

Open-path emission factors derived from DOAS and FTIR Measurements in the Mexico City Metropolitan Area

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Abstract:

A novel approach is presented that directly measures integral emission factors for numerous VOC, NO_x and SO₂ in the atmosphere, using collocated open-path Differential Optical Absorption Spectroscopy (DOAS) and Fourier Transform Infrared Interferometry (FTIR). Measurements were performed in two locations within the MCMA.

The problem:

In the MCMA mobile sources account for at least 50% of VOC and 80% of NO_x emissions [Molina and Molina 2002]. A major challenge arises from the high variability among emission factors [Zielinska et al. 1996, Sagabriel et al. 1996, Kean et al. 2001] derived from probing of individual vehicles, and the skewness of the distribution of emissions from in-use vehicles [Wenzel et al. 2000]. Emissions of volatile organic compounds (VOC), including formaldehyde, and NO_x (NO and NO₂) are important – though uncertain – input parameters to modeling photochemical smog formation.

Results:

- For two very different locations in the MCMA, about 10km apart, the mean emission factors of vehicle fleets in La Merced (downtown) and CENICA (low income residential / industrial area) agree generally within 50% or better (see Table 1).
- Slightly higher NO_x emissions factors are observed in La Merced compared to CENICA (see Table 1).
- Formaldehyde emission factors agree well (see Table 1).
- The average NO₂/NO ratio near CENICA is determined 7.3%.
- Combining DOAS and FTIR enables derive speciated emission factors for aromatic hydrocarbons, which are important SOA precursors.
- The day-to-day variability of open-path emission factors matches (or is below) the width of the distribution of emission ratios of the vehicle fleet, as measured by the ARI-mobile lab in mapping mode (see far right).
- Exceptionally constant open-path emission ratios are observed for benzene. The open-path approach lowers the uncertainty from vehicle to vehicle variability (see far right and below).
- Mean naphthalene emission factors agree well with available literature values (see Table 2).

Table 1: Spatial variability between La Merced and CENICA.

Compound X	CENICA		La Merced	
	X / CO ₂ [ppbv/ppbv]	EF [g/kg]	X / CO ₂ [ppbv/ppbv]	EF [g/kg]
NO	3.3 ± 0.4 × 10 ⁻³	6.2	4.8 ± 0.9 × 10 ⁻³	7.8
NO ₂	2.4 × 10 ⁻⁴	0.71		
NH ₃			2.4 × 10 ⁻⁴	0.22
N ₂ O	1.8 × 10 ⁻⁴	0.51	2.2 × 10 ⁻⁴	0.53
SO ₂	1.4 × 10 ⁻⁴	0.58		
CO	0.09	158	0.11	175
CH ₄			0.054	54.4
HCHO	1.8 ± 0.4 × 10 ⁻⁴	0.34	1.8 ± 0.6 × 10 ⁻⁴	0.34
C ₂ H ₂			1.2 × 10 ⁻³	2.02
Acetylene			1.1 × 10 ⁻³	1.91
Ethane			2.9 × 10 ⁻⁴	0.54
Propane			3.0 × 10 ⁻³	8.2
Butane	6.5 × 10 ⁻³	23.8		
Benzene	7.9 × 10 ⁻⁵	0.39		
Toluene	3.5 × 10 ⁻⁴	2.0		
m-Xylene	1.7 × 10 ⁻⁴	1.1		
p-Xylene	4.0 × 10 ⁻⁵	0.27		
Ethylbenzene	1.5 × 10 ⁻⁴	0.98		
Styrene	2.6 × 10 ⁻⁵	0.17		
Naphthalene	1.1 × 10 ⁻⁵	0.087		
Phenol	4.4 × 10 ⁻⁶	0.026		
p-Cresol	2.3 × 10 ⁻⁶	0.016		
Benzaldehyde	4.8 × 10 ⁻⁶	0.032		

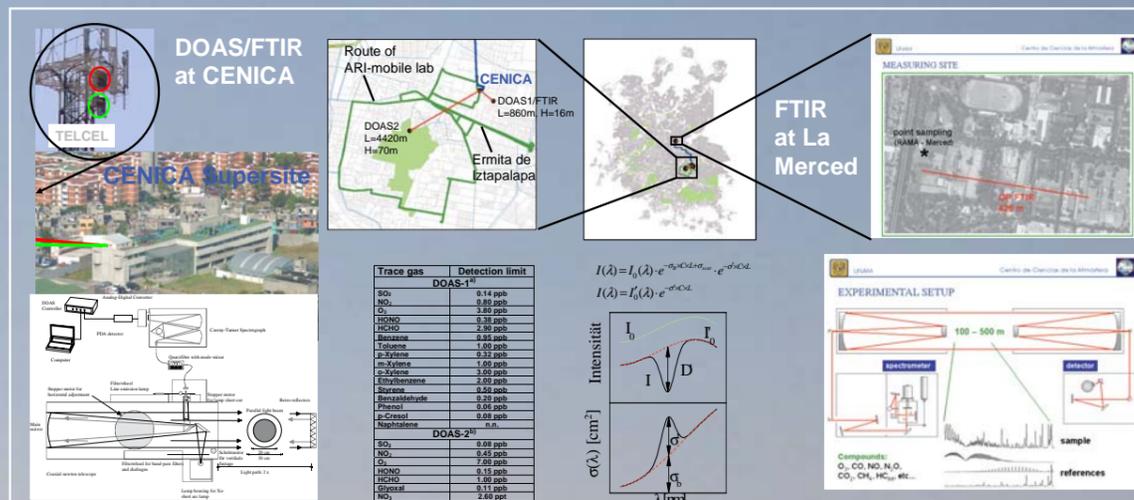
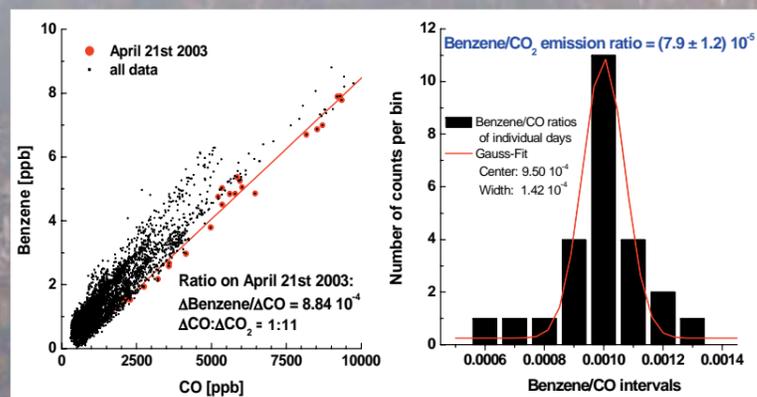
Table 2: Literature comparison emission factors for naphthalene

Location	Type of vehicle	EF [g/kg]	Reference
Ford Mc Henry Tunnel	LD	0.112	Sagabriel et al (1996)
Ford Mc Henry Tunnel	HD	0.086	Sagabriel et al (1996)
Tuscarora Mountain Tunnel	LD	0.050	Sagabriel et al (1996)
Tuscarora Mountain Tunnel	HD	0.022	Sagabriel et al (1996)
Mexico City	open-path	0.087	this work

Conclusions:

Open-path emission factors inherently average variable emissions among in-use vehicles and are representative for the overall vehicle fleet.

The approach was validated, and enables to derive low-cost fuel based emission inventories of numerous relevant trace gases.

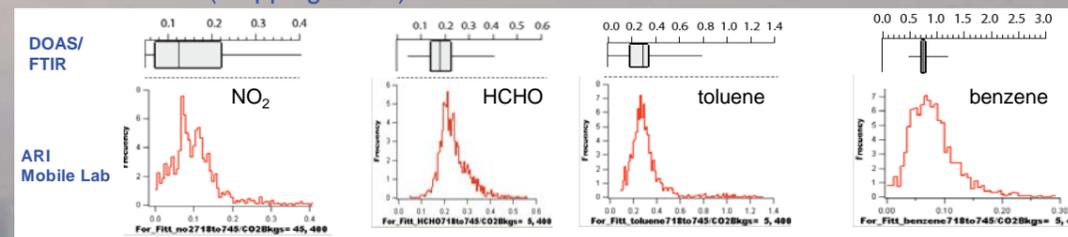


The approach:

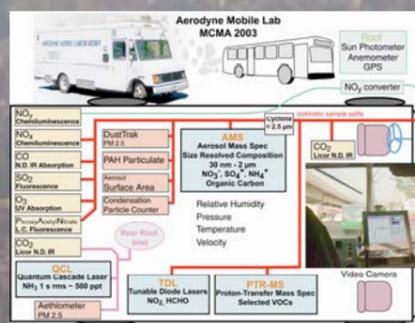
Elevated levels of air pollutants during morning rush hour were monitored in the UV/vis and IR spectral range, using Differential Optical Absorption Spectroscopy (DOAS) and Fourier Transform Infrared Interferometry (FTIR). High levels of CO during morning rush hour (5-7am CST) were correlated to accumulating trace gases emitted from mobile sources. CO is emitted – in contrast to CO₂ – almost exclusively from mobile sources (98%) and is readily detected by FTIR in both locations. Interference from photochemical sources was excluded using glyoxal (DOAS) as an indicator for the start of VOC chemistry. Trace gases were measured by FTIR (Grutter et al. 2004) and DOAS, including numerous aromatic hydrocarbons which are detected by their unique specific narrow-band (< 5 nm) absorption structures in the UV spectral range (Volkamer et al. 1998). Vehicle emissions of both NO_x species (NO and NO₂) were characterized at CENICA.

Validation experiment in a street canyon near CENICA (Ermita Iztapalapa)

The mobile lab (mapping mode) measured fresh emissions ratios near the FTIR/DOAS.



Mobile Laboratory Instrumentation & Modes of Operation



Stationary Sampling

High time resolution point sampling
Quality Assurance for conventional air monitoring sites

Mobile Sampling/Mapping

Motor vehicle pollution emission ratios
Large source plume identification
Ambient background pollution distributions

Chase

Detailed mobile source emissions characterization
Plume tracer flux measurements

