Volatile aromatic compounds in Mexico City atmosphere: levels and source apportionment

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RESUMEN

Se colectaron simultáneamente muestras de aire ambiente en tres sitios de la Ciudad de México durante el mes de marzo de 1997 con el fin de conocer las concentraciones y el origen de compuestos aromáticos utilizando el modelo de balance de masa de especies químicas (CMB). Los compuestos aromáticos volátiles representaron alrededor del 20% del total de hidrocarburos no metánicos presentes en las muestras matutinas colectadas. Las especies aromáticas volátiles más abundantes en el ambiente fueron el tolueno y los xilenos, seguidos por 1,2,4 trimetilbenceno, benceno, etilbenceno, metaetiltolueno, npropilbenceno, isopropilbenceno, 1,3,5 trimetilbenceno y estireno. Se llevaron a cabo campañas de muestreo en cruceros, en una estación de autobuses, un estacionamiento y algunos sitios en los que se utilizan disolventes y destilados de petróleo, para determinar los niveles de compuestos aromáticos volátiles a los que se expone la población. Se aplicó el modelo CMB para determinar la contribución de distintas fuentes a la presencia en la atmósfera de cada uno de los compuestos aromáticos más abundantes. El escape de vehículos fue la fuente principal de todos los compuestos aromáticos, especialmente los de gasolina, aunque el escape de vehículos a diesel y el asfaltado contribuyeron también en forma importante a la presencia de tolueno, xilenos, etilbenceno, propilbencenos y estireno. Las artes gráficas y el uso de pinturas impactó principalmente en la presencia de tolueno.

ABSTRACT

Samples of ambient air were simultaneously collected at three different sites of Mexico City in March of 1997 in order to quantify the most abundant volatile aromatic compounds and estimate the source contributions by application of the chemical mass balance model (CMB). Volatile aromatic compounds were around 20% of the total of non-methane hydrocarbons present in morning air samples. The most abundant volatile aromatic species in urban air were toluene and xylenes followed by 1,2,4 trimethylbenzene , benzene, ethylbenzene, metaethyltoluene, 1,3,5trimethylbenzene , styrene, npropylbenzene, and isopropylbenzane. Sampling campaigns were carried out at crossroads, a bus station, a parking place, and areas where solvents and petroleum distillates are used, with the objective of determining people's exposure to volatile aromatic compounds. The CMB was applied for estimating the contribution of different sources to the presence of each one of the most abundant aromatic compounds. Motor vehicle exhaust was the main source of all aromatic compounds, especially gasoline-exhaust, although diesel exhaust and asphalt operations also accounted for

toluene, xylenes, ethylbenzene, propylbenzenes, and styrene. Graphic arts and paint application had an important impact on the presence of toluene.

Key words: Mexico, volatile organic compounds, benzene, CMB

1. Introduction

The presence of volatile aromatic compounds in urban air is of environmental concern because they are precursors to photochemical smog including the production of secondary aerosols and the formation of ozone, as well as some of them have adverse effects on human health (Odum *et al.*, 1997). Several studies have been conducted in other countries to determine the atmospheric concentration of these compounds, mainly benzene, toluene and xylenes. Dann and Wang (1995) and Cheng *et al.* (1997) in Canada; Brocco *et al.* (1997) in Italy ; Grosjean *et al.* (1998) in Brazil; Thijsse *et al.* (1999) in Berlin; Rommelt *et al.* (1999) in Munich; Derwent *el al.* (2000) in the United Kingdom; Kourtidis *et al.* (2000) in Greece; Vukovich (2000) in the United States; Na and Kim (2001) in Korea. In Mexico the information about non-methane hydrocarbons (NMHC) and specifically of aromatic compounds in urban atmospheres is very scarce because measurements are difficult and expensive to undertake (Arriaga *et al.*, 1997; Sosa, 2001).

Volatile aromatic compounds are used as constituent in motor fuels, as chemicals intermediates, as solvents for fats, inks, oils, paints, plastics, etc. Their presence in the ambient air is associated to fuel incomplete combustion and to fuel and solvent evaporation. Increased concern for benzene as a significant environmental pollutant arises from public exposure to the content of benzene in gasoline, due to requirements for unleaded fuels for automobiles equipped with catalytic exhaust converters (Bravo, 2000). Benzene is a known human carcinogen and exposure has been linked to an increased risk of several forms of leukemia. Lynge *et al.* (1997) reported the association of leukemia and other forms of cancer to benzene exposure in gas stations. Long term exposure to benzene, toluene, ethylbenzene, xylene isomers (ortho, meta and para), trimethylbenzenes (TMB), and styrene, among other aromatics, may cause loss of appetite, nausea, weight loss, fatigue, headache, nervousness and irritability and has been associated to chronic respiratory diseases, dermatitis and other diseases (Sittig, 1991). The World Health Organization (WHO, 1987) considered no safe limit for benzene, but some countries have adopted an air quality guide values for it (i.e Germany with 2.5 μg/m^3/24 h). The WHO guideline recommended a safe limit for toluene of 7.5 μg/m^3/24 h).

On the other hand, volatile aromatic compounds have been associated to the formation of secondary organic aerosol (Odum *et al.*, 1997). Mugica *et al.* (2002b) used the maximum incremental reactivity coefficients determined by Carter (1994) to rank different NMHC in relation to ozone formation. Xylenes, toluene, 1,2,4trimethylbenzene, and 1,3.5trimethylbenzene ranked within the ten compounds that play a major role in ozone production in Mexico City. With the aim to control air pollution in Mexico City, the installation of catalytic converters in vehicles has been mandatory since 1991. As a consequence, lead in gasoline was eliminated and aromatic content increased. The content of aromatics in gasoline fuels on volume base has been controlled since 1994 to a maximum of 25%, and the content of benzene to a maximum of 1%. A gasoline vapors recovery program at gas stations has been implemented in Mexico City. Nevertheless, the atmospheric concentration of benzene in Mexico City has been reported as one of the highest in the world (Arriaga *et al.*, 1997). In 1995, the Federal District Administration conducted some studies in a specific site of Mexico City using a differential absorption spectrometer (OPSIS), founding a mean level of benzene of 45 μg/m^3.

The main purpose of this research was to investigate the origin of the most abundant aromatic volatile compounds in Mexico City atmosphere, as well as the exposure levels in specific sites.

Traditionally, the CMB model has been applied in many cities to determine how several sources contribute to the presence of NMHC (Watson *et al.*, 2001). In this study, the CMB model was used to determine the source apportionment to the presence of individual volatile aromatic compounds so it would be possible to establish specific control measures for each specific aromatic compound.

2.   Methodology

2.1   Sampling

The sampling of ambient air and sources was carried out according to the EPA TO-14 method using pre-evacuated SUMMA canisters (EPA, 1988). The stainless steel canisters employed were cleaned in the laboratory by repeated evacuation and pressurization with humidified helium chromatography grade. Three different places were selected for air ambient sampling in February and March, 1997: the first one, La Merced, is a commercial site near downtown; the second place, Xalostoc, is an industrial zone northeast Mexico City, and the third one, Pedregal, is a residential area located southwest Mexico City. Sampling time was from 6:00 to 9:00 A.M., and a total of 36 samples were collected in the stations located at a height of 2 to 3 meters above ground level. 56 additional samples were taken in La Merced with sampling periods of six hours, from 6:00 A.M. to 12:00 P.M. and from 12:00 P.M. to 18:00 P.M.

To characterize vehicular emissions, twelve samples were taken at ground level along three crossroads with a high density of traffic and seven samples were collected at a bus station. The sampling time was two hours (Sánchez *et al.*, 2001; Mugica *et al.*, 2001). Five samples were collected at a theater parking 20 minutes once the garage was full (Mugica *et al.*, 1998). Other exposure levels of aromatic compounds were measured at different sites where solvents and petroleum distillates are used. The selected places were: four graphic art workshops (one serigraphy and three offsets), three automotive painting sites, two places where architectonic coatings were being applied, two furniture shops where lacquers and varnishes were used. Sampling time period was 15 minutes. (Vega *et al.*, 2000b).

2.2   Analysis

Canister samples were analyzed using a Hewlett Packard Gas Chromatograph (5890 Model) with a flame ionization detector (FID) after concentration by collection in a cryogenically-cooled trap. The cryogenic method removes impurities and pre-concentrates the hydrocarbons in ambient air. The chromatographic capillary column used for C2-C14 hydrocarbon analysis was a J&W DB-1, made of fused silica, with an internal diameter of 0.32mm, length of 60m, and $1\mu m$ phase thickness. The oven temperature program was $-50°C$ for 3min, to $200°C$ at $8\mu C/min$. The chromatograph was calibrated by injecting known amounts of certified standard calibration gases onto the chromatography column.

3.   The CMB model

The CMB model allows the correlation of measured species concentrations in a site known as receptor and the emission sources that originate them. The CMB model consists of a least-squares solution to a set of mass-balance equations that express each receptor chemical concentration as a linear sum of products of source profiles abundances and source contributions. The source profiles abundances and the receptor concentrations with appropriate uncertainty estimates, are the input data for the CMB model. The CMB model calculates values for the contributions from each source type and the uncertainties of these values (Watson *et al.*, 1991). In recent years different source profiles have been developed in Mexico City to apply the CMB model (Mugica *et al.*, 1998,

2001; Vega *et al.*, 2000a,b). The base of the receptor model is the following equation, where the relationship between the concentrations of the chemical species measured in the receptor with those emitted in the source are expressed:

$$C_i = \sum_{j=1}^{P} F_{ij} * S_j$$

where C_i is the ambient concentration of the species i measured at the receptor site; P is the number of sources that contribute; F_{ij} is the fraction of source contribution; S_j is the calculated 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 this equation. The CMB software in current use is the CMB8, which operates in a Windows-base environment and accepts inputs and creates outputs in a wider variety of formats than previous CMB versions (Watson and Chow, 1998). One of the CMB8 output files is a table that shows the contribution of each source to the calculated ambient concentration for each species.

4.   Results

4.1   Ambient air concentrations

Table 1 shows the content of each type of organic groups at the three sites. Total volatile aromatic compounds accounted for 18 to 22% of the total NMHC. In average, La Merced was the most polluted area followed by Xalostoc. Pedregal had concentrations lower than one third of the other two sites, although it presented the highest percentage of aromatic compounds of the total NMHC.

Table 1. Contribution per group to the total of NMHC in ppbC %

Compounds	Xalostoc 6-9	Merced 6-9	Pedregal 6-9
Alkanes	54.0 ± 3.7	49.9± 5.4	55.8 ± 6.1
Olefines	13.0 ± 1.8	14.7± 1.4	14.9 ± 2.1
Oxigenated	1.2 ± 0.2	1.8 ± 0.3	1.8 ± 0.2
Halogenated	3.8 ± 1.1	4.1± 1.2	0.9± 0.2
Unknown	10.0 ± 2.9	10.6 ± 3.5	4.6 ± 1.1
Aromatics	18.0 ± 2.6	18.9 ± 3.3	22.0 ± 6.0
Total NMHC ppbC	3130 ± 1266	4106 ± 1574	1136 ± 361

Thirty-three aromatic compounds were detected, and the most abundant species in the three sites were in decreasing order: toluene, xylenes (ortho, meta and para isomers), followed by 1,2,4 trimethylbenzene, benzene, ethylbenzene, metaethyltoluene, 1,3,5 trimethylbenzene, npropylbenzene, isopropylbenzene, and styrene. These species account for 80% of the total aromatic compounds. Figure 1 and Figure 2 show the median, minimum and maximum aromatic compound concentrations in a box plot presentation of the three sites. In all cases the highest concentrations were found in La Merced and the lowest in Pedregal. Benzene was about 6% of the total of volatile aromatic compounds with concentrations up to 36 $\mu g/m^3$.

Table 2 shows the average concentration of each compound in La Merced, both in the morning and in the afternoon. Rush hours are mainly in the early morning, so the average of total NMHC concentrations contained in the six hour morning samples (6 A.M.-12 P.M) was 33% lower than the average concentrations of the three hour samples (6-9 A.M), although the volatile aromatic
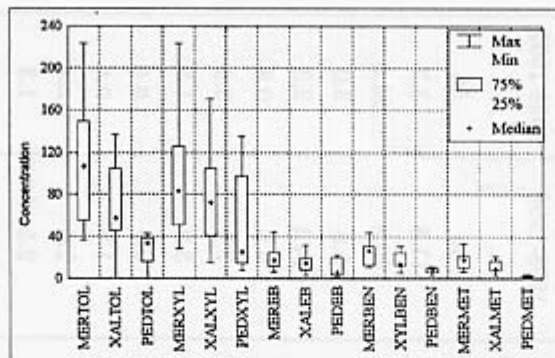
Fig. 1. Volatile aromatic compounds concentrations in Mexico City. Concentrations are in $\mu g/m^3$. MER: La Merced; XAL: Xalostoc; PED: Pedregal. TOL: toluene; XYL: xylenes; EB: ethylbenzene; BEN: benzene; MET: metaethyl-toluene.
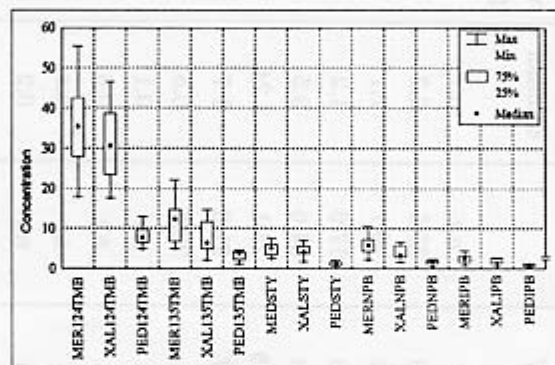

Fig. 2. Figure 2. Volatile aromatic compounds concentrations in Mexico City Concentrations are in $\mu g/m^3$. MER: La Merced; XAL: Xalostoc; PED: Pedregal. 124TMB: 1,2,4trimethylbenzene; 135TMB: 1,3,5trimethylbenzene; STY: styrene; NPB: npropylbenzene; IPB: isopropylbenzene.

concentrations in the six hour samples were only 20% lower than those observed in the three-hour morning samples. On the other hand, both NMHC and aromatic compound concentrations decreased around 50% from the morning to the afternoon due to an improved dispersion and as a result of photochemical reactions in the atmosphere. Arriaga's (1997) study reported that the aromatic compound concentrations did not present a decreasing trend from 1993 to 1996. The present study found that these concentrations have remained high.

Table 2 also shows the comparison with other studies carried out in different countries. Most of them show that the highest concentrations are observed in the early morning. It is important to stress that it is difficult to compare our results with those observed in other cities due to the differences in several factors, such as sampling sites and sampling periods; nevertheless, these data are presented to show how high the air pollution levels in Mexico City are.

4.2 Street and bus station levels

Table 3 shows the volatile aromatic concentrations found in several crossroads, a bus station, and a parking lot. Values are more than twice as concentrated than in ambient air. This implies that policemen, street vendors and pedestrians along the street or adjoining owners of highly traveled roads are exposed to high dose of volatile aromatics. The results of this study agree with

Table 2. Concentrations of volatile aromatic compounds in urban areas ($\mu g/m^3$)

Site	Mexico City Merced (1)	Mexico City Merced (1)	Mexico City Merced (1)	Rome Italy (2) (2)	Berlin (3) Germany Residen	Baltimore USA (4) b	Porto Allegre Brazil (5)	Seoul Korea (6) b
Sampling time	3 h Morning March 1997	6 h Morning Feb-March 1997	6 h Afternoon Feb-March 1997	Daily average 1992-1993	a 2 h day average summer	12 h 6:00AM-6.00PM weekdays 1994-1997	1 min 8:30 Morning 1998-1999	24 h Annual Mean 1998-1999
Samples	15	28	28	n.r	n.r	n.r	46	55
Benzene	25.2	20.9	10.8	35.5	2.2	7.2	11.8	3.2
Toluene	119.2	84.4	43.2	99.7	7.1	26.2	20.8	24.0
Ethylbenzene	20.7	18.7	10.8	17.6	1.2	5.3	5.8	3.0
m/p Xylene	73.1	68.1	37.8	54.6	3.5	16.1	14.1	2.3
o xylene	28.2	27.0	14.79	25.1	1.24	6.0	5.5	0.8
124 TMB	36.9	24.0	11.7	21.0	1.7	26.2	7.9	3.9
135 TMB	12.1	9.0	4.3	22.6	0.5	3.3	3.2	1.5
Isopropbenzene	2.6	2.0	0.9	n.r	0.1	1.0	0.9	n.r
Npropbenzene	6.1	4.8	2.3	n.r	0.6	1.8	1.8	n.r
Methyltoluene	18.1	13.8	6.4	n.r	n.r	n.r	2.6	n.r
Styrene	4.9	4.0	2.0	n.r	0.2	2.3	2.5	1.3
Tot NMHC ppbC	4106	2712	1211	n.r	138	n.r	577.4 c	234
Aromatics ppbC	779	618	315	n.r	22b	n.r	87.3 c	96

(1) This study
(2) Rome, Italy. Brocco et al., (1997)
(3) Berlin, Germany. Thijsse et al., (1999)
(4) Baltimore, Maryland, USA. Vukovich F., (2000)
(5) Porto Allegre, Brazil. Grosjean et al., (1998)
(6) Seoul, Korea. Na and Kim., (2001)
a: average of four sampling periods of 2h each (night, rush hours early morning, midday and evening.
b:μ concentrations were converted from ppb (original paper) to $\mu g/m^3$
c:$\mu g/m^3$.
n.r: Not reported

Table 3. Concentrations of volatile aromatic compounds emitted by mobile sources

	Mexico City Crossroads $\mu g/m^3$	Mexico City Bus station $\mu g/m^3$	Mexico City Parking garage $\mu g/m^3$
Sampling time	2 hours	2 hours	20 minutes
Samples	11	7	5
Benzene	64 ± 15	14 ± 3	83 ± 28
Toluene	207 ± 37	57 ± 12	358 ± 80
Ethylbenzene	42 ± 9	26 ± 28	69 ± 22
m/p xylene	143 ± 35	86 ± 100	280 ± 100
oxylene	54 ± 14	28 ± 29	104 ± 36
124 TMB	8± 3	9± 7	70± 4
135 TMB	18± 5	5± 2	29± 1
Isopropiylbenzene	4± 1	1 ± 1	15± 0
Npropylbenzene	10 ± 2	27 ± 1	6 ± 1
Methyltoluene	34 ± 9	6 ± 4	49 ± 2
Styrene	7 ± 1	1 ± 1	13 ± 2
% Aromatics	22.86	28.85	11.35

the benzene exposure study carried out by Meneses and Hernández-Avila (1999) who reported that street vendors are exposed to 83 $\mu g/m^3$ of benzene every day. Although the increased use of catalytic converters has lowered the level of volatile organic compounds from vehicle exhaust and the benzene content in fuels is controlled, several studies have confirmed that a substantial amount of benzene is produced by thermal decomposition of other aromatic compounds such as toluene, xylenes, and trimethylbenzenes in catalytic converters (Casinhas, 1999). Therewere, benzene and other aromatic compounds must be importantly decreased in fuel contents.

4.3 Solvents and petroleum distillate use

The use of solvents and distillates of petroleum in residential or commercial areas is of environmental concern because many of them are handled carelessly in the open air where not only workers, but also pedestrians, inhabitants and vendors are exposed to the emission of toxic vapors with a high content of aromatic compounds. Other closed sources located in residential areas such as dry cleaners and graphic art workshops (offset and serigraphy) lack emission control equipment because there are no national regulations; in this regard, adjoined owners or neighbors are exposed to NMHC emissions. Table 4 shows the mean concentrations and standard deviations found in these kinds of settings. Toluene's measured concentrations followed by xylenes' were very high in the graphic art workshops and where paint and varnishes are applied. Alkyl and trimethylbenzenes had the highest concentrations in dry cleaners.

4.4 Source apportionment

Vega *et al* (2000b) and Mugica *et al* (2002a) applied the CMB model to conduct source apportionment studies in Mexico City. These studies concluded that the major sources of NMHC were motor vehicle exhaust (50-64%), handling and distribution of LP gas (15-25%), and asphalting operations (9-12%). In this study the CMB model was applied to determine the source contribution of each of the most abundant aromatic species. Dry cleaners and degreasing were not included in the CMB analysis because an initial test showed negligible contributions to the total NMHC in the ambient air. In general, the measured and calculated mass of aromatic species had a good

Table 4. Volatile aromatic concentrations at some sites ($\mu g/m^3$)

	Serigraphy	Offset	Dry Cleaner	Degreasing	Automotive Painting	Architectural Coating	Varnishes
Samples	4	6	4	8	6	6	4
Benzene	606±568	1331±1168	75±43	23±14	180±122	531±270	221±74
Toluene	15004±10963	13309±12949	5215±3104	89±56	17182±9250	11951±3808	39973±23578
Ethylbenzene	2897±117	1071±964	424±227	19±10	558±395	512±214	475±375
m/p xylene	10152±530	3753±2280	1334±831	56±52	2019±1423	1816±1666	2871±1370
oxylene	3589±226	1315±1190	1044±806	24±20	671±456	591±561	338±108
124Trimethylbenzene	3±2	503±309	5872±3367	12±19	31±23	0±0	0±0
135 Trimethylbenzene	23±18	272±163	3648±2153	9±19	11±9	32±26	77±3
Isopropylbenzene	12±11	126±113	74±59	9±6	3±2	16±31	0±0
npropylbenzene	0±0.	229±207	1380±1220	9±6	6±5	0±0	0±0
metaethyltoluene	218±206	645±603	5214±3104	11±9	16±10	57±48	29±12
Styrene	43±42	134±127	129±91	8±7	333±164	141±87	104±62

concordance with deviations smaller than 20%, except 1,2,4 trimethylbenzene since only around 50% could be apportioned. This means that there are other sources not considered in the receptor model application.

Figures 3, 4 and 5 show the major sources for each species (calculated mass base) in the three sites. The contributions of vehicular emissions (gasoline, diesel and evaporative) for all the considered volatile aromatic species were quite similar for La Merced and Pedregal. The contributions to aromatic compounds from diesel exhaust and asphalt operations were highest in Xalostoc. In general, the gasoline vehicular exhaust was the major source of the considered aromatic compounds, with contributions up to 78% for metaethyltoluene, 76% for benzene, 70% for npropylbenzene, 68 % for 135 trimethylbenzene and isopropylbenzene, 65% for styrene and 60% for toluene. The contribution of this source was lower for ethylbenzene and xylenes, with an average of 42% and 24%. Other contributors to benzene were diesel-powered engines with around 10% in La Merced and Pedregal, and 19% in Xalostoc. The increased emissions of benzene in Xalostoc can be explained by the large number of industries located in the area that use diesel for the operation of boilers and engines. The contribution of evaporative sources to benzene was higher in Xalostoc (11%) than in La Merced (3%) and Pedregal (5%), maybe due to the presence of open tanks for industrial purposes.

In addition to gasoline exhaust emissions, about 20% of toluene was emitted by diesel exhaust sources, 13% in average by asphalt operations, and up to 11% by architectural coatings and graphic arts. As well as benzene, the major contribution of gasoline vapors to the concentration of toluene was found in Xalostoc (5.4% vs. 1.5% in the other two sites). In general, the contribution of diesel engines exhaust was very important to the presence of alkylated aromatics, such as xylenes, ethylbenzene and styrene, particularly in Xalostoc. Metaethyltoluene and 1,3,5 trimethylbenzene had the lowest contributions by this source (up to 8 and 15%). The contribution of evaporative emissions to other aromatic compounds than benzene was less to 5%, while the highest values were found in Xalostoc. Asphalt operations were important contributors to ethylbenzene, xylenes, 1,3,5 trimethylbenzene, isopropylbenzene, npropylbenzene, and styrene, with average percentages of 25, 24, 21, 18, 18, and 13%, respectively.

Emissions from cooking contributed with percentages less than 2% of aromatics, except for benzene, which reached up to 4% in some samples. These contributions can be explained by the presence of many complex compounds in the charcoal used in cooking. The contribution of landfills to volatile aromatic compounds was only found in La Merced, mainly for ethylbenzene and xylenes (both with 6%).

5. Conclusions

Non-methane hydrocarbons were measured in Mexico City in March, 1997 by means of gas chromatography. Ambient data collected from three sites in Mexico City show that the aromatic hydrocarbon fraction ranges from 18 to 22% of the total NMHC concentration. The composition of top species was similar from site to site. Benzene accounts for an average of 6% of the aromatic fraction, while toluene contributes 29%, and xylenes 24%. Exhaust and evaporative gases are the main sources of aromatic compounds in Mexico City atmosphere. The volatile aromatic concentrations at several crossroads and the parking garage were several times higher than ambient air concentrations, and entail a health risk for pedestrians, street vendors and policemen.

Although the CMB model estimations were found to have small contributions from sources which use solvents (such as graphic arts workshops and paint and varnishes application), this study showed that neighbors and people near these places are exposed to high concentrations of aromatic compounds, especially toluene. This suggests that regulatory initiatives to control exposure are also needed in these settings, as well as some regulations of toluene's content in solvents. Vehicles are the main source of all emissions of aromatic compounds. Thus, a strong reduction of aromatic
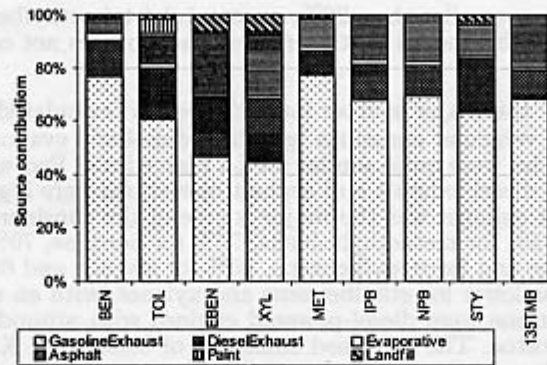
Fig. 3. Source contribution to individual aromatic compounds in La Merced
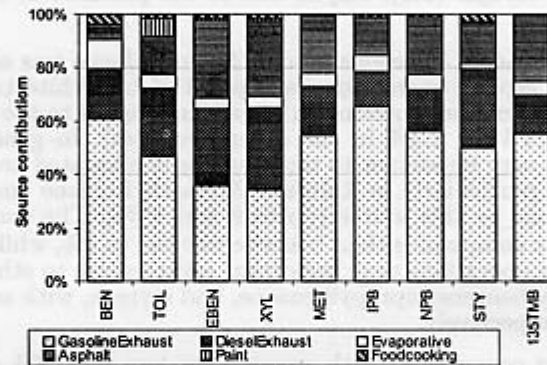

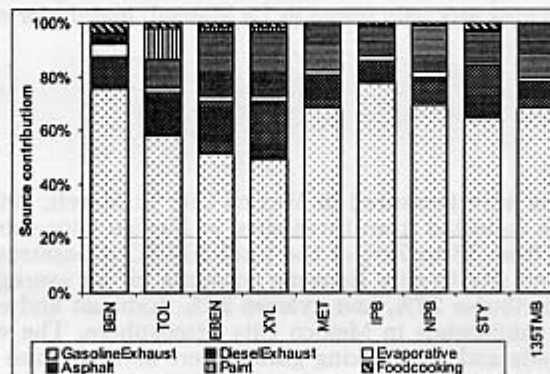Fig. 4. Source contribution to individual aromatic compounds in Xalostoc

Fig. 5. Source contribution to individual aromatic compounds in Pedregal

compound emissions from vehicle traffic appears to be mandatory. Asphalting operations should be also considered to diminish the presence of alkylbenzenes.

The continuous monitoring of volatile aromatic compounds, especially benzene, should be seen as an important and significant improvement of the existing network in order to upgrade its

response to an effective strategy to control pollution. Long-term measurements are needed to provide important information on hazardous and reactive pollutants, such as human exposure, exposure trends, and estimates of source contributions, as well as to evaluate the progress achieved through the application of control strategies.

Acknowledgements

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