Artículo

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Hazardous Volatile Organic Compounds in Vehicle Emissions from Reformulated Gasolines

J. Luis Jaimes-López,[a]* Julio Sandoval-Fernández,[b] Ángel Zambrano-García,[a] J. Luis Arriaga-Colina,[a] Emmanuel González-Ortiz, [a] Martín Llanos-Plata,[c] and Uriel González Macías[a]

[a] Dirección Ejecutiva de Investigación y Posgrado, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, México 07730, D. F. Tel.: (55) 7195-6756; fax: (55) 9175-6599. jjaimes@imp.mx

[b] Escuela Superior de Ingeniería Química e Industrias Extractivas, SEPI, Instituto Politécnico Nacional. Unidad Profesional Adolfo López Mateos, Zacatenco, Edif. 8, 2º piso. México, D. F.

[c] General Motors de México, S. de R.L. de C.V., Industria Minería No. 700, Col. Zona Industrial, Toluca, Edo. de México, C.P. 50000. México.

Abstract: Eleven reformulated gasoline fuels (RFGs) were evaluated by CVS tests on a chassis dynamometer to compare their effect on vehicle emissions of toxic volatile organic compounds (HVOCs). Fuel formulations were prepared by varying their contents of aromatics, benzene, olefins, sulfur and Reid vapor pressure. Two vehicles differing in combustion chamber and catalytic converter technologies (Euro 4 and Tier 1) were used. The CVS tests were conducted with an urban cycle designed to represent the typical driving conditions at the Mexico City Metropolitan Area (MCMA). It was used Electre analysis using three weight factors. Using a new gasoline with reduced contents of aromatics and olefins, preferentially below 19% and 8%, respectively, would potentially have a positive impact on the local air quality. This new gasoline should have a composition similar to F6, F3 or F13, but lower in sulfur content.
Key words: Toxic Compounds, vehicle emissions, reformulated gasoline, CVS tests, air quality

Resumen: Se evaluaron 11 Gasolinas Reformuladas (GRFs) por medio de pruebas CVS en un dinamómetro de chasis, para comparar su efecto sobre las emisiones de compuestos orgánicos volátiles tóxicos (COVTs), las cuales fueron preparadas variando el contenido de aromáticos, benceno, olefinas, azufre y presión de vapor Reid (PVR). Se usaron dos vehículos con tecnologías diferentes en la cámara de combustión y convertidor catalítico (Euro 4 y Tier 1). Las pruebas CVS se realizaron con el ciclo urbano, diseñado para representar las condiciones de manejo en el Área Metropolitana de la Ciudad de México (AMCM). Se utilizó el método Electre con tres factores de peso. Usando una nueva gasolina con contenido reducido de aromáticos y olefinas, preferentemente debajo de 19% y 8%, respectivamente, podría potencialmente tener un impacto positivo sobre la calidad del aire local. Esta nueva gasolina debería tener una composición similar a F6, F3 o F13, pero con un contenido más bajo en azufre.
Palabras Clave: Compuestos tóxicos, emisiones vehiculares, gasolinas reformuladas, pruebas CVS, calidad del aire.

Introduction

Recent studies on the presence of hazardous volatile organic compounds (HVOCs), such as benzene, ethyl benzene, *m-/p*-xylene and toluene, in the blood of Mexico City inhabitants indicate a relatively high exposition to these air pollutants [1,2]. Air pollution by HVOCs use to be high in urban/industrial areas with heavy consumption of petroleum products and weak pollution controls. Most of the anthropogenically emitted air VOCs in the Mexico City Metropolitan Area (MCMA) derive from intensive use of petroleum products like gasoline, diesel, liquefied petroleum gas (LPG), solvents and asphalt. Gasoline vehicle exhaust and LPG use are identified as the major local sources of air VOCs [3,4]. About 20% (102 ton) of the total VOCs released into the MCMA air in 2004 belonged to the hazardous type (HVOCs), and 25% of them (25.6 ton) derived from motor vehicles [5]. Thus, controlling for gasoline vehicle emissions is a practical way to further reduce the exposure of the local population to HVOCs and other air pollutants. This study is a contribution to the quest for developing cleaner fuels for the MCMA to reduce both human and environmental health risks.

The VOCs are a large group of chemicals composed basically by carbon and hydrogen. Some of them also contain bromine, chlorine, fluorine, nitrogen, oxygen or sulfur. Although many VOCs are innocuous, those known as hazardous VOCs (HVOCs) are toxic at relatively low doses (e.g. formaldehyde and toluene), carcinogenic (e.g. 1,3-butadiene and benzene) or precursors of secondary air pollutants like ozone [6]. Adverse effects from HVOCs depend on their environmental concentration, duration of exposure, compound strength or toxicity and individual sensitivity. Effects in humans range from minor, like eye irritation, and debilitating (asthma worsening) to fatal, including cancer. Some HVOCs also are known or suspected to cause immunologic, neurological, reproductive (reduction of fertility) and respiratory injuries. Consequently, they are listed as hazardous air pollutants (HAPs) by the American Environmental Protection Agency [7] and similar agencies in other countries.

Air monitoring has shown that total VOCs levels have declined consistently at the MCMA since the early 1990's, but they are still high compared to other large cities [8]. This decline is roughly consistent with reductions in VOCs emissions rates from local sources, which are mainly attributed to the renewal of the vehicle fleet, now equipped with better emission control systems, and quality improvements in gasoline fuels [5]. Nevertheless, the annual emissions of total VOCs at the MCMA were still over 500 thousand ton in 2004, compared, for instance, to 356 ton in Los Angeles, 415 ton in Minnesota and 268 ton in Washington, D.C. [9-11]. The most abundant air VOCs in the Mexican capital were propane and butane [12], and Blake and Rowland [13] suggested that leakages of these compounds from LPG usage may explain the high local levels of ozone. However, recent evidence indicates that neither propane nor butane could be responsible for such massive ozone formation because of their low photochemical reactivity [14]. Information on vehicle tailpipe emissions of HVOCs at the MCMA is very limited. A previous work estimated the HVOCs emissions from nearly 3.5 million gasoline vehicles in 3,130 ton/year [15]. These authors considered only benzene, 1,3-butadiene, formaldehyde and acetaldehyde, and reported increased emissions of these compounds with vehicle age and traveled distance, as well as a 22% reduction in benzene emissions from using Premium gasoline compared to the unleaded regular one.

There are two major successful technological strategies to reduce emissions of HVOCs and other air pollutants from mobile sources: engine physical improvements and fuel reformulation. Whereas vehicle improvements look for more efficient fuel combustion; i.e., a higher ratio between traveled distance and spent fuel volume, as well as conversion and filtering of the remaining pollutants; fuel reformulation restricts the formation of hazardous air pollutants by changing the chemical composition of fuels [16-18]. Gasoline is a complex mixture of mainly saturated and unsaturated hydrocarbons. The unsaturated ones, such as aromatics (e.g, benzene) and olefins (e.g. 2,2,4-trimethylpentane), are more reactive and likely to cause evaporative and combustion toxics. Sulfur is another natural component of gasoline which makes vehicle exhaust emissions to be toxic for humans and wildlife, and even corrosive for catalytic converters. Since emissions of less reactive and less toxic compounds are sought when a gasoline is reformulated, it is important to anticipate the expected chemical changes in the vehicle exhaust, and the extent to which they may affect formation of secondary pollutants and the human health. Such information can be obtained by experimenting with different reformulated gasoline fuels (RFGs) under real or proxy environmental conditions [19].

Here we report the results from controlled experiments comparing vehicle tailpipe emissions of HVOCs from two vehicles powered with 11 different RFGs. These vehicles represented two technologies: Tier 1, which is locally predominant [20] and Euro 4, which will soon enter into the local market. The RFGs with lower production of HVOCs in the vehicle emissions, and thus with lower potential toxicity, were selected by a multicriteria decision making technique (Electre method). In addition, new MCMA data on air HVOCs collected in May 2002 are provided and discussed.

Methods

VOCs monitoring in ambient air. Levels of VOCs in early morning air (06:00 to 09:00 h) were determined at six MCMA sites differing in anthropogenic emission sources: Xalostoc (XAL), Tlalnepantla (TLA) and Instituto Mexicano del Petróleo (IMP), located within or near major industrial areas in the North of the City; La Merced (MER), a commercial and services area near downtown; Cerro de la Estrella (CES), a site representing mixed residential and industrial activities in the southeast sector; and Pedregal (PED), a predominantly residential area in the southwest of the MCMA (Figure 1). Air sampling was done simultaneously from April 30th to May 16th, 2002, with precleaned stainless steel canisters. Because stable atmospheric conditions prevail during the early morning, the VOCs concentrations can be assumed to represent mostly within site emissions [4]. Seven samples per site were analyzed, except for Tlalnepantla (four), by gas chromatography at the IMP Atmospheric Chemistry Laboratory, utilizing method T-014 [21]. More than 280 VOCs species were detected, but only the hazardous and most abundant are reported herein.

Vehicle emissions tests. Contents of HVOCs in vehicle tailpipe emissions produced by 11 reformulated gasoline fuels (RFGs) were determined in exhaust samples from chassis dynamometer tests (Horiba ECDM-48 equipped with a constant volume sampler, CVS-45). A vehicle with Tier 1 technology and one Euro 4 were tested in the IMP Vehicle Emissions Laboratory from November 15th to December 2nd, 2001; and from March 19th to April 18th, 2002. All tests were done with the standardized Mex Urban cycle designed to represent the “typical” driving in Mexico City [22]. One fuel a day was tested per vehicle. Tests systematically started with the Euro 4 around 06:00 am and followed by the Tier 1 at 07:15 am. Fuels were shifted between vehicles in the next day. The major

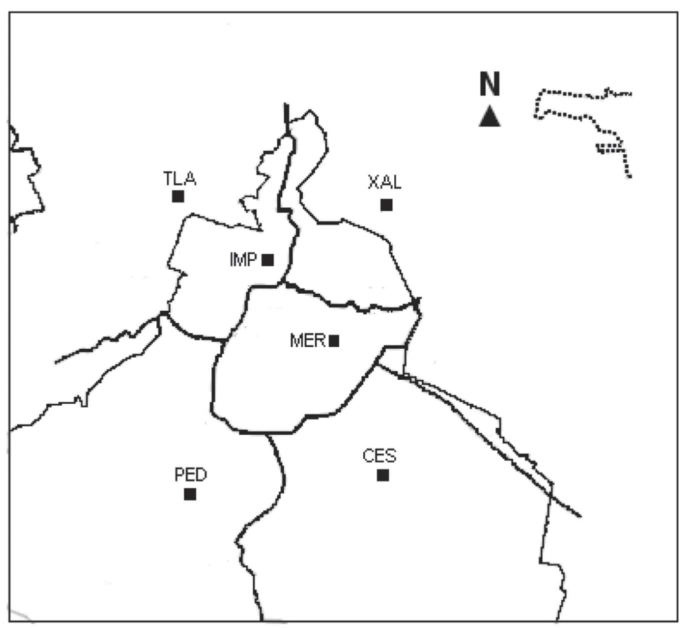

Fig. 1. Sampling sites in the MCMA (encircled). Cerro de la Estrella (CES), Instituto Mexicano del Petróleo (IMP), Merced (MER), Pedregal (PED), Tlalnepantla (TLA) and Xalostoc (XAL).

characteristics of the tested RFGs (F1-F13) and a reference gasoline similar to the one currently used in Mexico City are listed in Table 1 (Magna). They differed mainly in contents of aromatics, benzene, olefins, sulfur and Reid vapor pressure (RVP). Fuels were reformulated to meet with current Mexican Normativity.

Contents of VOCs in the vehicle emissions were determined at the IMP Motoquimia Laboratory by method TO-14 [23] using a chromatograph fitted with flame ionization detector (Agilent technologies, model 6890). Carbonyls (aldehydes and ketones) were sampled with dinitrophenyl hydrazine cartridges and analyzed by high performance liquid chromatography (HPLC, Agilent technologies, model 6890), according to method TO-11A [24].

Fuel ranking. Since it would be desirable that fuels offered in the MCMA produce lower amounts of hazardous pollutants in the vehicle exhaust, the experimental emission data were subjected to Electre analysis, a common technique to rank alternatives in decision making problems. In this case, a matrix with *m* alternatives (RFGs) and *n* attributes (emitted HVOC species) was processed through concordance and discordance concepts [25]. Prior to Electre analysis, this matrix was standardized by column to 1-100 values, and assigning 100 to that RFG producing the lowest amount of a compound. The remaining values were obtained by lineal interpolation. This matrix was processed according to:

$$C_{a/b} = \left[\sum_{j=1}^{m} w_j \left(u_{aj} / u_{bj} \right) \right] / \sum_{j=1}^{m} w_j$$

Where:

$C_{a/b}$ = Concordance of alternative *a* respect to alternative *b*.
w_j = Weighting factor for each evaluation criterion
u_{aj} = Score or value of alternative *a* for each criterion
u_{bj} = Score or value of alternative *b* for each criterion

Discordance is defined as:

$D_{a/b}$ = (Maximal opposition difference between alternatives *a* and *b*) / *d*

Where:

$D_{a/b}$ = Discordance between alternatives *a* and *b*
d = Maximum opposition value

Electre allows us weighting each criterion (HVOC species) according to its importance in the problem context, toxicity in this case. Three data matrices were submitted to Electre analysis: one unweighted ($W_0 = 1$), and two weighted by compound toxicity indexes for noncancer effects (herein W_1) and for integrated total hazard value (herein W_2), according to Scorecard [26]. These weighting factors are shown in Table 2. Scorecard [26] defines a noncancer risk score for a chemical released to air as the hazard index resulting from one pound release of that chemical to air normalized by the hazard index for a one pound release of toluene to air. Thus, W_1 units are pounds of toluene equivalents. The total hazard value used herein (W_2) is the IRCH value (Indiana Relative Chemical Hazard Ranking System), which is composed by a variety of measures relating

Table 1. Physicochemical properties of tested RFGs.

TEST	RF	F1	F2	F3	F4	F5	F6	F8	F9	F10	F12	F13
SG, 20/4	0.73	0.73	0.73	0.74	0.73	0.73	0.72	0.73	0.75	0.74	0.73	0.74
RVP, psi	8.8	6.9	6.7	6.7	6.7	8.3	10.8	10.9	11.0	6.4	6.4	7.7
RON	91.1	91.7	91.7	91.0	91.0	91.7	90.9	91.8	93.19	91.6	91.4	91.0
MON	83.9	83.5	83.7	83.9	83.5	84.3	84.7	83.7	83.0	84.0	84.0	83.9
(RON+MON)/2	87.5	87.6	87.6	87.5	87.7	87.7	87.9	87.4	88.1	87.8	87.7	87.5
IET, °C	38.0	40.8	38.9	41.6	43.7	37.6	33.3	34.3	34.9	37.8	37.7	36.4
a 10%, ºC	70.6	71.5	68.8	67.5	62.0	57.0	45.1	51.6	48.3	65.1	69.8	57.6
a 50%, °C	115	108	106	105	109	104	107	105	106	103	107	103
a 90% , °C	172	164	166	164	166	163	165	165	168	178	161	162
EET, °C	207	203	205	202	203	205	201	203	204	203	198	200
AROMATICS, % vol	27.9	17.2	20.7	18.7	21.8	19.9	18.0	22.6	37.3	18.2	17.1	23.6
BENZENE, % vol	1.2	0.9	1.4	0.9	1.4	1.4	1.0	1.4	1.4	0.6	0.5	0.2
OLEFINS, % vol	12.5	7.2	7.5	6.6	6.1	6.9	7.2	15.2	15.4	2.8	8.5	9.1
OXYGEN, % vol	0.3	0.0	1.0	2.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.3
SULFUR, ppm	720	440	410	400	330	420	370	415	400	90	805	27

RF, reference gasoline; F1…Fn , reformulated fuels; SG, specific gravity; RON, research octane number; MON, motor octane number; IET, initial ebullition temperature; EET, end ebullition temperature.

Table 2. Inhalation (W_1), total hazard (W_2) and carcinogenicity (W_3) factors used as toxicity weighting factors for HVOC in tailpipe vehicle emissions. Data source: Scorecard (2007).

HVOCs	W_1	W_2	W_3
Benzene	8.1	48	1
Ethylbenzene	0.14	24	-
p-xylene	0.53	23	0.53
Naphthalene	18	29	-
o-xylene	0.54	26	-
Toluene	1	29	-
1,2-Dibromoethane	1500	39	6.2
1,2-Dichloroethane	4.2	39	2.5
Chlorobenzene	0.95	32	-
p-Dichlorobenzene	9.2	33	1.4
Trichloroethylene	1	41	-
n-Hexane	0.03	31	-
1,3-Butadiene	2.2	41	0.53
Styrene	0.08	33	-
MTBE	0.0045	29	0.03
Formaldehyde	16	43	0.02
Acetaldehyde	9.3	38	0.01

a chemical's toxicity and physicochemical properties such as vapor pressure, tendency to bioaccumulate, corrosivity, and so on [26].

Results and discussion

HVOCs in ambient air. Table 3 summarizes the average concentration of total VOCs and specific HVOCs in morning ambient air during the monitoring period. Levels of total VOCs were significantly higher at the two heavily industrialized and densely populated sites in the north of the MCMA, Tlanepantla (TLA) and Xalostoc (XAL), and lower at the residential Pedregal (PED) in the southwest. Merced, IMP and CES had intermediate total VOCs levels, but these were twice as higher as for PED. This north to southwest difference is consistent with previous reports on these pollutants in the MCMA, e.g. [8]. These early May (2002) data were 35-39% lower than March levels reported in morning ambient air for previous years [8]. This could be explained either by the usually higher ambient temperature during May, which promotes dilution of air pollutants at earlier hours in the morning, or by actual decreases of vehicle emissions in recent years. Arriaga and colleagues [8] already observed a significant declining trend for total VOCs for the Xalostoc site. Such a decline, estimated in 21% for the period 1994-2004, has been attributed to the renewal of the local vehicle fleet, to the use of better emission control systems and improvements in the quality of gasoline [5].

On average, the HVOCs represented 19 to 28% of the total VOCs present in ambient air (Table 3). Levels of HVOCs also were higher at TLA and XAL (> 700 ppbC), intermediate at Merced, IMP and CES (> 500 ppb C), and lower at PED

Table 3. Average HVOCs concentration (ppbC) in morning ambient air (6:00-9:00 am) at six sites in Mexico City. Sampling period: April 30th to May 15th, 2002. Only compounds with concentration above the detection levels were included. N = 7, except for TLA (4). Compare data by row: values with the same letter did not differ (Tukey mean comparisons after ANOVA, $p < .05$).

HVOCs	TLA	XAL	MER	CES	IMP	PED
Benzene	35.6 a	30.7 ab	29.7 ab	28.5 ab	23.0 ab	11.9 b
Ethylbenzene	36.4 a	27.1 a	21.9 ab	26.3 a	22.4 ab	8.5 b
m-/p-xylene	125.6 a	94.8 a	67.5 ab	79.0 ab	74.2 ab	25.7 b
Naphthalene	3.5 ab	4.0 ab	5.5 a	4.6 ab	3.7 ab	1.9 b
o-xylene	45.1 a	36.2 a	27.2 ab	29.8 ab	28.2 ab	10.1 b
Toluene	177.4 ab	262.0 a	138.5 ab	151.6 ab	147.9 ab	51.8 b
1,2-dichloroethane	12.7 ab	12.0 a	12.3 a	11.5 ab	9.1 ab	4.4 b
Chlorobenzene	2.5 ab	3.6 a	3.6 a	3.1 ab	2.8 ab	1.1 b
p-dichlorobenzene	3.1 ab	4.5 ab	7.9 a	4.0 ab	4.7 ab	1.7 b
Perchloroethylene	7.0 a	3.1 ab	1.7 b	1.1 b	3.3 ab	0.4 b
Trichloroethylene	3.3 ab	4.8 a	5.3 a	4.7 a	4.1 ab	1.7 b
2,2,4-trimethylpentane	49.2 ab	35.8 ab	44.9 ab	48.2 a	28.5 ab	18.2 b
n-hexane	34.6 a	38.1 a	28.2 ab	24.8 ab	24.0 ab	9.3 b
1,3-butadiene	6.1 a	4.5 ab	4.9 ab	5.0 ab	3.7 ab	1.9 b
Styrene	20.9 a	7.2 ab	8.1 ab	6.6 ab	12.9 ab	3.0 b
MTBE	40.2 a	38.0 a	43.0 a	44.4 a	27.5 ab	3.1 b
Formaldehyde	79.7	70.9	86.1	68.7	60.6	29.8
Acetaldehyde	48.4	39	48.2	41.7	36.8	20
TOTAL HVOCs	**731.3**	**716.4**	**584.6**	**583.5**	**517.2**	**204.6**
TOTAL VOCs	**2628**	**2515**	**2490**	**2001**	**2268**	**1054**
% HVOCs	**27.8**	**24.6**	**20.1**	**25.9**	**25.7**	**19.4**

(205 ppbC). At the TLA monitoring site, located near a large industrial area and avenues with heavy vehicle traffic, HVOCs represented 28% of the total VOCs. Ten HVOCs had their highest concentrations at this site: benzene, ethyl benzene, *m-/p*-xylene, *o*-xylene, 1,2-dichloroethane, perchloroethylene, 2,2,4-trimethylpentane, 1,3-butadiene, styrene and acetaldehyde. Compounds like perchloroethylene, a toxic and carcinogen solvent, and styrene, which is used to fabricate rubber, polystyrene plastics and resins products derive mostly from industries, and to some extent from gasoline vehicles. At XAL, HVOCs represented 25% of the total VOCs. Xalostoc showed the highest levels of toluene, chlorobenzene, trichloroethylene and *n*-hexane. Near to downtown (Merced), the HVOCs represented 20% of the total VOCs, being naphthalene, formaldehyde, *p*-dichlorobenzene and chlorobenzene the most abundant species. At the residential PED site, the HVOCs contributed 19% of total VOCs. Thus, the ratio HVOCs: VOCs declined from north to south, a trend reported for other gaseous air pollutants in Mexico City, e.g. [27].

All sites considered, the most abundant HVOCs were toluene > *m-/p*-xylene > formaldehyde > 2,2,4-trimethylpentane > MTBE. This resembles the HVOC abundances of the tailpipe emissions from Tier 1 vehicles (toluene > *m-/p*-xylene > benzene > MTBE > 2,2,4-trimethylpentane (Table 4), which is consistent with the view that gasoline vehicles are the most important local VOCs source [3,28]. Figure 2 illustrates a grouping exercise of sampling sites according to their chemical similarity with the tailpipe emissions of Tier 1 when fueled with the reference gasoline (RF). This grouping showed that HVOCs at PED were chemically more similar to Tier 1 emissions than the rest of sites; i.e, the morning air at this site was mainly polluted by gasoline vehicle emissions. At the other sites, the HVOCs appeared to derive from more mixed sources. Interestingly, the morning HVOCs levels were lowest at PED, a site characterized by having the most frequent and severe ozone events in Mexico City at afternoon hours. Several authors have explained this situation by transfer of O_3 precursors from the north of the city into this southern site [8,12].

HVOCs in vehicle tailpipe emissions. Tier 1 and Euro 4 vehicles did not differ significantly in total VOCs and total HVOCs emissions when fueled either with the reference gasoline (RF) or RFGs. Some significant differences occurred, however, for specific HVOCs (Table 4). When fueled with RF, Euro 4 emitted on average 117% more benzene, 22% more toluene and 55% more *2,4*-trimethylpentane than Tier 1 (Table 4). This result indicates that the gasoline currently used in Mexico City may not be appropriated for Euro 4 cars because it may lead to higher inputs of HVOCs into the local air. Since Euro 4 also had higher emissions of benzene (62%), ethyl benzene (48%) and toluene (88%) than Tier 1 when fueled with RFGs (Table 4), further studies on suitable fuels would be advisable prior to

Table 4. Content of HVOCs (average ± one SD, ppbC) in tailpipe emissions from two vehicles (Tier 1 and Euro 4) fueled with reference (RF) or reformulated gasoline (RFG). Probabilities associated to *t*-tests for independent (RF) and paired samples (RFG): * $p < .05$; ** $p < .01$; *** $p < .001$.

	RF		RFG	
HVOCs	Tier 1	Euro 4	Tier 1	Euro 4
Benzene	15.0 ± 3.75	32.5 ± 7.07***	16.2 ± 7.56	26.3 ± 10.16**
Ethylbenzene	14.0 ± 4.99	15.7 ± 4.69	9.3 ± 2.96	13.8 ± 5.90*
m-/p-xylene	42.7 ± 22.06	47.5 ± 20.06	26.5 ± 7.44	39.1 ± 27.59
Naphthalene	4.1 ± 4.37	3.8 ± 6.70	2.5 ± 2.82	2.9 ± 4.48
o-xylene	15.8 ± 8.27	18.5 ± 7.86	9.3 ± 2.90	17.5 ± 11.51*
Toluene	41.3 ± 8.54	50.2 ± 8.13*	49.4 ± 25.17	48.0 ± 15.09
1,2-dibromoethane	1.9 ± 1.33	2.7 ± 1.76	2.8 ± 1.98	3.4 ± 2.36
1,2-dichloroethane	3.1 ± 1.25	2.7 ± 0.43	2.1 ± 1.51	2.5 ± 1.28
Chlorobenzene	0.8 ± 0.62	1.1 ± 0.49	0.6 ± 0.47	1.1 ± 0.63
p-dichlorobenzene	0.4 ± 0.43	0.9 ± 0.57	0.5 ± 0.36	0.5 ± 0.42
Trichloroethylene	1.0 ± 1.24	0.8 ± 0.75	1.6 ± 1.62	0.5 ± 0.58
2,2,4-trimethylpentane	6.4 ± 1.92	9.4 ± 3.01*	30.9 ± 16.61	33.3 ± 16.97
n-hexane	4.7 ± 1.19	5.3 ± 0.7	4.7 ± 2.71	5.3 ± 1.33
1,3-butadiene	2.6 ± 0.82	2.4 ± 0.45	2.5 ± 0.58*	1.9 ± 0.70
Styrene	1.7 ± 1.40	2.6 ± 3.05	1.8 ± 1.62	1.7 ± 2.02
Methyl tert-butil ether (MTBE)	14.8 ± 5.86	14.5 ± 4.00	11.3 ± 9.62	12.4 ± 7.48
Formaldehyde			24.1 ± 6.64***	7.3 ± 1.57
Acetaldehyde			11.2 ± 3.39**	5.5 ± 1.75
TOTAL HVOCs	**170.3 ± 45.95**	**210.7 ± 49.49**	**207.3 ± 28.7**	**223.0 ± 61.02**
TOTAL VOCs	**671.1 ± 275.24**	**774.4 ± 284.41**	**633.3 ± 271.25**	**657.9 ± 242.49**
% HVOCs	**27.0 ± 7.05**	**28.3 ± 4.72**	**36.0 ± 10.19**	**35.6 ± 9.52**

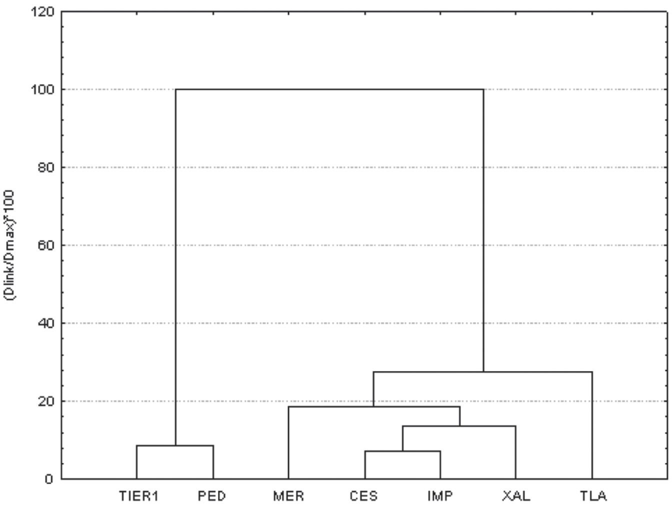

Fig. 2. Site similarity with tailpipe emissions from Tier 1. Grouping technique: cluster analysis of standardized HVOCs data by Ward method and Euclidean distance. Aldehydes not included.

a massive introduction of Euro 4 vehicles in the Mexico City area.

With respect to the emissions of specific HVOCs, Tier 1 emitted mostly *m/p*-xylene > toluene > *o*-xylene > benzene > MTBE when operated with the reference gasoline (Table 4). The same compounds also were the most abundant in Euro 4 emissions: toluene > *m/p*-xylene > benzene > *o*-xylene > MTBE (Table 3). When powered with RFGs, Tier 1 emitted mostly toluene > 2,4,4-trimethylpentane > *m/p*-xylene > formaldehyde > benzene; whereas Euro 4 emitted mainly toluene > *m/p*-xylene > 2,4,4-trimethylpentane > benzene > *o*-xylene.

According to European technological standards, Euro 4 cars are designed to work with unleaded gasoline having the following composition: low sulfur (50 ppm), aromatics (35% vol) and olefins (18% vol), and RVP = 8.7 to minimize both toxic emissions and sulfur damage to vehicle components. The Euro 4 tested vehicle, however, emitted less HVOCs with fuels containing lower than specified aromatics (17-18.2%) and olefins (2.8-8.5%), as well as low benzene content (0.5-1.0%). Surprisingly, one of the RFGs which produced less HVOCs with Euro 4 was F12, the one with the highest sulfur content (805 ppm) (Table 5). This car had higher HVOCs emissions with F9, F2 and F8, which had 21-37% aromatics, 1.4% benzene, 7.5-15.4% olefins, intermediate 27-370 ppm sulfur, and RVP (6.4-10.8 psi). In contrast, Tier 1 produced lower amounts of HVOCs with RFGs having higher levels of those components: 17-37% aromatics, 0.9-1.4% benzene, 6.6-15.4% olefins, 400-440 ppm sulfur, and RVP (6.7-11 psi), and it produced higher amounts of HVOCs with F8, F10 and F12, which contained 17-23% aromatics, 0.5-1.4% benzene, 8.5-15.4% olefins, 400-805 ppm sulfur contents, and RVP (6.4-10.9 psi).

Reformulated gasoline comparisons. Tables 5 and 6 summarize the total VOCs, total HVOCs and specific HVOCs produced by 11 RFGs. Data variability was rather large because of the compositional differences among fuels. Total VOCs from Euro 4 ranged from 428 (F5) to 1097 (F2) ppbC, and this range was slightly wider for the Tier 1 car, 450 (F10) to 1374

Table 5. Euro 4 tailpipe emissions of HVOCs (ppbC) when fueled with reformulated fuels (F1-F13).

HVOCs	F1	F2	F3	F4	F5	F6	F8	F9	F10	F12	F13
Benzene	20.73	29.91	18.54	21.91	22.22	18.13	44.55	46.25	17.47	27.46	22.39
Ethylbenzene	14.54	17.89	8.51	13.84	12.41	7.43	14.51	28.17	7.64	10.85	16.42
m-/p-xylene	48.37	55.86	23.40	46.28	77.53	20.23	42.52	84.89	0.62	1.32	29.24
Naphthalene	1.32	12.90	3.10	1.02	0.84	0.05	10.46	1.00	0.05	0.63	0.05
o-xylene	17.79	24.11	9.04	18.07	41.40	7.64	16.90	33.71	6.86	6.91	10.21
Toluene	47.39	53.85	39.53	43.46	34.35	35.90	48.02	86.29	38.76	38.71	61.37
1,2-dibromoethane	6.84	6.46	5.03	6.17	2.25	2.19	2.34	1.57	3.34	0.05	1.00
1,2-dichloroethane	2.08	2.17	2.19	1.62	2.25	5.58	4.16	2.87	2.03	2.11	0.96
Chlorobenzene	1.39	1.87	1.53	1.38	0.71	0.05	1.09	1.89	1.01	1.03	0.05
p-dichlorobenzene	0.55	1.46	0.05	0.65	0.17	0.05	0.70	0.90	0.40	0.80	0.29
Trichloroethylene	0.05	0.05	0.05	0.05	1.12	0.95	1.17	1.44	0.05	0.05	0.05
2,2,4-trimethylpentane	58.40	57.87	40.69	44.14	24.83	22.55	24.27	9.55	36.54	38.81	8.78
n-hexane	4.15	4.07	4.71	3.51	7.05	5.78	7.17	7.17	4.63	4.55	5.02
1,3-butadiene	3.24	2.44	2.79	1.54	1.48	1.60	1.09	1.82	1.07	1.99	1.42
Styrene	0.90	6.33	0.71	1.19	0.90	0.34	5.09	0.54	0.51	1.65	0.91
Methyl tert-butil ether	0.05	13.94	12.86	0.05	13.94	16.56	27.12	15.91	12.50	12.55	10.73
Formaldehyde	7.32	5.74	8.91	8.30	7.27	6.89	5.30	4.77	7.05	9.28	9.28
Acetaldehyde	4.83	3.75	7.99	6.81	6.20	4.55	5.03	3.05	4.44	5.09	8.71
TOTAL HVOCs	**239.9**	**300.7**	**189.6**	**220.0**	**256.9**	**156.5**	**261.5**	**331.8**	**145.0**	**163.8**	**186.9**
TOTAL VOCs	**703.3**	**1,097.0**	**584.1**	**607.2**	**427.7**	**443.6**	**1,007.8**	**907.8**	**454.9**	**576.8**	**426.5**
% HVOCs	**34.1**	**27.4**	**32.5**	**36.2**	**60.1**	**35.3**	**25.9**	**36.5**	**31.9**	**28.4**	**43.8**

Table 6. Tier 1 tailpipe emissions of HVOCs (ppbC) when fueled with reformulated fuels (F1-F13).

HVOCs	F1	F2	F3	F4	F5	F6	F8	F9	F10	F12	F13
Benzene	10.92	12.26	15.87	11.66	13.17	13.66	37.92	17.83	12.64	14.56	17.44
Ethylbenzene	9.05	7.64	6.95	10.09	9.12	7.64	9.78	11.69	7.58	6.07	16.80
m-/p-xylene	28.45	20.79	18.80	31.85	39.00	22.44	33.47	30.85	17.88	16.77	31.00
Naphthalene	0.05	6.21	2.65	6.72	0.05	0.80	6.01	4.61	0.05	0.05	0.49
o-xylene	9.98	8.44	7.55	12.97	12.03	7.65	10.72	10.17	3.53	6.61	12.88
Toluene	35.06	34.14	30.02	41.37	33.91	32.84	34.94	40.39	98.58	91.36	71.13
1,2-dibromoethane	0.05	4.81	3.22	5.21	2.89	1.80	2.36	1.10	5.95	2.89	0.05
1,2-dichloroethane	1.55	1.45	1.38	1.56	2.89	3.33	5.75	2.66	1.01	1.91	0.05
Chlorobenzene	0.95	1.08	1.09	0.05	0.78	0.84	0.05	0.05	1.10	0.79	0.05
p-dichlorobenzene	0.53	0.55	0.70	0.78	0.20	0.05	0.58	0.05	1.29	0.62	0.29
Trichloroethylene	1.04	1.27	0.05	0.05	1.06	1.23	1.56	0.62	5.29	4.02	1.73
2,2,4-trimethylpentane	46.80	47.07	29.46	41.59	27.96	18.13	22.11	6.20	46.68	49.02	4.62
n-hexane	3.15	3.08	3.05	3.17	7.17	7.90	9.91	5.97	1.76	1.64	5.39
1,3-butadiene	3.19	3.27	1.56	2.89	2.34	2.66	2.74	1.94	1.62	2.37	2.59
Styrene	0.74	2.48	0.60	2.56	0.37	0.37	4.14	0.26	3.68	4.06	0.32
Methyl tert-butil ether	0.05	9.83	10.31	0.05	16.06	20.52	31.93	14.92	7.91	0.72	11.65
Formaldehyde	23.80	20.77	23.31	15.00	30.96	25.69	28.61	29.83	10.36	25.26	31.45
Acetaldehyde	9.60	11.07	12.22	6.30	10.80	10.67	11.42	14.19	18.82	6.78	11.41
TOTAL HVOCs	**185.0**	**196.2**	**168.8**	**193.9**	**210.8**	**178.2**	**254.0**	**193.3**	**245.7**	**235.5**	**219.3**
TOTAL VOCs	**488.35**	**578.06**	**484.71**	**677.75**	**1374.11**	**495.75**	**836.24**	**528.28**	**449.72**	**602.29**	**451.55**
% HVOCs	**37.9**	**33.9**	**34.8**	**28.6**	**15.3**	**35.9**	**30.4**	**36.6**	**54.6**	**39.1**	**48.6**

ppbC (F5). In contrast, the range of total quantified HVOCs was wider for Euro 4, 145 (F10) to 332 ppbC (F9), than for Tier 1, 169 (F3) to 254 (F8). The largest reductions in emissions of total HVOCs from RFGs, compared to the reference gasoline, were 36% (F10), 31% (F6) and 29% (F12) for the Euro 4 vehicle, and 22% (F3), 16% (F6) and 11% (F1) for Tier 1, which indicates that Euro 4 was more efficient in reducing tailpipe emissions of these hazardous compounds for some fuels. Those five RFGs would be tentatively good candidates to reduce emissions of HVOCs from these vehicles. However, in selecting alternative fuels several other factors should be considered. These include toxic emissions, characteristics of the actual vehicle fleet they are intended for, ambient conditions as well as technical and economical considerations. Electre is a multicriteria method that allows us to quantitatively consider these and other decision factors. Herein, only toxicity by HVOCs was taken into account.

Table 7 shows how Electre ranked the tested RFGs from best to worst when considering HVOCs production directly (W_0), or weighted by noncancer inhalation toxicity (W_1) and

Table 7. Electre fuel ranking based on vehicle tailpipe emissions of HVOCs. Toxicity weighting factors: W_0, W_1, W_2.

W_0	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th
EURO 4	F10	F12	F6	F13	F1	F4	F9	F2	F3	F5	F8
TIER 1	F3	F1	F4	F13	F9	F10	F6	F12	F2	F8	F5
E50/T50	F3	F4	F6	F13	F10	F12	F1	F5	F9	F2	F8
E25/T75	F4	F1	F3	F5	F6	F9	F10	F12	F13	F8	F2
W_1	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th
EURO 4	F12	F10	F13	F6	F9	F2	F5	F8	F1	F3	F4
TIER 1	F1	F3	F9	F4	F6	F10	F12	F13	F5	F8	F2
E50/T50	F13	F6	F12	F9	F3	F10	F4	F1	F8	F5	F2
E25/T75	F13	F6	F9	F12	F3	F4	F10	F1	F8	F5	F2
W_2	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th
EURO 4	F10	F6	F1	F13	F2	F3	F4	F5	F9	F12	F8
TIER 1	F1	F3	F4	F6	F9	F10	F13	F5	F12	F8	F2
E50/T50	F6	F3	F4	F13	F10	F12	F1	F5	F9	F2	F8
E25/T75	F3	F1	F4	F13	F6	F9	F10	F12	F5	F2	F8

total environmental hazard (W_2). These rankings are presented by individual vehicles and average emissions from both vehicles, assuming vehicle fleet scenarios composed by 50% Euro 4 and 50% Tier 1 cars (E50/T50), and 25% Euro 4 with 75% Tier 1 (E25/T75). When all HVOC species were given the same importance ($W_0 = 1$; i.e., without toxicity consideration), the best three RFGs for Euro 4 were F10 > F12 > F6, and F3 > F1 > F4 for Tier 1. This Euro 4 result was similar to that from direct comparisons shown in the previous section (Table 4), but it varied slightly in the case of Tier 1, since Electre selected F4 instead of F6 (Table 5). These selections indicate that each vehicle require a different gasoline formulation to obtain the best reduction in HVOCs emissions.

When HVOCs were weighted by non-cancer toxicity via inhalation (W_1), Electre selected again F12 and F10 for Euro 4 as lower producers of toxics, but selected F13 as third option instead of F6. For Tier 1, it selected F1 and F3, but selected F9 instead of F4 (Table 7). These selections can be traced to the relatively low amounts of *1,2*-dibromoethane and naphthalene, the first and second most potent noncancer toxics measured. However, F12 would not be a good fuel choice because of its high proportion of sulfur (805 ppm), which could translate into emissions of toxic sulfur compounds (e.g., SO_2 and sulfates) and possible misfunction of vehicle catalytic converters. Furthermore, F12 also produced relatively high amounts of such toxics as formaldehyde, ethyl benzene and *p*-dichlrobenzene (Table 4). Thus, F13 and F6 would be potentially the best options for Euro 4 vehicles according to Electre.

When weighing HVOCs emissions by total hazard values (W_2), Electre selected F10 > F6 > F1 for Euro 4, and F1 > F3 > F4 for Tier 1. Thus, under all weightings, Electre ranked F10 as a good option for Euro 4, and F1 and F3 for Tier 1. These three RFGs would be thus promissory options to protect human and environmental (ecosystem) health by lowering air pollution by HVOCs.

Because vehicle pollutant emissions depend on the vehicle-fuel couple, to obtain the largest reduction in pollutant emissions it would be desirable to count on fuels tailored specifically for each vehicle technology. However, because producing specific fuels for every technology in a particular vehicle fleet could be economically and technically unaffordable for any petroleum refinery system and the final consumer, it may be more attractive to find one or two RFGs with low toxic emissions with all or most vehicle types. We looked for such a minimum set of RFGs by applying Electre to the average emissions of the two tested vehicles and by plotting the standardized HVOCs emissions weighted toxicity.

After averaging the HVOCs emissions from both cars directly (E50/T50), Electre selected: F3 > F4 > F6 for W_0; F13 > F6 > F12 for W_1; and F6 > F3 > F4 for W_2. Thus, F6 was selected under the three weightings, and F3 was the second best option. Therefore, assuming a vehicle fleet composed by half Euro 4 and half Tier 1 vehicles, F6 and F3 may help in reducing emissions of HVOCs. When assuming a vehicle fleet composed by 75% Tier 1 and 25% Euro 4 vehicles (E25/T75), Electre selected F4 > F1 > F3 for W_0; F13 > F6 > F9 for W_1; and F3 > F1 >F4 for W_2. In this case, fuels composed like F1, F3 and F4 would be good choices.

Figure 3 is a graphical alternative to visually assess RFGs by production of HVOCs without averaging emissions between vehicles. These subplots allowed us to detect which RFGs worked better than average with both tested vehicles in terms of reducing total HVOCs emissions and their associated potential toxicity. Figure 3 includes a fourth weighing factor, W_3, standing for potential cancer effects [26]. These subplots are subdivided into four sections by dotted lines crossing at the average emission value of each vehicle. Thus, fuels at the upper right section performed better than average with both vehicles; i.e., they produced less HVOCs or potential toxicity. Fuels at the lower left corner caused higher than average HVOC emissions and potential toxicity in both vehicles. Those at the lower right section worked fine with Tier 1, but not with Euro 4. Finally, fuels at the upper left corner did well with Euro 4 and bad with Tier 1. According to this figure, only F6 produced lower than average HVOCs emissions and potential toxicity with both cars under all weightings. In contrast, F2 produced higher than average HVOCs amounts and potential toxicity with both cars in all cases. Fuel 12 did well with both cars under W_0, W_2 and W_3, but did well only with Euro 4 under W_1. Fuel 13 did better than average for both cars under W_1, W_2 and W_3, and fine only with Euro 4 under W_0. The rest of RFGs (F1, F3, F4, F5, F8, F9 and F10) did well only with one or another vehicle. However, some of the latter RFGs may cause higher than average potential toxicity and/or carcinogenicity with one or another vehicle. For instance, F4 was associated to higher than average potential inhalation toxicity (W_1) and carcinogenic potential (W_4); F5 had higher than average HVOCs emissions with both cars, and tended to lower toxicity only with Euro 4. Fuel 8 would not be a good choice because it produced high amounts of carcinogenic HVOCs with both cars, though it did relatively well for inhalation noncancer effects.

Considering all Electre exercises, F3, F6 and F1 would be the best RFG options to lower tailpipe emissions of HVOCs. In contrast, the graphical technique suggested F6, F13 and F12 as the best options. With exception of F13, all of these RFGs were formulated with low contents of aromatics (<19%), low to median olefins (6.6 to 9.1%) and low to median benzene (0.2 to 1.0%). This indicates the environmental importance of lowering aromatics, benzene and olefins in alternative gasoline fuels. This view was confirmed by the composition of RFGs ranked as worst options: F2, F8, and to some extent F9, since they had 20.7-37.3% aromatics, 7.5-15.4% olefins and 1.4% benzene. It was not clear whether sulfur contents and the Reid vapor pressure affected the emissions of HVOCs. This result is in agreement with previous observations by Schifter and colleagues [20], who reported no effect of sulfur content on the emissions of total toxic VOCs measured as benzene, 1,3-butadiene, formaldehyde and acetaldehyde. Sulfur itself is a toxic expected to appear in vehicle tailpipe emissions in proportion to its content in gasoline. Most RFGs tested herein were designed with relatively high (330 to 440 ppm) to very high

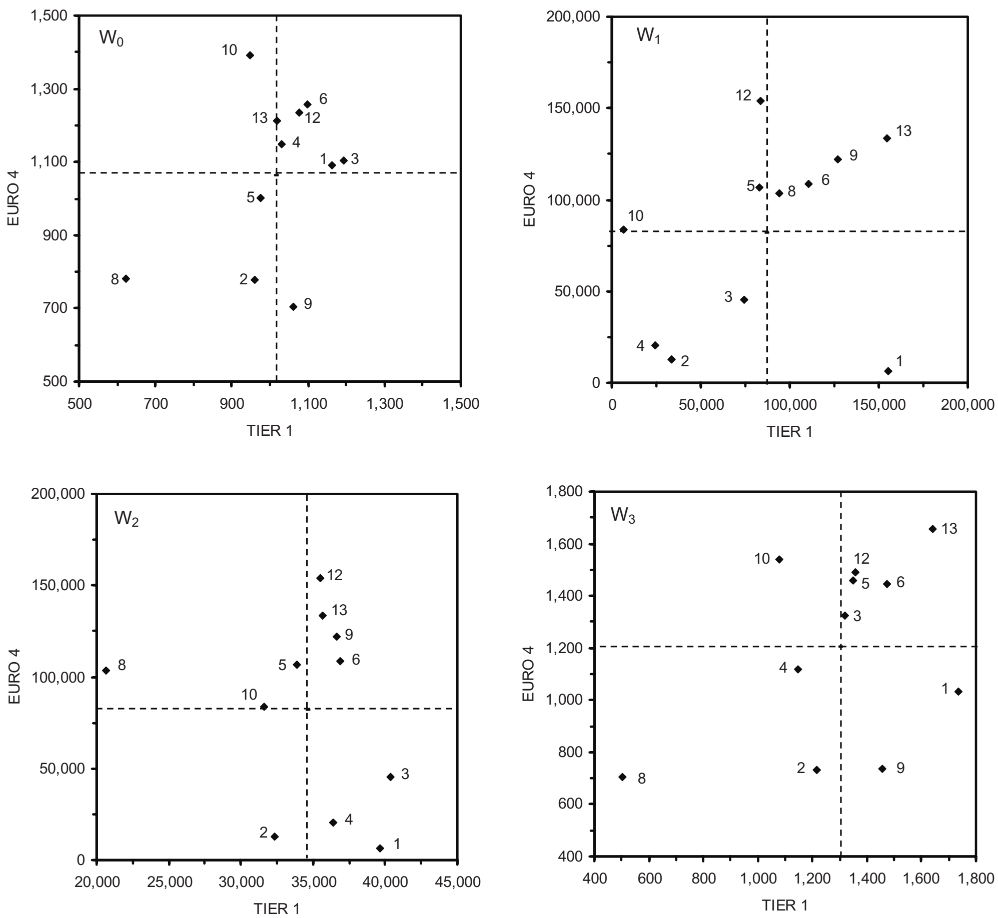

Fig. 3. Euro 4 and Tier 1 HVOCs exhaust emissions and toxicity weightings. W_0, standardized unweighted emissions; W_1, standardized data weighted by HVOC toxicity via inhalation; W_2, standardized data weighted by Total Hazard Value; W_3, standardized data weighed by potential cancer effects. Dotted lines cross at the average vehicle emission. Fuels at the upper right corner were better than average with both vehicles; those at the lower left corner performed worst than average with both vehicles; fuels at the upper left corner did fine only with Euro 4; fuels at the lower right corner did fine only with Tier 1.

(805 ppm, F12) sulfur contents, except F13 and F10, with 27 and 90 ppm, respectively. The Reid vapor pressure is known to affect evaporative rather than combustion emissions and values below 10 psi would be preferred in order to reduce evaporative emissions.

Summarizing, both Electre and the graphical approach selected F6 as one of the best RFGs tested. This was due to the comparatively low amounts of the most toxic and/or carcinogenic HVOCs produced by F6, like benzene, *1,2*-dibromoethane and *1,3*-butadiene (Tables 5 and 6). Fuel 1, which was selected by Electre worked fine with Tier 1, but it tended to produce higher than average potential toxicity and carcinogenicity with Euro 4 (Figure 3, W_1, W_2 and W_3). Fuel 3, also selected by Electre, presented some total hazard inconveniences for Euro 4 (Figure 3, W_2) because of its emissions of aldehydes, *p*-dichlorobenzene, chlorobenzene and naphthalene, but it did relatively well with both cars in terms of carcinogenic potential (Fig. 3, W_3). Fuel 13 reduced total potential toxicity and carcinogenicity by HVOCs; however, in some comparisons Electre ranked this fuel in between the good and bad options because of its relatively high emissions of aldehydes, trichloroethylene, *p*-dichlorobenzene, and other compounds of lower toxicity. Fuel 12 worked better with Euro 4, but it should be discarded because of its high sulfur content, which could be an environmental concern and cause problems to vehicle catalytic converters.

Conclusions

This study produced new data on the HVOCs in morning ambient air at the MCMA and in experimental tailpipe emissions from 11 RFGs for two vehicle technologies relevant to this urban area. Although the HVOCs levels in ambient air were still high, the data were consistent with a declining trend observed since the past 10-15 years for these compounds.

Their spatial distribution also agrees with previous reports for total VOCs: at downtown and the industrial north of the city, levels were 2-3 times as higher as at the south portion. These levels could be further lowered at the MCMA by using a new RFG. This new gasoline must contain as reduced contents of aromatics and olefins as possible, preferentially below 19% and 8%, respectively. According to our results, introducing RFGs such as F6, F3 and F13 in the MCMA would potentially have a positive impact on the local air quality and, consequently, on the population's health by lowering the present levels of HVOCs in ambient air. However, some further experimental and modeling studies would be required to discard potential emissions of other hazardous pollutants not considered herein (e.g., PAHs, metals and SO_2).

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