained here, while Table 10 presents a comparison of the EFs on a mass emitted per volume of fuel burned basis between a study conducted in Los Angeles, CA and our study. EFs data from tunnel studies in Mexico is scarce; only one additional study is reported in the primary literature (which is commented in the next section of this paper). That is the reason why this comparison is presented, even though we acknowledge that many factors will make the values different between studies (e.g., vehicle technology, fuel composition and quality, existence of inspection and maintenance programs, ambient conditions, etc.). From the information presented we can at least say that the values obtained here are in the order of magnitude of what others have observed in their studies.

Table 9. EF comparison among several tunnel studies (EF in g/km-veh).

Species	Tunnels				
	Tuscarora[7]	Fort McHenry[7]	Taipei[10]	Gubrist[11]	LLT
Ethene	14.50 ± 1.1	22.06 ± 2.1	26.23 ± 4.9	24.14 ± 6.1	34.6 ± 1.8
Acetylene	3.94 ± 1.5	7.56 ± 1.3	11.56 ± 3.0	12.83 ± 3.2	21.5 ± 0.6
Ethane	1.00 ± 1.0	5.44 ± 0.5	4.27 ± 1.0	4.29 ± 0.9	7.4 ± 5.7
Propane			2.4 ± 0.8	0.15 ± 1.2	18.8 ± 2.0
Isobutane			4.57 ± 0.9	1.71 ± 1.0	11.9 ± 5.7
1-Butene/Isobutene	5.25 ± 0.8	5.63 ± 0.6	8.27 ± 1.6	1.92 ± 0.6	9.7 ± 4.1
1,3-Butadiene			2.56 ± 0.4	1.61 ± 0.2	3.1 ± 5.6
n-Butane	5.06 ± 1.1	6.50 ± 1.1	6.56 ± 2.0	9.7 ± 5.3	28.7 ± 3.2
trans-2-Butene			1.61 ± 0.4	1.44 ± 0.6	2.0 ± 0.8
Isopentane	14.50 ± 3.6	32.06 ± 2.5	12.5 ± 4.1	18.22 ± 7.3	49.4 ± 9.7
n-Pentane	5.44 ± 1.4	9.69 ± 0.9	9.52 ± 3.1	6.16 ± 4.5	27.2 ± 3.3
trans-2-Pentene			2.76 ± 0.8	1.22 ± 0.8	2.8 ± 0.3
2,3-Dimethyl butane	1.38 ± 0.4	3.81 ± 0.4	1.33 ± 0.7		3.4 ± 0.2
2-Methyl pentane	4.75 ± 1.4	10.38 ± 0.8	5.27 ± 1.7		15.0 ± 1.1
3-Methyl pentane	3.00 ± 0.9	5.81 ± 0.5	6.39 ± 1.5		7.2 ± 0.8
n-Hexane	2.38 ± 0.7	4.75 ± 0.4	4.18 ± 1.6	1.73 ± 0.6	9.3 ± 5.0
Methyl cyclopentane	0.00 ± 0.1	3.56 ± 0.4	0.36 ± 0.1		4.7 ± 1.4
Benzene	9.25 ± 0.9	14.88 ± 1.1	12.21 ± 3.3	10.38 ± 2.3	17.3 ± 2.3
2-Methyl hexane	1.75 ± 0.6	3.63 ± 0.4			4.2 ± 2.1
3-Methyl hexane	1.50 ± 0.4	4.94 ± 0.9	2.94 ± 0.4		4.5 ± 1.6
2,2,4-Trimethyl pentane	3.88 ± 0.7	11.63 ± 0.9	0.29 ± 0.2		14.1 ± 4.9
n-Heptane			1.46 ± 0.2	0.93 ± 0.4	3.5 ± 5.3
2,3,4-Trimethyl pentane	1.31 ± 0.3	4.19 ± 0.3			3.7 ± 1.3
Toluene	14.31 ± 2.3	28.69 ± 2.6	29.02 ± 5.0	16.02 ± 4.8	44.6 ± 4.7
Ethyl benzene	2.81 ± 0.6	7.06 ± 1.4	5.88 ± 1.6	3.6 ± 0.9	6.1 ± 2.0
m- and *p*-Xylene	10.56 ± 2.2	24.00 ± 4.9	8.95 ± 2.4	10.78 ± 3.0	16.7 ± 3.0
o-Xylene	4.06 ± 0.9	8.81 ± 1.6	7.88 ± 2.1	4.77 ± 0.6	7.7 ± 1.5
3- Ethyl toluene	3.19 ± 0.7	9.25 ± 2.1			3.2 ± 0.5
1,2,4-Trimethyl benzene	5.31 ± 1.3	15.19 ± 3.4			4.3 ± 2.9

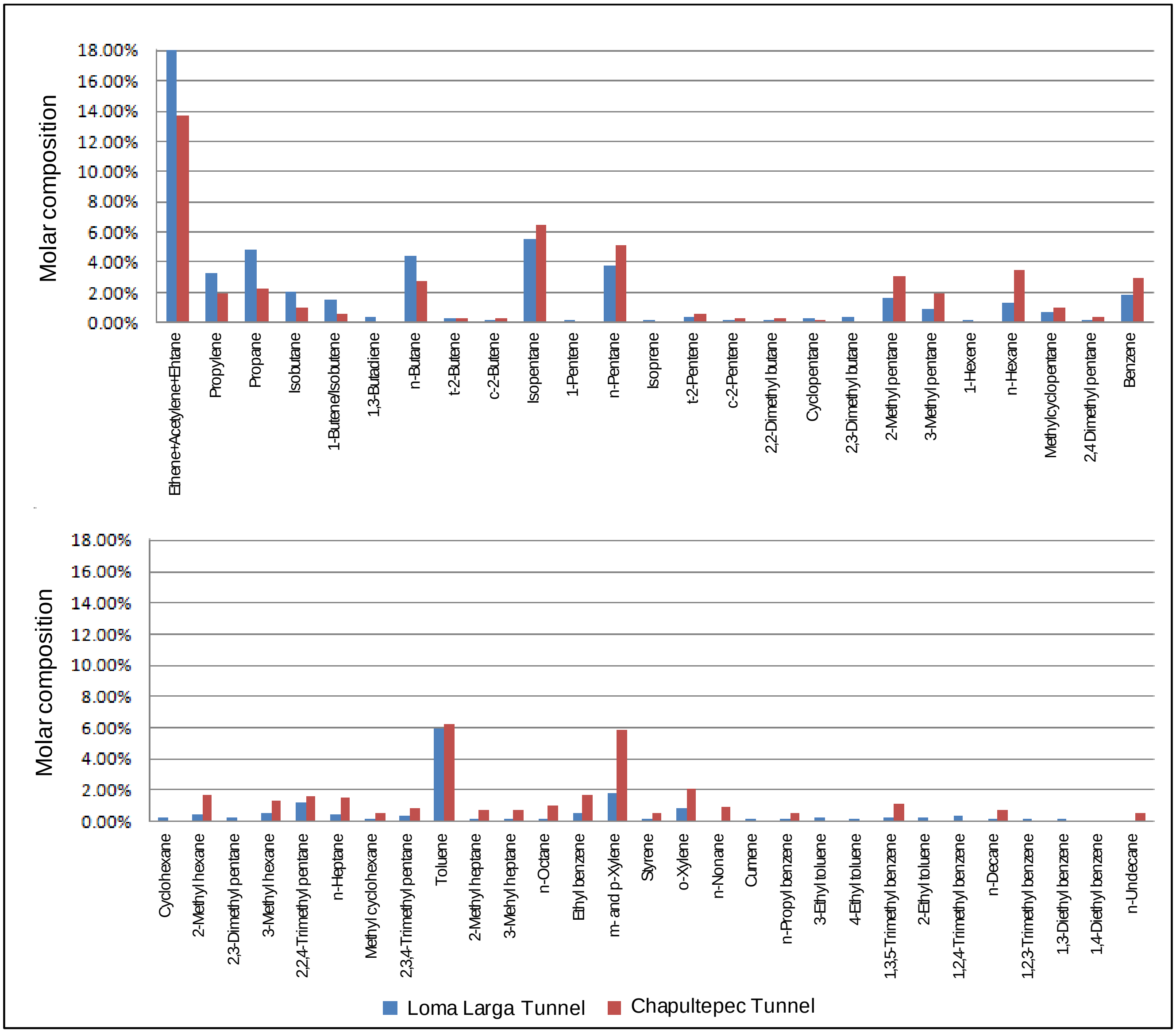
Table 10. EF (g/L) comparison between the LLT and values from a Los Angeles, CA tunnel.

Species	Los Angeles[15]	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	1179
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

Comparison with the Chapultepec Tunnel Study. In 1996, a tunnel study was conducted in the Chapultepec Tunnel, located in Mexico City, to estimate VOC EFs.[16] Given the difference in years between the studies, it is expected to have differences in the results 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 one reported in the primary literature conducted in the country before the one we are presenting here. In addition, the composition of the vehicular 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.

Figure 4 illustrates the chemical profiles found for both studies. In the LLT study, two- and four-carbon species had higher contribution values than in the CTS (ethene, ethane, acetylene, propylene, propane, *i*-butane, *i*-butene, *n*-butane). Five and six-carbon species showed two to three times higher contributions in the CTS with respect to the LLT study (*n*-Pentane, *t*-2 pentene, *i*-pentane, 2-methylpentane y 2-methylpentane), as well as the contribution of xylenes. Six or more carbon species (toluene, cumene, *n*-proyl benzene, styrene) showed similar contribution values. These results 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.

Figure 5. VOC chemical profiles comparison: CTS (1996)[16] vs LLT Study (2009).



CONCLUSIONS

In order to create a confident emissions 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 EFs and speciated VOCs 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 experimental set-up, the results obtained are a good estimate for gasoline-powered light-duty vehicles of the MMA. Overall, EFs (mg/km-veh) for CO_2, CO and TNMOC for the sampled vehicular fleet tended to be higher than those reported in other tunnel studies, while NOx estimates were lower. Results for CO and NOx have to be used with caution due to the uncertainty associated with the estimation procedure used to derive them. In addition, the data collected did not allowed to statistically differentiate the EFs from the bores, though the EFs from the up-slope bore tended to be higher. 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 tracer species, particularly for the ethene/acetylene ratio. This ratio is relevant since it indicates that the sampled fleet tends to be composed of vehicles with a functioning catalytic converter. Average estimated fuel consumption for the experiments resulted in 12.3 ± 2.3 km/L, which also corresponds well with what would be expected of the type of fleet sampled.

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KEYWORDS

Photochemical precursors
Mobile sources
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