

Volatile organic compounds in the downtown area of Mexicali, México during the spring of 2005: analysis of ambient data and source-receptor modeling

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RESUMEN

La calidad del aire de la ciudad fronteriza de Mexicali no es satisfactoria, principalmente debido a los altos niveles de partículas suspendidas (PS) finas y ozono (O_3) que se registran ahí. Esto también influye en la calidad del aire de las ciudades del Valle Imperial en California. En abril de 2005 se llevó a cabo una campaña de monitoreo para obtener concentraciones de compuestos orgánicos volátiles (COV) en aire ambiente y así obtener información de los niveles y posibles fuentes de estos precursores de O_3 y PS finas. Contenedores de seis litros (*canisters*) se emplearon para tal fin en un sitio localizado en la región centro de la ciudad, para posteriormente analizar las muestras y obtener concentraciones de 54 especies preseleccionadas. Las muestras se tomaron diariamente durante tres periodos de tiempo: 6-9, 13-16 y 20-23 h tiempo local. La concentración promedio de compuestos orgánicos no metánicos totales (CONMT) fue de 560 ppbC, siendo las muestras de la mañana las que reportaron los mayores valores promedio (795) y las muestras del mediodía los menores valores (257 ppbC). Los compuestos aromáticos contribuyeron con alrededor de 24% del valor de CONMT reportado. Correlaciones entre especies indican una importante influencia de fuentes antrópicas locales en las mediciones (p. ej., una proporción de 2.1 entre xilenos y benceno). Adicionalmente, una alta correlación entre productos típicamente emitidos por motores de combustión interna (p. ej., acetileno-etileno $R^2 = 0.90$, etileno-propileno $R^2 = 0.94$, benceno-etileno $R^2 = 0.75$) y una contribución consistente de más del 15% de estas especies (etileno, acetileno, propileno y benceno) indican un importante aporte de fuentes móviles. Esto se comprueba a través de la aplicación de un modelo receptor, el Chemical Mass Balance, a los datos observados. Las estimaciones indican que las fuentes móviles a gasolina contribuyen con un 56% del nivel de COV observado, mientras que las emisiones de gas LP contribuyen con un 18, las emisiones de escape de vehículos diesel con un 6 y productos generales de consumo con un 5.

ABSTRACT

The border city of Mexicali has some of the worst air pollution in México, mainly due to the high levels of fine particulate matter (PM) and O_3 registered. This also impacts the air quality of communities across the border in California's Imperial Valley. A field campaign was conducted in April of 2005 to obtain ambient concentrations of volatile organic compounds (VOC), and thus obtain insight on the levels and sources of these O_3 and fine PM precursors. Six-liter stainless steel canisters were deployed at a site located in the downtown area of the city to obtain ambient air samples that were then analyzed for 54 selected target species. Samples

were collected on a daily basis at three different sampling times: 6-9, 13-16, and 20-23 h LT. Average total non-methane organic compounds (TNMOC) concentration was 560 ppbC, with the morning samples having the highest reported average concentration (795) and the afternoon the lowest (257 ppbC). Aromatics contributed around 24% to the TNMOC concentration. Correlation between different species indicates strong influence of local anthropogenic sources (e.g., xylenes-benzene ratio of 2.1). In addition, high correlations between typical products from internal combustion engines (e.g., acetylene-ethene $R^2=0.90$, ethene-propylene $R^2=0.94$, benzene-ethene $R^2=0.75$) across all samples and a consistent contribution of more than 15% of these species (ethene, acetylene, propylene and benzene) indicate major contribution from mobile sources. This is supported by receptor modeling results obtained through the application of the Chemical Mass Balance model to the ambient data. Source apportionment estimates indicate a 56% contribution of gasoline-related mobile source emissions to the VOC that were measured, 18 contribution from LPG emissions, 6 from diesel exhaust, and 5 from consumer products.

Keywords: Air pollution, emission sources, ambient air monitoring, Chemical Mass Balance, US-México border region.

1. Introduction

Volatile organic compounds (VOC) are typically abundant in urban atmospheres. The main anthropogenic sources of these chemical species are emissions from mobile sources, fugitive gasoline emissions, chemical and petrochemical industry, gaseous fuels leaks, and in general operations where solvents are used (e.g., architectural coatings, industrial and commercial painting processes, printing processes, dry cleaning, degreasing processes, graphic arts, etc.). VOC can have a variety of harmful health effects. At high exposure levels, several VOC can cause central nervous system depression (e.g., drowsiness, stupor) (Maroni *et al.*, 1995), and can be irritating upon contact with the skin (Hodgson *et al.*, 1991) or to the mucus membranes if inhaled (Mølhav, 1991), while other are proven carcinogenic substances (Jones, 1999). In addition to the health risks, VOC contribute to ozone and fine particulate matter formation in the troposphere (Russell *et al.*, 1995; Robinson *et al.*, 2007). In the oxidation process of VOC that leads to tropospheric ozone formation, semi-volatile organic compounds are formed which then can condensate onto preexisting aerosols. This process is relevant since the hygroscopic properties of such aerosols change as the ratios of inorganic, organic and inert species present in the individual aerosols change, with corresponding impacts on the optical and radiative-forcing properties of the polluted air (Kanakidou *et al.*, 2005).

The city of Mexicali, Baja California, is located in the western United States-México border (Fig. 1). Mexicali is a very dynamic city, with intense industrial and commercial activities. From a more regional perspective, Mexicali is located in the valley of Mexicali, adjacent to California's Imperial Valley, where the cities of Calexico, El Centro and Brawley are located. This region as a whole (Imperial Valley and the Valley of Mexicali) is also characterized by intense agricultural activity. Its location, coupled with an ongoing increase in population, and in industrial and commercial facilities, makes of the Mexicali-Imperial Valley border area a key region in the national as well as the international economic arenas. Currently, this border region is home to more than 1 million people, most of them living in the Mexican side of the border (Quintero Núñez *et al.*, 2006). However, this growth has derived in important environmental problems for Mexicali. The city has had some of the worst air pollution in the border region of México and this also impacts the air quality of communities across the border in California's Imperial Valley (INE, 1999; Quintero Núñez *et al.*, 2006). In a recent report from México's Instituto Nacional de Ecología, Mexicali has been placed as the most polluted city in the country with respect to PM_{10} and CO, and the sixth

with respect to O_3 (Zuk *et al.*, 2007). In addition, Mendoza *et al.* (2006) found that $PM_{2.5}$ levels in Mexicali can be also quite high, with a strong organic carbon component.

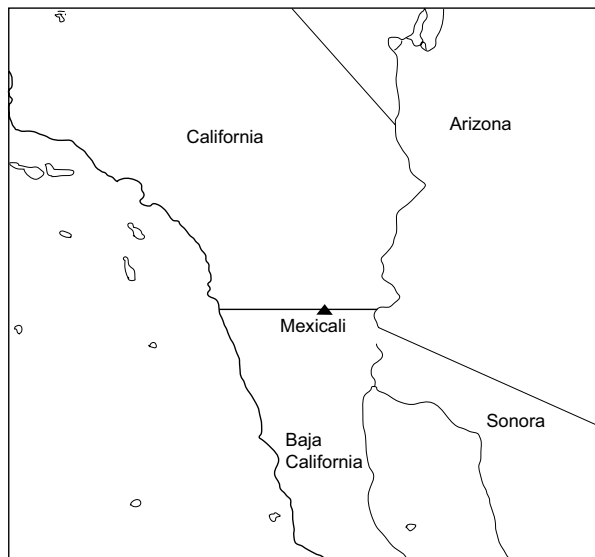


Fig. 1. Geographic location of the city of Mexicali in the western international border between México and the United States.

In the city of Mexicali the prevailing weather, as well as for most of the valley, is very arid. Typical conditions include clear skies, low humidity, extremely hot summers, mild winters, and low precipitation usually occurring during the winter and summer months (GEBC, 1999). These conditions are determined to a great extent by the presence of a semi-permanent subtropical cyclonic system in the Pacific Ocean near the California coast and the topography of the valley. Near-sea level altitude and a mountain range to the west of the valley acts as a shadow to the humid air flow from the ocean. During the spring months, the area is influenced by high pressure cells that foster stagnant wind conditions, which provoke the accumulation of air pollutants in the urban area (Vanoye García, 2007). Ground-level wind-flow patterns are dictated by the topographic orientation of the valley, which is northwest to southeast. About two-thirds of the time winds are from the northwest and one-third from the southeast; rarely winds are from other directions (GEBC, 1999). A past study also found a 2 m/s wind-speed threshold below which wind direction tended to be erratic (with the corresponding accumulation of pollutants), and above which pollutants dispersion was favored (Chow *et al.*, 2000).

Past air quality studies in Mexicali includes a VOC monitoring campaign during the summer of 1997 as part of the Southern California Ozone Study (SCOS97; Zielinska *et al.*, 1999). The main goal of that study was to establish boundary conditions for the regional air quality modeling domain set for SCOS97, and provide some information on VOC levels in the main cities of the California-México border region. A key finding of the ambient data analysis includes a large contribution from mobile sources to the total VOC observed. A second monitoring campaign was conducted during the summer of 1999, and the data collected was used for more detailed source apportionment calculations (Fujita *et al.*, 2004). Results of this second study indicate a contribution of nearly 40% of gasoline vehicles to the total ambient non-methane hydrocarbons, followed by natural gas fugitive emissions, propane combustion and diesel exhaust. Solvent emissions from

surface coatings and biogenic emissions were generally insignificant. The present study provides updated information on the levels of VOC in the ambient air of downtown Mexicali during a spring episode, and an analysis on the main sources that contribute to the observed concentrations through receptor modeling. The information is relevant to address the impacts of the growth of the city on air pollution, assess eventually the effectiveness of the air quality improvement programs set forth for the region by the state of Baja California (GEBC, 1999) and the Border 2012 Program (Quintero-Núñez and Sweedler, 2004), and help decision-makers orient further emission control policies for the region.

2. Experimental and modeling methods

2.1 Sampling campaign

Ambient air samples were collected at the Universidad Autónoma de Baja California (UABC) site from the routine air quality monitoring network of the city of Mexicali (Fig. 2). The UABC site is located within a University campus. The samples were obtained at the same location where the rest of the instruments of the site grab their samples: on top of a two-story building, mainly surrounded by open spaces, a few buildings and a small parking lot. The area where the UABC is located is predominantly residential, although several commercial facilities are located in the district.

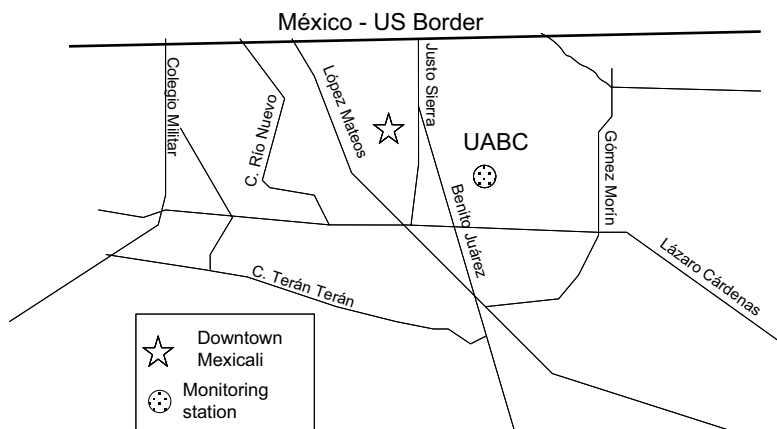


Fig. 2. Location of the UABC monitoring site.

A field campaign was conducted in April of 2005 to obtain ambient concentrations of VOC. Sampling activities started April 13 and ended April 22. Samples were collected on a daily basis at three different sampling times: 6-9, 13-16 and 20-23 h LT. The monitoring periods were selected to capture early morning, fresh VOC emissions, afternoon aged air masses, and early night emissions. The samples were collected in six-liter stainless steel SUMMA[®]-polished canisters. The sampling train included the following components, all constructed of stainless steel: a sampling inlet, a sintered metal particle filter, a critical orifice, a mass-flow controlling device calibrated for 3-hour sampling periods, a vacuum gauge and a canister. In addition, the sampling inlet was connected to a 1.5 m teflon sampling line to elevate the sampling point to a distance above the building top similar to the sampling points of the rest of the station monitoring devices. Prior to sampling, a leak test was conducted to insure proper connection between the components of the sampling train. A total of 33 valid samples were collected during the monitoring campaign.

The chemical analysis of the samples was based on methods contained in the United States Environmental Protection Agency's (US EPA) technical guidance documents (US EPA, 1998) using GC/dual capillary columns and dual FID, and was performed by Air Toxics LTD (Folsom, California). The method involves cryogenic cooling of the ambient air samples to obtain up to 50 mL of a condensate. After concentrating the sample, the concentrated aliquot was flash vaporized and swept through a water management system to remove water vapor. Following dehumidification, the sample was passed directly in to the GC system for analysis. Fifty-four target species were selected for analysis (Table I). The list resembles the Photochemical Assessment Monitoring Stations (PAMS) program target list of the US EPA. Each analysis was reported in ppbC using propane as the calibrate. Total non-methane organic compounds (TNMOC) were determined by summing the area count of all target and non-target peaks in the C2 through C12 range and applying the response factor of propane. Quality assurance/quality control specifications indicated by the analytical laboratory included 100% of laboratory blanks and 10% sample duplicates. Reporting limit was between 10 and 20 ppbC.

Table I. Target species list for chemical analysis.

Species	Mnemonic ^a	Species	Mnemonic
Total non methane organic compounds	TNMOC	Benzene	BENZ
Ethane	ETHA	Cyclohexane	
		2-Methylhexane / 2,3-Dimethylpentane	2-MYH/2,3-DMP
Ethene	ETHE	3-Methylhexane	3-MYH
Propane	PRPA	2,2,4-Trimethylpentane	2,2,4-TMP
Propylene	PRPE	<i>n</i> -Heptane	HEPA
Isobutane	ISOB	Methylcyclohexane	
Acetylene	ACET	2,3,4-Trimethylpentane	
<i>n</i> -Butane	BUTA	Toluene	TOLU
Trans-2-Butene		2-Methylheptane	
1-Butene		3-Methylheptane	
Cis-2-Butene		<i>n</i> -Octane	
Cyclopentane		Ethyl Benzene	EBEN
Isopentane	ISOP	<i>m</i> , <i>p</i> -Xylene	MPXY
<i>n</i> -Pentane	PNTA	Styrene	STYR
1,3-Butadiene		<i>o</i> -Xylene	OXYL
Trans-2-Pentene		<i>n</i> -Nonane	
1-Pentene		Cumene	
Cis-2-Pentene		Propylbenzene	
2,2-Dimethylbutane	2,2-DMB	3-Ethyltoluene/4-Ethyltoluene	3-ETYT/4-ETYT
2,3-Dimethylbutane		1,3,5-Trimethylbenzene	
Isoprene		2-Ethyltoluene	
2-Methylpentane	2-MYP	1,2,4-Trimethylbenzene	1,2,4-TMB
3-Methylpentane	3-MYP	<i>n</i> -Decane	
1-Hexene		1,2,3-Trimethylbenzene	
<i>n</i> -Hexane	HEXA	1,3-Diethylbenzene	
Methylcyclopentane/2,4-Dimethylpentane	MECY/2,4-DMP	1,4-Diethylbenzene	
		<i>n</i> -Undecane	

^aOnly mnemonics for detected species are listed.

2.2 Source-receptor modeling

Receptor models are mathematical procedures for identifying and quantifying the contribution of sources of air pollutants to a given receptor location. Receptor models do not use pollutant emissions, meteorological data or chemical transformation mechanisms to estimate the contribution of sources to receptor concentrations as chemical-transport models do (Russell and Dennis, 2000). Instead, receptor models use chemical and physical characteristics of gases and particles measured at the source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations (Watson, 1984).

In this study, the Chemical Mass Balance (CMB) receptor model version 8 (US EPA, 2004), was employed to obtain source contribution estimates to the VOC ambient air concentrations observed at the UABC monitoring site. CMB has been described in the literature (e.g., Cooper *et al.*, 1984; Gordon, 1988) and has been used extensively in source apportionment studies that involve VOC species (Watson *et al.*, 2001). Briefly, CMB solves a set of linear equations that express the chemical concentration at each receptor site as a linear combination of the product of source profile abundances and source contributions. Thus, known concentrations of component i (e.g., a given VOC species), C_i , will be:

$$C_i = \sum_{j=1}^J F_{ij} \times S_j \quad i = 1, \dots, I \quad (1)$$

where F_{ij} are the known source composition factors (source profiles) of species i in source j , and S_j the unknown contribution of source j . The number of chemical species (I) must be greater than or equal to the number of sources (J) for a unique solution to these equations. CMB uses the effective variance weighted solution, which can be superior to the classic weighted least-squares, and has been described by Cooper *et al.* (1984) and Henry (1992). This technique provides realistic estimates of the uncertainties of the source contributions (owing to its incorporation of both source profile and receptor data uncertainties) and gives greater influence to chemical species with smaller values of uncertainty in both the source and receptor measurements than to species with higher values of uncertainty.

Source profiles employed in this study were the ones derived and reported by Fujita *et al.* (2004) for a VOC source apportionment study conducted for the same region in the '90s. Source profiles database was enhanced by profiles derived by others for California (Censullo, 1996; Fujita *et al.*, 2002) and México City (Mugica *et al.*, 1998) CMB applications. One-sigma uncertainties of the original data were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of 15%. The assigned uncertainties were the larger of the two values based on recommendations by Fujita *et al.* (2004). Table II lists the source profiles that were used for source apportionment in this study with a brief description and assigned mnemonics. Categories of source profiles include gasoline and diesel exhaust, liquid and vapor gasoline, commercial natural gas and liquefied petroleum gas, surface coatings, consumer products, and isoprene as a biogenic marker. The actual source composition profiles used are presented in Table III.

Table II. Source profile descriptions used in this study.

Profile	Description	Source represented	Reference
MEXI_BAM	Mexicali /Calexico background – AM	Regional background	Fujita <i>et al.</i> (2004)
MEXI_BPM	Mexicali /Calexico background – PM	Regional background	Fujita <i>et al.</i> (2004)
MEXI_GEX	Mexicali surface streets, diesel and background subtracted	Gasoline vehicle exhaust-México	Fujita <i>et al.</i> (2004)
MEX_GLIQ	Mexicali gasoline composite	Liquid gasoline -México	Fujita <i>et al.</i> (2004)
MEX_GVAP	Mexicali gasoline composite -calculated headspace vapor	Gasoline fugitive emissions-México	Fujita <i>et al.</i> (2004)
CAL_GVAP	Calexico gasoline composite -calculated headspace vapor	Gasoline fugitive emissions-US	Fujita <i>et al.</i> (2004)
CAL_GLIQ	Calexico gasoline composite	Liquid gasoline-US	Fujita <i>et al.</i> (2004)
MEXI_LPG	Mexicali propane	Propane fugitive emissions-México	Fujita <i>et al.</i> (2004)
WEOzHDD1	Truck stop in South Coast Air Basin at 1-10 and 1-5 background subtracted scaled to MTBE	Diesel vehicle exhaust	Fujita <i>et al.</i> (2002)
WEOzLDV1	Average of Pasadena freeway samples in the South Coast Air Basin with background subtraction	Gasoline vehicle exhaust-US	Fujita <i>et al.</i> (2002)
CNG_J	Natural gas from Juárez	Natural gas fugitive emissions	Fujita <i>et al.</i> (2002)
Prop_E	LPG from Super energy Propane and Westex Conversion	Propane fugitive emissions-US	Fujita <i>et al.</i> (2002)
MZO26	Propane fired gas grill exhaust-México City	Propane combustion exhaust	Mugica <i>et al.</i> (1998)
CPcomp95	EPA composite consumer products 9/29/95	Consumer products	Censullo <i>et al.</i> (1996)
Painting	Surface coating operations-average (EPA 9021)	Surface coatings	Censullo <i>et al.</i> (1996)

Table III. Source composition profiles used for CMB source apportionment (expressed as weight percentages).

Species ^{a†}	Source profiles														
	MEXI_BAM	MEXI_BPM	MEXI_GEX	MEX_GLIQ	MEX_GVAP	CAL_GLIQ	CAL_GVAP	MEXI_LPG	WEOzHDDI	WEOzLDV1	CNG_J	Prop_E	MZO26	Cpcomp95	Painting
ETHA	0.0823	0.0999	0.0093	0.0	0.0	0.0	0.0	0.0915	0.0	0.0586	0.7628	0.0731	0.0073	0.0	0.0
ETHE	0.0472	0.0	0.0507	0.0	0.0	0.0	0.0	0.0	0.1374	0.0705	0.0	0.0	0.0395	0.0022	0.0
PRPA	0.0712	0.1027	0.0351	0.0	0.0	0.0	0.0	0.8095	0.047	0.0179	0.1539	0.9191	0.5579	0.1329	0.0
PRPE	0.0151	0.0073	0.0246	0.0	0.0	0.0	0.0	0.0001	0.0293	0.0359	0.0	0.0025	0.0627	0.0	0.0
ISOB	0.0063	0.0057	0.0125	0.0059	0.0622	0.0019	0.0211	0.0155	0.0193	0.0071	0.0221	0.0042	0.0719	0.4237	0.0
ACET	0.0375	0.0564	0.1299	0.0	0.0	0.0	0.0	0.0	0.0486	0.0547	0.0	0.0	0.0077	0.0	0.0
BUTA	0.0242	0.0504	0.0375	0.018	0.1368	0.0142	0.1149	0.0811	0.0183	0.0181	0.0368	0.0011	0.1882	0.0787	0.0
ISOP	0.0513	0.0732	0.1232	0.1156	0.3491	0.1316	0.42	0.0004	0.0479	0.0949	0.0127	0.0	0.0	0.0	0.0558
PNTA	0.0211	0.031	0.0343	0.0354	0.0809	0.0478	0.1154	0.0	0.0288	0.0297	0.0118	0.0	0.0	0.0005	0.0558
2,2-DMB	0.0034	0.0081	0.0185	0.0249	0.0361	0.0085	0.0131	0.0	0.0072	0.0101	0.0	0.0	0.0	0.0	0.0
2-MYP	0.0105	0.0233	0.0394	0.0582	0.0578	0.0575	0.0602	0.0	0.0164	0.0348	0.0	0.0	0.0	0.0005	0.0
3-MYP	0.0166	0.0397	0.0251	0.037	0.0327	0.0358	0.0334	0.0	0.0077	0.0212	0.0	0.0	0.0	0.0	0.0
HEXA	0.1363	0.2034	0.0237	0.0328	0.024	0.0309	0.0239	0.0	0.0	0.0152	0.0	0.0	0.0	0.047	0.0245
MECY	0.0197	0.0267	0.0109	0.0148	0.0098	0.0355	0.0248	0.0	0.0061	0.0211	0.0	0.0	0.0	0.0	0.0066
2,4-DMP	0.0055	0.0013	0.0062	0.009	0.0044	0.0277	0.0143	0.0	0.0047	0.012	0.0	0.0	0.0	0.0	0.0093
BENZ.	0.0633	0.0261	0.0389	0.0295	0.014	0.0103	0.0051	0.0	0.0152	0.0332	0.0	0.0	0.0	0.0	0.0093
2-MYH	0.003	0.0044	0.0156	0.0279	0.0093	0.0279	0.0098	0.0	0.0079	0.0164	0.0	0.0	0.0	0.0011	0.0051
2,3-DMP	0.0057	0.0048	0.009	0.013	0.0045	0.047	0.0173	0.0	0.0058	0.0188	0.0	0.0	0.0	0.0	0.0007
3-MYH	0.0122	0.0298	0.016	0.0308	0.0096	0.0293	0.0097	0.0	0.0106	0.018	0.0	0.0	0.0	0.0	0.0006
2,2,4-TMP	0.0072	0.0057	0.0238	0.0	0.0	0.0	0.0	0.0	0.0175	0.031	0.0	0.0	0.0	0.0	0.0
HEPA	0.0067	0.0034	0.0118	0.0234	0.0055	0.0183	0.0046	0.0	0.01	0.0127	0.0	0.0	0.0	0.0312	0.1318
TOLU	0.0488	0.0581	0.0789	0.1081	0.0163	0.1077	0.0172	0.0	0.0908	0.0839	0.0	0.0	0.0	0.1925	0.4173
EBEN	0.0256	0.005	0.0177	0.0283	0.0015	0.0205	0.0012	0.0	0.018	0.0161	0.0	0.0	0.0	0.0033	0.0268
MPXY	0.0135	0.0133	0.0593	0.0	0.0	0.0	0.0	0.0	0.0672	0.0659	0.0	0.0	0.0	0.0186	0.0118
STYR	0.0366	0.0	0.0008	0.0	0.0	0.0	0.0	0.0	0.0612	0.0047	0.0	0.0	0.0	0.0005	0.0001
OXYL	0.0066	0.0068	0.0229	0.0364	0.0014	0.0298	0.0012	0.0	0.0222	0.0229	0.0	0.0	0.0	0.0142	0.0436
1,2,4-TMB	0.1076	0.0438	0.0232	0.0442	0.0006	0.0376	0.0005	0.0	0.0411	0.0244	0.0	0.0	0.0	0.0	0.0055

^aSee Table I for species mnemonics.

3. Results

3.1 TNMOC Results

Results of the campaign show an average TNMOC concentration of 560 ppbC (standard deviation = 489 ppbC). Table IV presents the basic statistics for the TNMOC concentrations measured during the three monitoring periods: morning, afternoon and night. Putting into context the level of VOC present in Mexicali's ambient air, morning average TNMOC concentration obtained in Mexicali during the campaign was approximately half of the average reported morning (also 6-9 h samples) total non-methane hydrocarbons concentration reported for México City during a spring of 2003 campaign (Molina *et al.*, 2007).

Table IV. Basic statistics for TNMOC concentrations (all values in ppbC).

	Average	Standard deviation	Maximum	Minimum
Morning (N = 10) ^a	795	618	2000	100
Afternoon (N = 10)	257	129	540	110
Night (N = 9)	631	535	1500	150

^aN: number of valid data.

Results indicate that, in general, TNMOC concentrations were higher during the morning hours, followed by the nighttime and lower during the afternoon. The variation of individual chemical species tended to follow the same pattern. From a temporal perspective, Figure 3 presents the variation of the morning, afternoon and nighttime TNMOC concentrations and wind conditions (speed and direction) during the whole monitoring campaign. A valley on the TNMOC time series plot between the night of April 16 and the morning of April 20 (Saturday through Wednesday) indicates an episode of prevailing relatively low concentrations. Of note, the sample taken during the nighttime period of April 19 was invalidated due to sampling problems. Meteorological conditions during this period included winds that were on average higher than those of the previous and latter days. This condition could have favored lower concentrations by diluting the pollutants at a rate higher than the one at which they were being emitted. Figure 4 presents a scatter plot of TNMOC versus wind speed data. It can be observed that a threshold exists between wind speeds of 1 and 2 m/s above which concentrations fall below 500 ppbC; the great majority of these events occurred precisely during the April 16-20 period (Fig. 4). These findings are in line with the ~2 m/s wind speed threshold reported by Chow *et al.* (2000) and described earlier. Wind direction during the first part of the referred period was dominated by sustained southeasterly winds, while the latter part was dominated by sustained northwesterly winds. Less stable wind direction behavior was observed during the other days where winds were generally below 1 m/s. This is also in line with the conditions mentioned earlier that favor pollutants accumulation.

Given that the low-TNMOC period occurred during a weekend-weekday transition, it is possible that traffic changes could have influenced the observed concentrations. A traffic study conducted in Mexicali during June 2004 (Tejeda-Honstein *et al.*, 2005) reported that, considering the 22 most important roadways in Mexicali, any given day between Monday and Friday represents $14.6\% \pm 0.2\%$ of the total weekly traffic. Traffic on Saturdays and Sundays averaged 14.5 and 12.4% of the total weekly traffic, respectively. Thus, it is not expected that weekend-weekday traffic differences could be a major factor influencing the observed drastic changes in VOC concentrations. In addition, Tejeda-Honstein *et al.* (2005) also report a rather constant hourly traffic density profile from ~8

to ~20 h, with highest traffic occurring between 13 and 19 h. Thus daily variation in the results appears to be, again, mainly due to meteorological factors rather than possible changes in traffic.

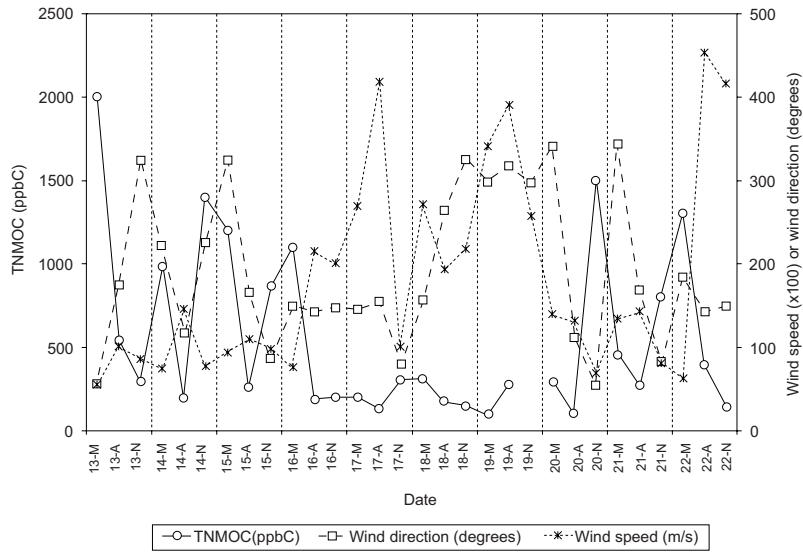


Fig. 3. TNMOC, mean wind speed and wind direction time series, from 13 to 22 April 2005 (Sampling period, M: morning, A: afternoon, N: night).

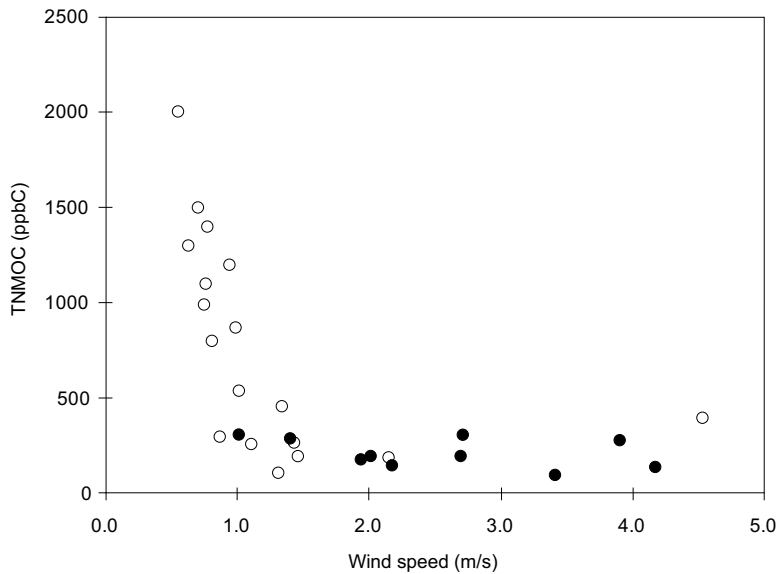


Fig. 4. Mean wind speed and TNMOC scatterplot. Filled circles represent data for the period April 16 (night) through April 20 (morning); hollow circles represent the rest of the data.

3.2 Individual species results

From a species-wise perspective, of the 54 species analyzed only 27 were detected (including TNMOC) in the ambient air samples, and in particular during the afternoon periods only four species were detected: propane, isopentane, 3-methyl hexane and styrene. Figure 5 shows the concentration distribution of individual organic compounds observed during the morning and night sampling periods; the afternoon period is not presented due to the small number of species detected. The same trend, observed for the concentration levels of the TNMOC data, was observed for the individual species and is not presented to be brief: high levels detected for the morning period, while the afternoon concentrations were the lowest detected. The species consistently with the highest concentration (on a ppbC basis) were propane, isopentane, toluene, and m,p-xylene. In addition, the aromatic species, mainly benzene, toluene, ethylbenzene (BTEX), xylenes and 1,2,4-trimethylbenzene, contributed approximately 24% of the total average of TNMOC concentration.

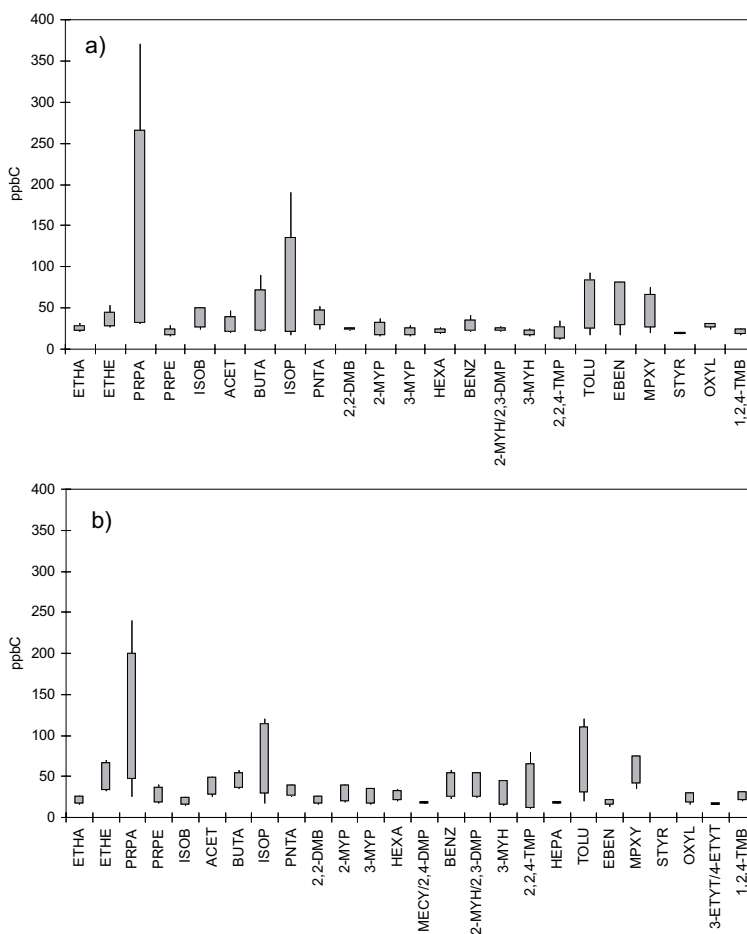


Fig. 5. Concentrations of individual organic compounds observed during two of the sampling periods: a) morning and b) night. Bars represent $\pm 1\sigma$ of the samples, while endpoints of the lines represent maximum or minimum values observed. (See Table I for definitions of species mnemonics.)

Vehicles fueled by liquid petroleum gas (LPG) are known to represent an important source of propane emissions (Duffy and Nelson, 1996; Na *et al.*, 2004). However LPG leaks in transportation lines, refueling and containers, as well as commercial and domestic consumption, have proven to be also a considerable source of propane in Mexican cities (Blake and Rowland, 1995; Gamas *et al.*, 2000; Shifter *et al.*, 2000). These last sources can be thought to be major contributors to the high propane concentrations observed, given that LPG is not used extensively in Mexicali's vehicular fleet. Regarding isopentane, it is a major component of gasoline and even though it is present in exhaust emissions, the main source of isopentane in TNMOC ambient concentrations can be related to gasoline vapors (McLaren *et al.*, 1996).

3.3 Correlation between species

A normal correlation analysis between individual species was conducted with the purpose of identifying, in a preliminary way, the sources of the pollutants identified. For that matter, species were classified in two groups: aromatic and aliphatic. For each case, the correlations between TNMOC and individual species were also considered. Correlation coefficients (R^2) were evaluated into three correlation ranges: good ($0.80 < R^2 < 1.0$), moderate ($0.50 < R^2 < 0.80$), and weak ($R^2 < 0.50$) (Devore, 2000). The strongest correlation between aromatic species was obtained for the xylenes (Table V). Moderate correlations were obtained for toluene and the xylenes, and benzene and 1,2,4-trimethylbenzene. The rest of the correlations for this chemical family were weak. The correlations between TNMOC and the aromatics indicate moderate correlations for toluene, the xylenes and ethylbenzene, while for 1,2,4-trimethylbenzene and benzene the correlation was weak.

Table V. Correlation coefficients (R^2) for aromatic species.^{a, b}

	TNMOC	BENZ	TOLU	MPXY	OXYL	EBEN	1, 2, 4-TMB
TNMOC		0.16	0.71	0.78	0.67	0.64	0.05
BENZ	10		0.45	0.46	0.38	0.29	0.79
TOLU	15	10		0.76	0.67	N.V. ^c	0.28
MPXY	10	8	10		0.95	0.40	0.06
OXYL	6	6	6	6		0.18	0.04
EBEN	6	5	5	5	5		0.35
1, 2, 4-TMB	6	6	6	6	4	4	

^aThe normal correlation coefficients are given in the upper triangle, and the number of data points correlated is given in the lower triangle. ^bSee Table I for species mnemonics. ^cNo value.

Correlation coefficients between aliphatic species are shown in Table VI. The species that present the stronger correlations are those associated typically with emissions from internal combustion engines. For example, the correlations between acetylene and ethene ($R^2 = 0.90$) and ethene and propylene ($R^2 = 0.94$) indicate a high probability that the origin of these species could be the same and could be attributed to exhaust of gasoline vehicles (Barletta *et al.*, 2002; Chan *et al.*, 2002; Na *et al.*, 2004). Other correlations that support this hypothesis are the ones between aromatic and aliphatic species, e.g. benzene-ethene ($R^2 = 0.75$) and acetylene-benzene ($R^2 = 0.84$) (Zielinska *et al.*, 1999). Even more, a consistent contribution of more than 15% of these mobile emissions tracers (i.e., ethene, acetylene, propylene and benzene) to the TNMOC concentration indicates major contribution from mobile sources.

Table VI. Correlation coefficients (R^2) for aliphatic species.^a

	TNMOC	ETHE	PRPE	ACET	ETHA	PRPA	ISOB	BUTA	ISOP	PNTA	2,2-DMB	2-MYP	3-MYP	HEXA	2-MYH /2,3-	3-MYH	2,2,4-TMB
TNMOC		0.18	0.12	0.06	0.02	0.64	0.02	0.04	0.62	0.23	0.41	0.05	0.83	0.16	0.64	N.V.	0.44
ETHE	10		0.94	0.90	N.V.	0.05	0.23	0.07	0.06	0.04	0.12	0.47	0.68	0.79	0.45	0.36	0.29
PRPE	10	10		0.82	N.V.	0.09	0.19	0.06	0.04	0.02	0.15	0.45	0.70	0.79	0.50	0.38	0.28
ACET	8	8	8		0.22	0.01	N.V.	0.75	0.63	0.38	0.93	0.78	0.89	0.66	0.45	0.51	0.38
ETHA	8	8	8	7		0.10	0.72	0.56	0.51	0.53	0.83	0.30	0.02	0.07	0.02	0.07	0.08
PRPA	21	10	10	8	8		0.02	0.01	0.35	N.V.	0.38	0.01	0.51	N.V.	0.01	0.06	0.01
ISOB	6	6	6	5	6	6		0.60	0.83	0.84	0.44	0.08	0.04	0.03	0.14	0.01	0.20
BUTA	10	10	10	8	7	10	6		0.93	0.49	0.41	0.69	0.13	0.19	N.V.	0.17	N.V.
ISOP	17	10	10	8	8	16	6	10		0.65	0.40	0.62	0.24	0.19	N.V.	0.14	0.01
PNTA	10	10	10	8	8	10	6	10	10		0.67	0.31	0.21	0.11	N.V.	0.27	0.03
2,2-DMB	6	6	6	4	5	6	5	6	5	6		0.48	0.25	0.35	0.04	0.27	N.V.
2-MYP	9	9	9	7	7	9	5	9	9	9	5		0.80	0.70	0.53	0.58	0.32
3-MYP	8	7	7	5	5	7	5	7	8	7	6	6		0.84	0.84	0.91	0.61
HEXA	9	9	9	8	7	9	6	9	9	9	5	8	6		0.49	0.36	0.24
2-MYH/2,3-	6	6	6	5	6	6	5	6	6	6	5	5	5	6		0.92	0.81
3-MYH	7	5	5	5	5	5	5	5	6	5	4	4	4	5	4		0.83
2,2,4-TMB	8	8	8	7	7	8	5	8	8	8	5	7	6	8	6	4	

^aSee notes in Table V for details.

3.4 Source-receptor modeling

CMB was applied to valid ambient VOC samples that were obtained at the UABC monitoring site in Mexicali. VOC concentrations obtained in the field campaign were reported by the analytical laboratory in ppbC, and were converted to $\mu\text{g}/\text{m}^3$ at local temperature and pressure conditions during the sampling period to be consistent with the source profiles used.

When using receptor models, the relative proportions of chemical species must change little between the source and the receptor, otherwise, this fundamental assumption in the formulation of the receptor modeling would be violated. VOC are typically oxidized in the lowest two kilometers of the troposphere and can have lifetimes ranging from minutes to several months. Thus, in CMB calculations only species with lifetimes in the atmosphere greater than that of toluene (~9 hours during the summer) are recommended as fitting species in samples from urban source areas (Fujita *et al.*, 2004). An exception to this is isoprene. This species is included as a fitting species despite its high reactivity because it serves as a marker for biogenic emissions. Selection of fitting species in our application was based on recommendations by Fujita *et al.* (2004). For the particular case of the afternoon samples, no source apportionment was attempted since not enough data were available (i.e., not enough species were identified in the samples to apply the CMB model).

Acceptable fits for the source profiles used were achieved for only 13 samples: seven morning samples (April 13-16, 18, 21 and 22) and six nighttime samples (April 13-15, 17, 21 and 22). The other 20 samples did not have enough species reported to complete the requirements of the receptor model and calculate the source contributions. Figures 6 and 7 show the source contributions to TNMOC estimated in this study for the morning and night periods, respectively, in percents of the measured concentration. The most significant source for the morning period was gasoline mobile sources (exhaust emissions plus fugitive gasoline emissions); it represents, on average, 42% of the contributions for the morning period, except for April 18 (a Monday) where the most important source were consumer products. For the night period, the most significant source was again gasoline mobile sources (~70% average contribution). However, it is interesting to note that for the morning

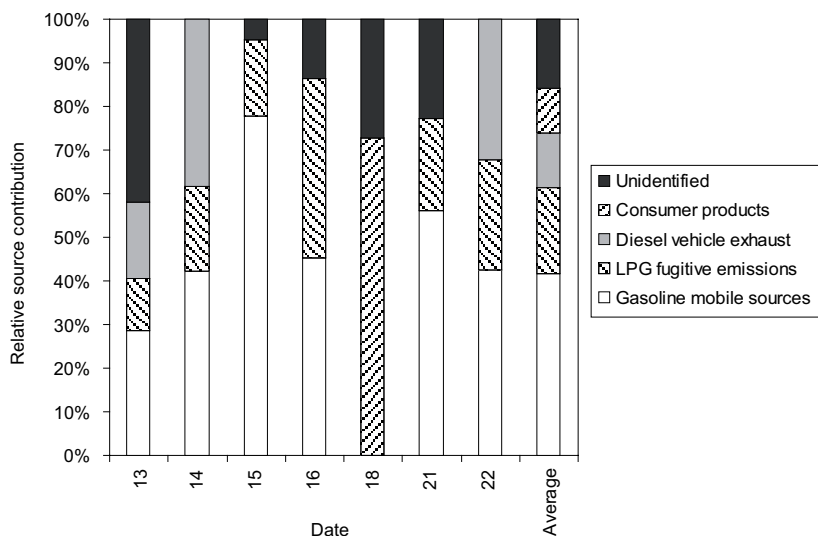


Fig. 6. Source contributions to ambient TNMOC: morning periods, April 2005.

samples CMB got a better fit using Mexicali-derived profiles (exhaust, fugitive and composite emission profiles), while for the night samples CMB got a better fit using US-derived profiles. Only in one day (April 13), CMB got a better fit in the night sample using the profile obtained from Mexican vehicle exhausts. The “Mexican gasoline vehicle exhaust” profile (MEXI_GEX) was derived from '90s fleet. The result might be an indication that the current fleet has modernized and has become similar to the US fleet from the '90s. Another aspect to note is that on April 17, a Sunday, CMB estimates that the main source affecting the site (~50% contribution) was LPG fugitive emissions. This can be an indication of the strong commercial activity from restaurants and other food establishments during that day, as well as a decrease in traffic. In addition, recall that during the April 17-20 period rather low VOC concentrations were obtained; some of the day-to-day variation observed during this period could be a result of such condition.

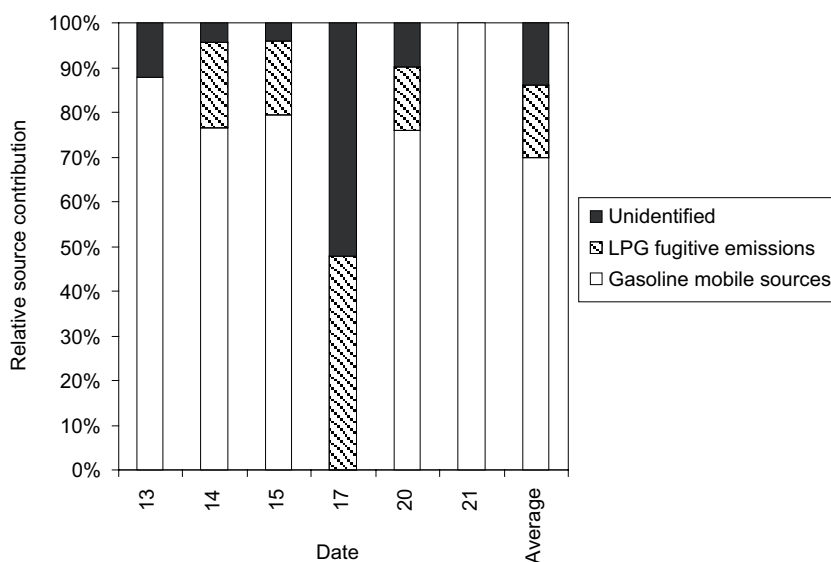


Fig. 7. Source contributions to ambient TNMOC: night periods, April 2005.

4. Discussion

4.1 VOC observations

Plausible origins of the VOC detected in monitoring site can be further explored analyzing the relationship between VOC and CO concentrations, since CO can typically be associated with mobile emissions (exhaust emissions; Barletta *et al.*, 2002). A moderate correlation ($R^2 = 0.66$) was found between average CO and TNMOC concentrations (Fig. 8). CO concentrations used were those registered also at the UABC site, and the average periods were the same as the VOC sampling periods used. Higher correlations were obtained for the nighttime data ($R^2 = 0.93$) and the afternoon data ($R^2 = 0.75$). Correlation for the morning data resulted in $R^2 = 0.61$. This is an indication that pollutants sampled at the UABC site have a high probability of having their source in combustion processes, and particularly, mobile sources, across all times.

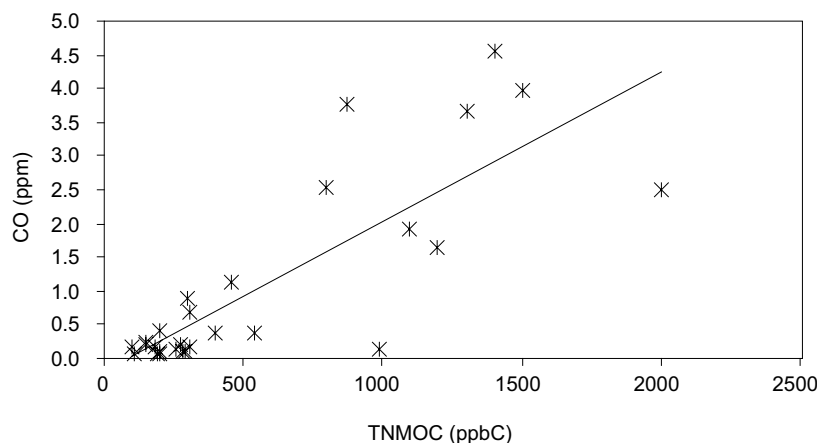


Fig. 8. Correlation between average TNMOC and CO concentrations.

Vehicle exhausts typically contain aromatic compounds, in particular benzene, toluene and xylenes. However, toluene and xylenes are also found in solvent emissions while benzene is not (Na *et al.*, 2004, 2005). This explains the moderate correlations observed among benzene and the rest of the BTEX species, i.e. toluene and xylene emissions cannot be completely attributed to mobile sources. Nonetheless, the average ratio between benzene (B) and toluene (T) concentrations can give further insight into the characteristics of the main source of pollutants at the site. B:T ratios of 0.41 and 0.42 for the morning and night periods, respectively, were obtained. With this, it can be inferred again that vehicle emissions, and in particular those from non-catalytic vehicles, were the major sources of TNMOC in Mexicali (Barletta *et al.*, 2002; Chan *et al.*, 2002). The ethene-acetylene ratio is also a well-known indicator to distinguish between emissions from catalytic and non-catalytic converter vehicles. Emissions from non-catalytic converter units usually have an ethene-acetylene ratio close to unity, while catalyst-equipped vehicles have a ratio of 3 or greater (Duffy *et al.*, 1996; Sagebiel *et al.*, 1996; Barletta *et al.*, 2002). For the ambient air samples obtained in this study, ethene to acetylene ratios of 0.82 and 0.79 were obtained for the morning and night periods, respectively, confirming that non-catalytic converter vehicles constitute the main TNMOC sources in Mexicali. This is in line with the fact that Mexicali's vehicular fleet is quite old and that there is evidence that a majority of the vehicles have tampered pollution control devices. For example, in the study of GEBC (1999) it was detected that 95% of the vehicles were from 1990 or older.

Of particular interest is also to compare the results obtained here with those reported in past studies where VOC concentrations and possible sources were also analyzed at the same monitoring location. Zielinska *et al.* (1999) analyzed VOC obtained from ambient air samples in Mexicali during a field campaign in the summer of 1997, and also concluded that motor vehicle emissions were the main source of these pollutants. Fujita *et al.* (2004) conducted a field campaign in the summer of 1997, used source apportionment techniques to analyze the data, and concluded that gasoline vehicles were consistently the largest contributor to ambient total non-methane hydrocarbons (TNMHC). Table VII shows a comparison of pollutant concentrations in Mexicali between the three studies. It can be noted that the ethene-acetylene ratio has increased from 0.62 in 1997 to 0.82 in 2005. This can be an indication of a slight decline in the relative contribution of

non-catalytic converter vehicles to the total emissions. Also, consistently the three studies report a xylenes-benzene ratio close or greater than 2, which indicates the influence of fresh emissions at the site (Roberts *et al.*, 1997). Thus, results suggest that the main source of VOC in downtown Mexicali continues to be gasoline-powered vehicles from nearby sources.

Table VII. Comparison of pollutant concentrations and relevant ratios obtained from two past studies and this study for the same monitoring site in downtown Mexicali.

Time period (horas)	1997 ^a		1999 ^b		2005 ^c		
	6-9	13-16	6-9	13-16	6-9	13-16	20-23
NMHC	1358.1	256.6	693	250			
TNMOC					795	257	535
Ethene/acetylene	0.62	0.62	0.62	0.7	0.82		0.78
Xylenes ^d /benzene	2.7	2.5	2.23	1.81	1.81		2.12

^aZielinska *et al.* (1999); ^bFujita *et al.* (2004); ^cThis study; ^dSum of *o*- and *m*, *p*-Xylene.

Finally, a correlation analysis between early morning TNMOC measurements and O₃ concentrations can give some insight on the influence of the VOC emissions in the generation of this secondary species. In general, relatively weak to weak correlations between early morning TNMOC measurements at the UABC site and O₃ at the same site and at a monitoring site in Calexico, CA were obtained. The highest correlations were for average O₃ at UABC ($R^2 = 0.49$) and peak O₃ at Calexico ($R^2 = 0.37$) (Fig. 9). TNMOC versus peak ozone at UABC yielded an R^2 of 0.21, and for average O₃ at UABC during the afternoon monitoring period yielded an R^2 of 0.25. TNMOC at UABC versus average afternoon O₃ at Calexico resulted in an R^2 of 0.30. These results imply that TNMOC emitted in downtown Mexicali contribute to the chronic pollution of O₃ in Mexicali, and are one of the possible causes of ozone peaks in Calexico which is far enough for the pollutants to react. A detailed source-receptor analysis is needed to determine more accurately the impact of the transport of these emissions.

4.2 Source-receptor results comparisons

The CMB receptor model was used to determine the contributions of sources in Mexicali to ambient VOC at the UABC site, for the period April 13 to 22, 2005. In a past source apportionment study by Fujita *et al.* (2004) that used data obtained at the same site but for different period (September 22 to 27, 1999), specific source profiles explained 75% of the mass on average while the rest was attributed to unidentified sources. In our study, on average, 86% of the mass was explained by the source profiles used. In addition, Fujita *et al.* (2004) estimated that gasoline vehicles were consistently the largest contributor, accounting for about 40% of ambient TNMOC during the morning periods, followed by natural gas of LPG sources with 18% contribution, and negligible contributions from other sources. In our study, gasoline mobile sources contribution was estimated at 56%, followed by fugitive LPG emissions (18%), diesel vehicles (6), and consumer products (5). In the Fujita *et al.* (2004) study, the “background source” did not showed up as a contributor in the morning periods, and for the afternoon periods it was assigned a small contribution (1.5 to 4.4%). In our study the background source was not an important source, probably indicating significant changes in the source profiles of surroundings sources in the last six years.

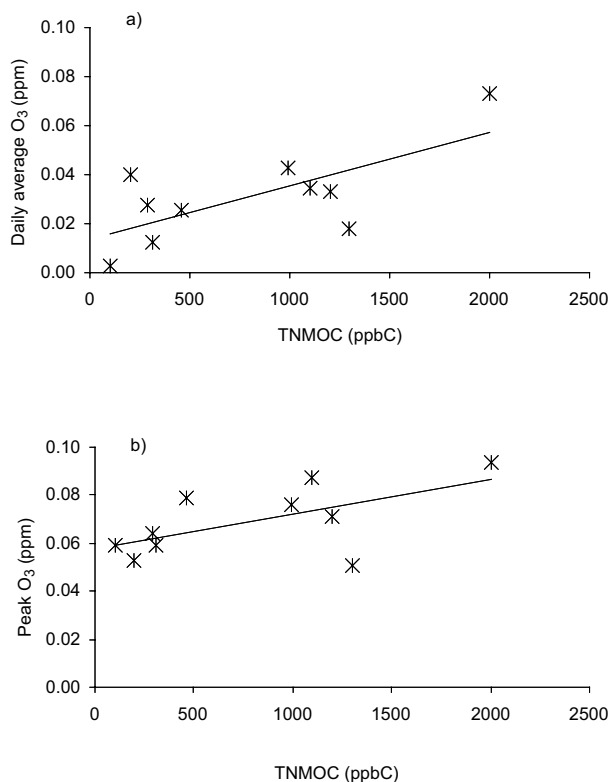


Fig. 9. Correlation between early morning TNMOC in UABC and a) daily average O₃ concentration in UABC, and b) peak O₃ concentration in Calexico.

The previous figures can be compared to the relative contribution of mobile sources to the total hydrocarbons or VOC emissions reported in emissions inventories for the city or municipality of Mexicali. For example, the 1996 official inventory for the city (GEBC, 1999) indicated that 60% of the total emitted hydrocarbons came from mobile sources (70% if emissions from fuel transportation and storage activities are included), while 15% came from LPG sources; 35% of the emissions came directly from light-duty vehicles. In more recent inventory efforts, data from base years 1999 (ERG *et al.*, 2004) and 2004 (Tejeda-Honstein *et al.*, 2005) estimated ~95% contribution of gasoline-powered vehicles to total mobile VOC emissions, the rest being diesel sources. According to the CMB results obtained here, ~90% of the mobile VOC emissions had their source in gasoline sources and the rest in diesel sources. Even though the inventories are from different years and different methodologies were used to derive them, the contribution of mobile sources and LPG sources appear to be in the same range proving consistency in the trends observed by the different studies.

Comparing the results obtained in our CMB application with others, it can be seen that the source contributions for VOC species in downtown Mexicali resembles that of other major cities. For example, Brown *et al.* (2007) report that in Los Angeles, CA mobile-related emissions accounted for 70-80% of the fitted contribution, while solvent use accounted for 17% or less of the fitted contribution. In a study conducted in Beijing, China in August of 2005 (Song *et al.*, 2007), source

contributions to ambient VOC observations were as follow: 52% gasoline-related emissions, 20 petrochemicals, 11% LPG, 5% natural gas, 5 painting, 3 diesel vehicles, and 2 biogenic emissions. Jorquera and Rappenglueck (2004) estimated that near 70% of ambient VOC concentrations observed in Santiago, Chile were due to mobile sources, ~11% were due to LPG losses, and ~6% to diesel exhaust. Finally, CMB application to data obtained in México City (Vega *et al.*, 2000; Mugica *et al.*, 2002) resulted in contributions in the range of 50 to 64% from motor vehicle exhaust, 15-25% from LPG sources, and 9-12% from asphaltting operations. In all previous cases, the receptor sites were in a great majority located in residential or commercial areas with important traffic influence, as was the case for the UABC site. In a review paper by Watson *et al.* (2001), it was reported that, considering the results of 103 references, gasoline-related mobile emissions (exhaust plus evaporative and fugitive emissions) contributed in general to up to 50% or more of the ambient VOC measured in most of those studies.

5. Conclusions

A monitoring campaign was conducted in April of 2005 to quantify the levels of VOC at a site located near the downtown district of the border city of Mexicali. TNMOC concentrations obtained were higher in the early morning samples, followed by the nighttime samples and lower for the afternoon samples. This same pattern was followed by the individual species detected. The species registered with the highest concentrations (on a ppbC basis) were propane, isopentane, toluene and the xylenes. The presence of propane and isopentane can indicate an important contribution of LPG-related source as well as gasoline evaporation. However, the main source of the organic species sampled appears to be vehicle exhaust emissions, and in particular vehicles with no catalytic converter. This is supported by the ethene-acetylene ratios obtained (~0.8), and the high correlation between ethene, propylene and benzene. This hypothesis is also supported by a benzene-toluene ratio of ~0.4, and a strong correlation between TNMOC and CO measurements obtained at the same site. A xylenes-benzene ratio close to 2 indicates influence of nearby sources to the observed ambient VOC concentrations, most probably vehicular traffic and commercial activities given the location of the monitoring site. In addition, source-receptor modeling results also indicate that mobile sources (56%) and fugitive LPG sources (18) can be pointed out as main contributors to the observed VOC at the UABC site. In general, main sources of VOC in downtown Mexicali appear to have not changed in the past ten years given the results of two other studies conducted in 1997 and 1999, though the increase in the ethene to acetylene ratio might indicate slight decline in the relative contribution of non-catalytic converter vehicles to the total emissions. The results obtained in this study can help further efforts on assessing the effectiveness of air quality improvement programs of the region, and help orient future policies. Also, results can serve to more detailed top-down emissions inventory validation studies, such that those inventories can be used with more confidence in more detailed air quality modeling efforts.

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