2010

TECNOLÓGICO DE MONTERREY®

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

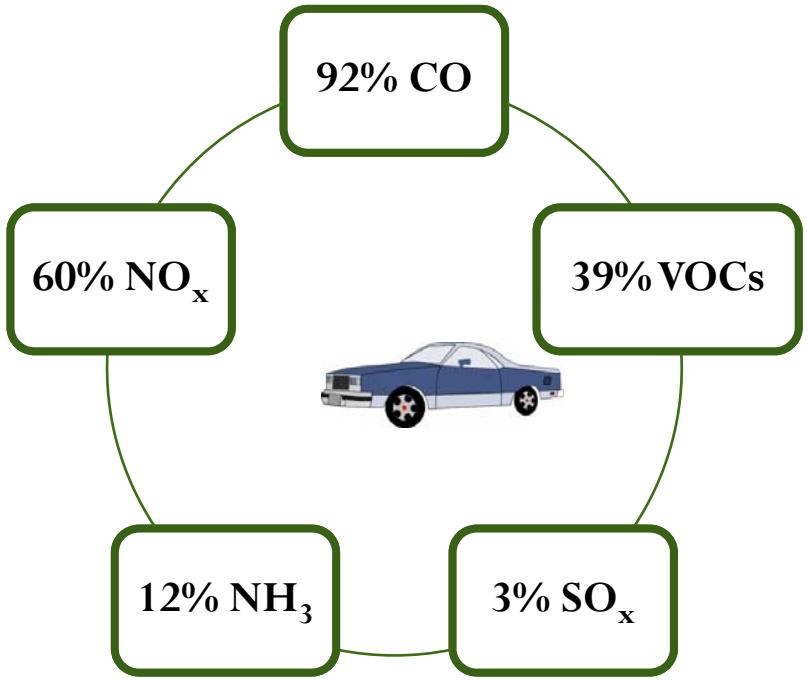


Alejandro E. Araizaga, Yasmany Mancilla and Alberto Mendoza
Department of Chemical Engineering, Tecnológico de Monterrey

Session 06 | Mobile Sources | 2010

Monterrey Metropolitan Area (MMA)

- According to the 1999 official emissions inventory…

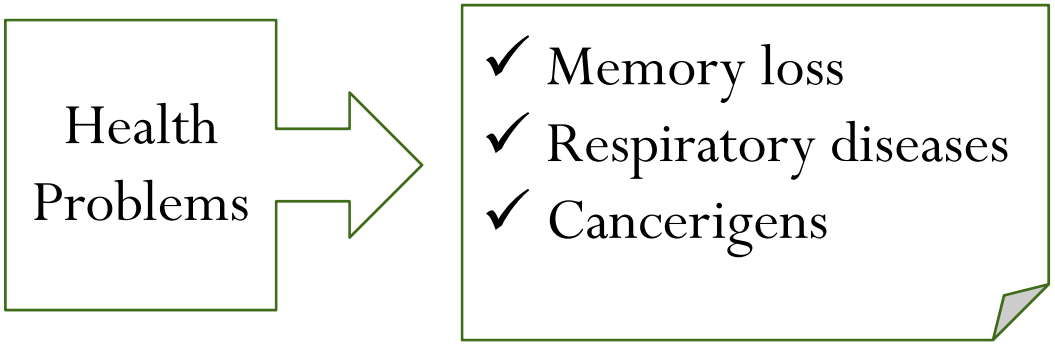


=

69% of the gaseous emissions

Volatile Organic Compounds (VOCs)

- VOCs can provoke:



- In addition:

$$\text{VOCs and } NO_x + \text{sunlight} \longrightarrow O_3 + \text{SOA}$$

- Few studies outside Mexico City have been conducted to characterize the emissions of local sources.

What is the aim of this tunnel study?

- Characterize VOC emissions from mobile sources in the MMA using as experimental set-up a road tunnel.

Monterrey Metropolitan Area (MMA)

The Túnel de la Loma Larga (TLL)

Tunnel studies around the world

Baltimore, USA

Los Angeles, USA

The Loma Larga Tunnel (LLT)

Cross-sectional Area of 113.5 m^2

±3.5% slope

2.0 h sampling periods

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				√	√	√

Six non-consecutive days campaign (June 2009)

Measurement Description

- At each sampling location

Testo 435 device

• [CO_2] , pressure, temperature and %RH

Testo 425 device

•Thermal Anemometer



- NO_x measurements

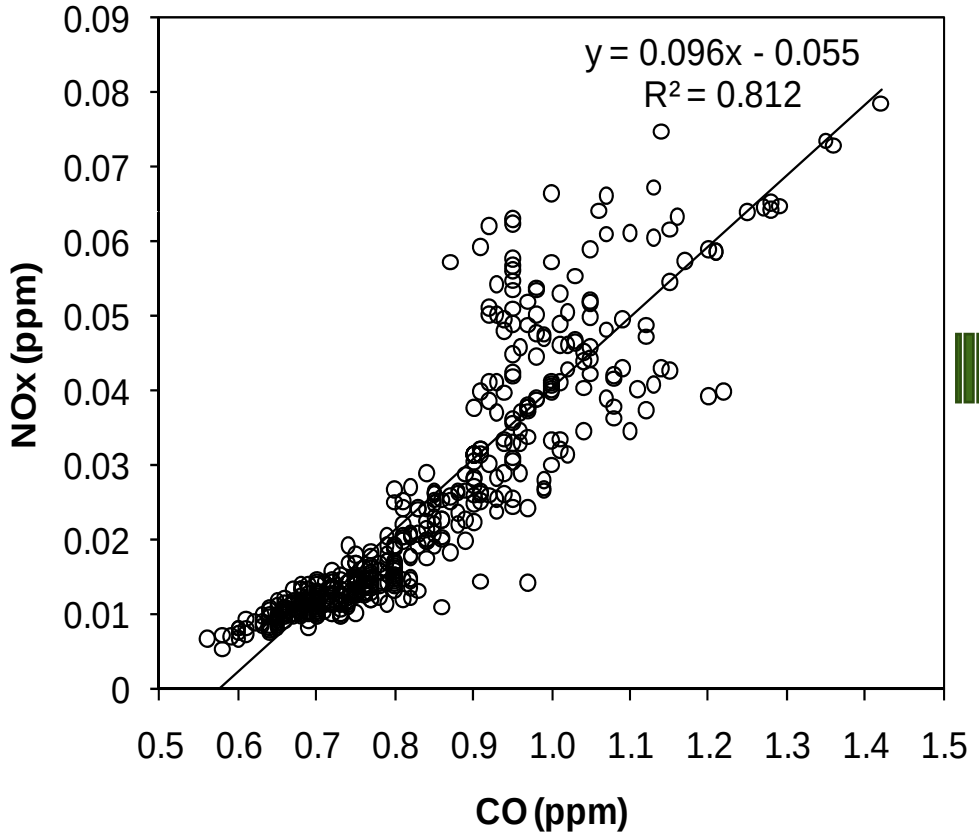
Shimadzu NOA-7000 device

• "Inlet" = Levels reported by the Obispado air quality station.

• "Outlet" = NOA-7000

CO Measurements

- NOx levels were used as surrogate for CO concentrations



$$\left(\frac{CO}{NOx}\right)_{Obispado} = \left(\frac{CO}{NOx}\right)_{Tunnel}$$

June 2009 Obispado station data

VOC Measurements

- 6 L SUMMA® Stainless-steel canisters, mass-flow controllers (2 hrs)

Aliphatics

No.	Compound	No.	Compound
1	Ethane	15	Cyclohexane
2	Propane	16	2,3-dimethylpentane
3	Isobutane	17	3-methylhexane
4	Butane	18	2,2,4-trimethylpentane
5	*t*-2-butane	19	Heptane
6	Cyclopentane	20	Methylcyclohexane
7	Isopentane	21	2,3,4-trimethylpentane
8	Pentane	22	2-methylheptane
9	2,2-dimethylbutane	23	3-metihyheptane
10	2,3-dimetihybutane	24	Octane
11	2-methylpentane	25	Nonane
12	3-methylpentane	26	Decane
13	Hexane	27	Undecane
14	Methylcyclopentane/2,4-Dimethylpentane		

Aromatics

No.	Compound	No.	Compound
1	Benzene	9	2,4-ethyltoluene
2	Toluene	10	1,3,5-trimethylbenzene
3	Ethylbenzene	11	2-ethyltoluene
4	*m,p* -xylene	12	1,2,4-trimethylbenzene
5	Styrene	13	1,2,3-trimethylbenzene
6	*o* -xylene	14	1,3-diethylbenzene
7	Cumene	15	1,4-diethylbenzene
8	Propylbenzene		

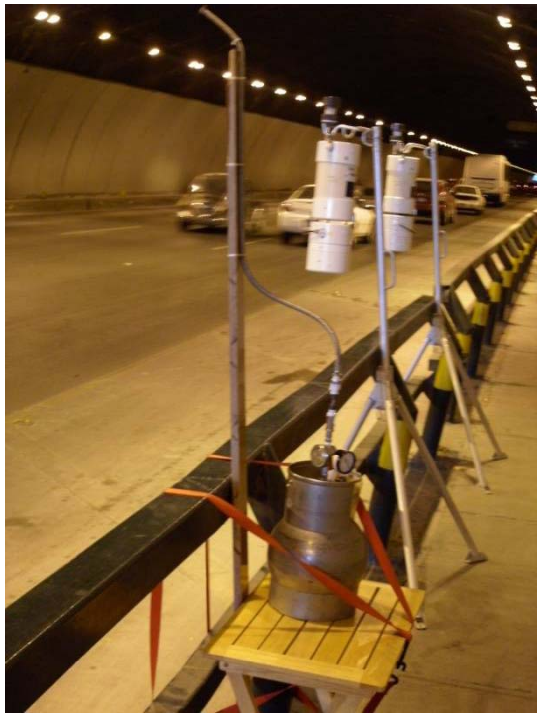
Olefins

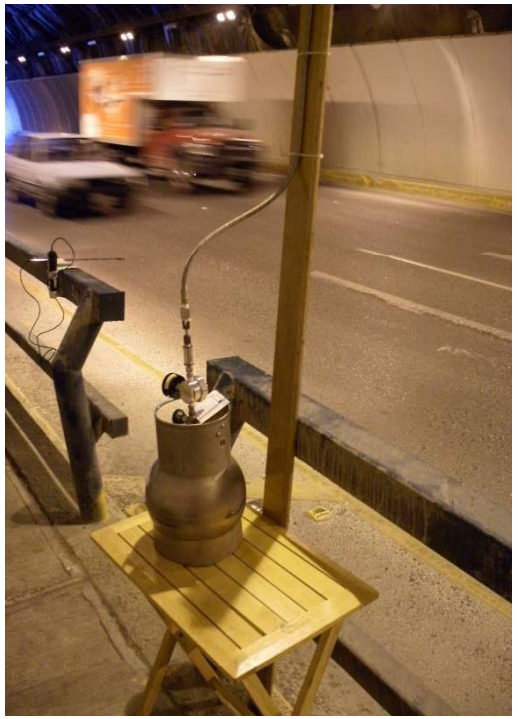
No.	Compound	No.	Compound
1	Ethene	7	*t*-2-pentene
2	Propylene	8	1-pentene
3	Acetylene	9	*cis*-2-pentene
4	1-butene	10	Isoprene
5	*cis*-2-butene	11	1-hexene
6	1,3-butadiene		

- Chemical analysis:

High Resolution GC-MS for 53 compounds (TO-15);
TNMOC by GC-FID (TO-12)

Devices on site





Emission Factor Estimation

EF: mass emitted per distance traveled per vehicle

$$EF_k = \frac{\left(C_{k,e}V_e - C_{k,i}V_i\right)}{N \cdot L}$$

Where:

- C_k = Concentration of pollutant *k* at the exit, *e*, and inlet, *i*, sampling points.
- V = Air volumetric flow.
- N = Total number of vehicles that traverse during the sampling period.
- L = Distance between two sampling stations.

More about EFs…

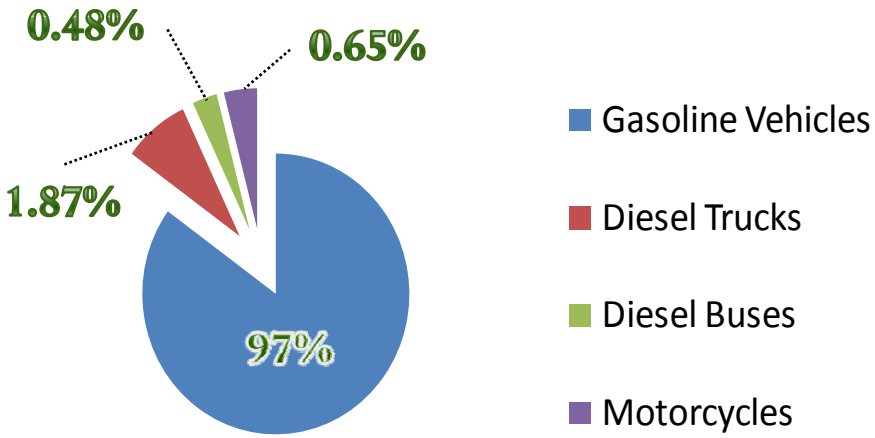
EF: mass emitted per volume of fuel burned

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

Where:

- ΔC_k = Concentration difference of the species *k* between the two sampling points.
- ΔC_{CO2}, ΔC_{CO} and ΔC_{TNMOC} = The carbon-equivalent concentration differences of CO_2, CO and Total Non-Methane Organic Compounds.
- w_c = Carbon mass fraction in the fuel.
- ρ_g = Density of gasoline.

Experimental Field Conditions



- Total of 87,393 vehicles
- 97% were gasoline-powered vehicles

- Average vehicle velocities were as low as 42 km/h and as high as 76 km/h

Main Species EFs

▪Comparison of EFs (g/veh-km) with other tunnel studies

Species	Tunnel					
	LLT	Taipei[a]	Chung-Cheng [a]	Gubrist[b]	Fort McHenry[c]	Tuscarora[c]
CO_2	182.7 ± 44.0				175.63 ± 0.9	145.00 ± 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

[a] Hwa et al. (2002). [b] Legreid et al. (2007). [c] Pierson et al. (1996).

Slope Effect

Uphill vs. Downhill

CO_2: 190 g/km-veh vs. 175 g/km-veh

TNMOC: 1.5 g/km-veh vs. 0.8 g/km-veh

Main Species EFs…

- Comparison of EFs (g/L) with other tunnel studies

Species	Tunnel						
	LLT	Callahan (Boston)[a]	Lincoln (NY)[a]	Deck Park (Phoenix)[a]	Sepulveda (LA)[a]	Fort McHenry[b]	Tuscarora[b]
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

Average Fuel Consumption = 12.3±2.3 km/L

Main Species EFs…

- Comparison of EFs : 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

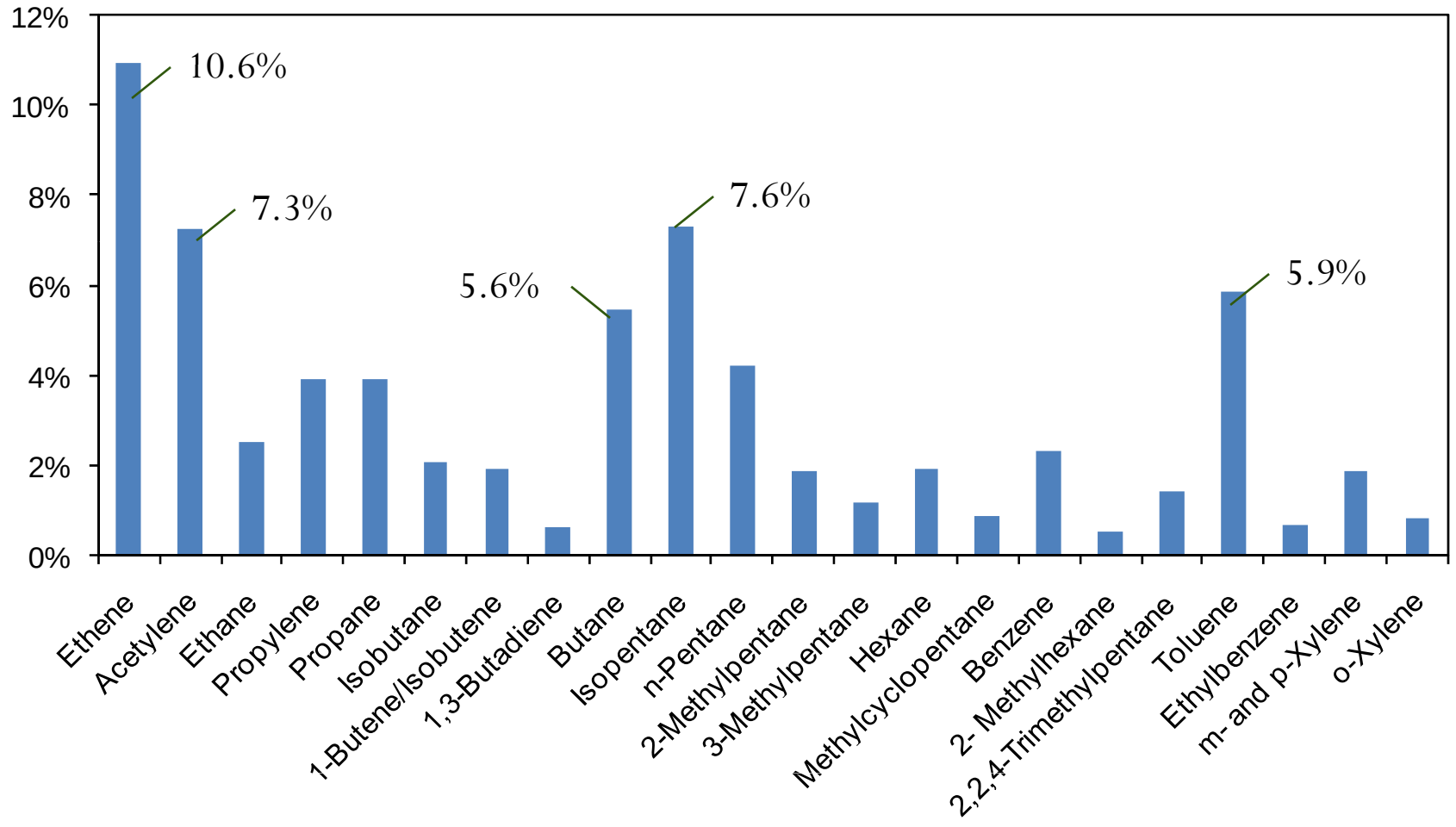
CO: Whithin the range values

NO_x: Half the value

HC: Twice the value

Chemical Profile

- Average chemical speciation of VOCs emitted inside the LLT.



Main Species EFs…

- 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

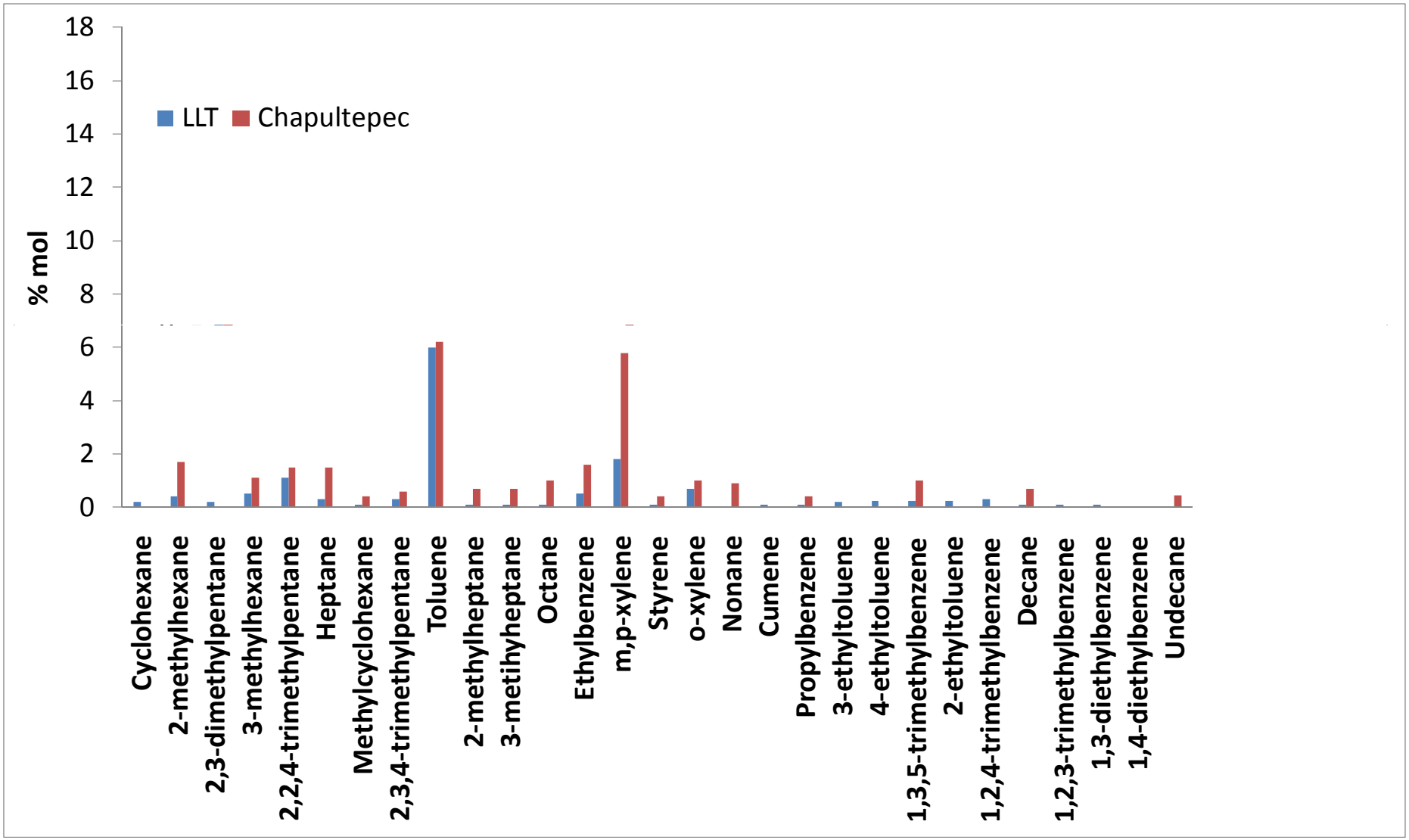
Range from 1.1 to 2.4 ⇨ Working Catalytic Converter

VOCs EFs (mg/km-veh)

Compound	*Tunnel Tuscarora*	*Tunnel Fort McHenry*	*Tunnel Taipei*	*Tunnel Gubrist*	*LLT*
★**Ethene**	**14.50 ± 1.1**	**22.06 ± 2.1**	**26.23 ± 4.9**	**24.14 ± 6.1**	**32.38 ± 1.5**
★**Acetylene**	**3.94 ± 1.5**	**7.56 ± 1.3**	**11.56 ± 3.0**	**12.83 ± 3.2**	**19.54 ± 0.5**
Propane			2.4 ± 0.8	0.15 ± 1.2	17.46 ± 1.8
Isobutane			4.57 ± 0.9	1.71 ± 1.0	10.32. ± 5.4
★**Isopentane**	**14.50 ± 3.6**	**32.06 ± 2.5**	**12.5 ± 4.1**	**18.22 ± 7.3**	**47.47 ± 9.5**
Pentane	5.44 ± 1.4	9.69 ± 0.9	9.52 ± 3.1	6.16 ± 4.5	25.77 ± 3.4
Hexane	2.38 ± 0.7	4.75 ± 0.4	4.18 ± 1.6	1.73 ± 0.6	8.51 ± 5.0
Methylcyclopentane	0.00 ± 0.1	3.56 ± 0.4	0.36 ± 0.1		4.11 ± 1.7
★**Benzene**	**9.25 ± 0.9**	**14.88 ± 1.1**	**12.21 ± 3.3**	**10.38 ± 2.3**	**15.92 ± 2.0**
2-Methylhexane	1.75 ± 0.6	3.63 ± 0.4			6.82 ± 2.5
3-Methylhexane	1.50 ± 0.4	4.94 ± 0.9	2.94 ± 0.4		4.28 ± 1.9
2,2,4-Trimethyl pentane	3.88 ± 0.7	11.63 ± 0.9	0.29 ± 0.2		13.37 ± 5.0
Heptane			1.46 ± 0.2	0.93 ± 0.4	2.78 ± 4.4
2,3,4-Trimethyl pentane	1.31 ± 0.3	4.19 ± 0.3			2.81 ± 1.8
★**Toluene**	**14.31 ± 2.3**	**28.69 ± 2.6**	**29.02 ± 5.0**	**16.02 ± 4.8**	**42.93 ± 3.9**
Ethylbenzene	2.81 ± 0.6	7.06 ± 1.4	5.88 ± 1.6	3.6 ± 0.9	5.36 ± 2.3
m,p-Xylene	10.56 ± 2.2	24.00 ± 4.9	8.95 ± 2.4	10.78 ± 3.0	14.50 ± 3.5
o-Xylene	4.06 ± 0.9	8.81 ± 1.6	7.88 ± 2.1	4.77 ± 0.6	5.93 ± 1.6

★ Tracers for mobile emissions

Mexico city tunnel Vs. LLT



Conclusions…

- To create a confident inventory.
- To derive EFs and speciated VOCs profiles for the MMA.
- First study that reports this type of data for MMA.
- A good estimate for gasoline-power LD vehicles.
- EFs for CO_2, CO and TNMOC tended to be higher than those reported in other tunnel studies, while NOx estimates were lower.
- High correlation between typical tracer species.

Acknowledgements

- Grant from the Mexican National Council for Science and Technology (CONACYT)

- Additional funding was provided by the Research Chair in Air Pollution Engineering (Tecnológico de Monterrey).

- Alejandro Araizaga received additional support (scholarship) through the Mexican Institute of Chemical Engineers (IMIQ) and Yasmany Mancilla through CONACYT.

- The support from the municipality of Monterrey during the field campaign conducted in this study.

THANK YOU!

Alberto Mendoza

mendoza.alberto@itesm.mx

TECNOLÓGICO DE MONTERREY

Departamento de Ingeniería Química
DEPARTMENT OF CHEMICAL ENGINEERING