

# Measurements of Atmospheric Pollutants (Aromatic Hydrocarbons, O<sub>3</sub>, NO<sub>x</sub>, NO, NO<sub>2</sub>, CO, and SO<sub>2</sub>) in ambient air of a site located at the northeast of Mexico during summer 2011

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**Abstract:** - Volatile organic compounds (aromatic hydrocarbons: benzene, ethyl benzene and p-xylene), O<sub>3</sub>, NO<sub>2</sub>, NO, NO<sub>x</sub>, CO, SO<sub>2</sub> and meteorological parameters were measured in ambient air of a site located in the Metropolitan Area of Monterrey, México. A total of 69 samples were collected for aromatic hydrocarbons and analyzed by Gas Chromatography with Flame Ionization Detection (GC-FID). Criteria pollutants concentrations were determined by automatic analyzers and meteorological parameters were measured by a portable meteorological station. A marked diurnal variation was found for the three measured aromatic hydrocarbons. The highest concentrations occurred during the morning sampling period (from 09:00 to 10:30 h) followed by the midday sampling period (from 12:00 to 13:30 h) and showing the lowest concentrations during the afternoon sampling period (from 15:00 to 16:30 h). Mean concentrations for benzene, ethyl benzene and p-xylene were: 0.9, 1.06 and 1.63 µg m<sup>-3</sup>, respectively. Aromatic hydrocarbons abundance showed the following order: p-xylene > ethyl benzene > benzene. All criteria pollutants showed concentration values lower than the maximum permissible values requested by the air quality Mexican standards, only ozone showed levels approaching to the standard value. A relation among criteria pollutants, meteorological parameters and aromatic hydrocarbons was found using a Principal Component Analysis (PCA), identifying some associations among the pollutants originated in common sources. Air pollutants maximum concentrations were found when winds blew from NE. Important industrial sources and avenues with high vehicular traffic are located in this direction. These sources could contribute to the levels measured in the studied site. This site did not show a clear pattern of VOC's/NO<sub>x</sub> sensitivity to ozone formation during the study period.

**Key-Words:** - Volatile organic compounds, Aromatic hydrocarbons, Air pollutants, Monterrey, Mexico, Principal Component Analysis, Ozone.

## 1 Introduction

The monitoring of pollutants is a relevant issue in the environmental and health protection. For instance, regarding acoustical noise, Guarnaccia et al. [1] presented a comparison between experimental data and predictive models, showing the weak and strength points of a software approach. In addition, an integrated method, that takes into account several different pollutants and introduces a Health Quality Index, is proposed by Quarteri et al. [2]. In order to understand the importance and role of Volatile Organic Compounds (VOCs) on the formation of tropospheric ozone it is necessary to measure the concentrations of these pollutants in air

[3-5]. Ozone is produced in the troposphere by the oxidation of VOCs in the presence of sunlight and nitrogen oxides (NO<sub>x</sub>=NO+NO<sub>2</sub>). Ozone is a recognized greenhouse gas [6] and is unhealthy at enhanced concentrations [7]. Tropospheric ozone is considered as the most phytotoxic atmospheric pollutant due to its oxidant capacity. It is present in high concentrations in the Northern Hemisphere and causes damages in crops, forests and sensible vegetation [8-10]. It affects the respiratory system of animals and humans [11]; and is the third most important greenhouse gas, behind the CO<sub>2</sub> and CH<sub>4</sub>. The relation between ozone and its two main precursors, NO<sub>x</sub> (NO+NO<sub>2</sub>) and volatile organic

compounds (VOC), represents one of the major scientific challenges associated with urban air pollution [12]. It is generally known that for some conditions the process of ozone formation is controlled almost entirely by NO<sub>x</sub> and is largely independent of VOC, while for other conditions ozone production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NO<sub>x</sub>. However it is difficult to determine whether ozone production during specific events is associated with NO<sub>x</sub>-sensitive chemistry or VOC-sensitive chemistry. VOC's compounds includes several sub-groups like halogenated compounds, carbonyl compounds, non-methane hydrocarbons and aromatic hydrocarbons. The importance of each of these compounds groups lies in their potential of ozone formation in the presence of sunlight. For all these reasons, it is important to know the levels of VOC's and criteria pollutants in the atmosphere of urban sites in order to establish strategies and control policies for tropospheric ozone.

In Mexico there are air quality standards for O<sub>3</sub>, NO<sub>2</sub>, NO, NO<sub>x</sub>, CO, SO<sub>2</sub>, Pb and particulate matter [13-21]. However, there is not a standard for volatile organic compounds, even some of them "such as benzene" has been classified as carcinogenic by the International Agency for Research on Cancer [22]. Ambient air concentrations of aromatic hydrocarbons in urban areas have been reported from several authors around the world [19-21]. However, in Mexico, most of the studies about these compounds have been focused to Mexico City and its Metropolitan Area [26-28]. Little information has been registered about other important urban and industrialized areas in Mexico. At the northeast of the country, it is located an important industrial area named Metropolitan Area of Monterrey (MAM). Important industrial activities are carried out and few studies about carbonyls in ambient air have been reported for this area [29]. The main municipality within this area is Monterrey city, which is the third largest city in México. It is located in Nuevo Leon State (at 25°40'N latitude and 100°18'W longitude), with an average altitude of 537 m above sea level, and with an area of 580.5 km<sup>2</sup> (Fig. 1). MAM is constituted by 12 cities or municipalities (Apodaca, Escobedo, García, Guadalupe, Cadereyta, Juárez, Salinas Victoria, San Nicolás de los Garza, San Pedro Garza García, Santa Catarina, Monterrey and Santiago). This area is considered a high profile center of education, tourism and business with a population of 4 000 000 inhabitants and 85% of its territory in urban area. This study is focused on San Nicolás de los Garza

located at the over the north of the MAM where industrial activities and vehicular fleet are common potential pollution sources. More than 60% of total emissions of NO<sub>x</sub>, CO, HC and Pb are due to vehicular fleet, and 92% of SO<sub>2</sub> emissions are due industrial activities [30]. This study reports aromatic hydrocarbons concentrations and its relation with criteria air pollutants (O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, CO and SO<sub>2</sub>) measured during summer-2011 in one site located within the Metropolitan Area of Monterrey (MAM) in Nuevo León, Mexico. A correlation analysis between carbonyls and criteria air pollutants was made and supported by a principal compound analysis (PCA). In addition, the influence of local meteorological conditions was studied by meteorological parameters measurements. The probable origin of air pollutants measured was inferred from the 24-h air mass trajectories calculated for the studied period using the HYSPLIT model from NOAA, in order to identify the possible sources contributing to air pollutants levels during the study period in this area.

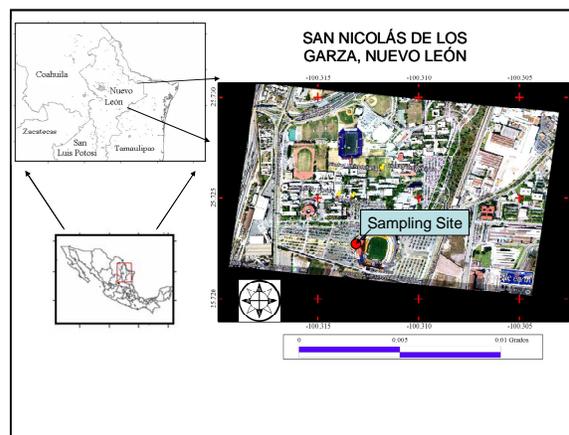


Fig.1. Sampling site location.

## 2 Materials and Methods

### 2.1 Sampling site location

MAM has a humid subtropical climate. Its weather is hot in the summer (temperature reaches 35 °C in August), though reasonably pleasant in spring and autumn. The average temperature in winter is 8 °C. Rainfall is scarce, but more prominent during May - September. Humidity in winter can be high, although without showers. Snowfall is a very rare event. The annual average precipitation is 615 mm.

The weather patterns over the area are influenced by frontal systems coming from the north of the continent. The specific sampling site was located in the facilities of the Mechanical and Electrical Engineering School of the Autonomous University of Nuevo León State within the MAM in the municipality of San Nicolás de los Garza (25° 43' 30" N; 100° 18' 48" W) (Fig. 1). The site was located within an industrial, residential and commercial area where also there are three avenues with high vehicular traffic.

## 2.2. Sampling Method

### 2.2.1. Aromatic Hydrocarbons (AH)

69 samples were collected during summer 2011 (from August 08 to September 23). Benzene, ethyl benzene and p-xylene were measured in ambient air.

Samples of air were collected within glass tubes containing 226-01 Anasorb CSC (SKC): length 70 mm; inner diameter 4.0 mm; outer diameter 6 mm packed in the first section with 100 mg of activated carbon and 500 mg in the second one, separated by a glass wool section (Method INSHT MTA/MA-030/A92) [31]. The downstream end of the glass tube was connected to a calibrated flow meter. Ambient air was passed through the glass tubes at a flow rate of 200 ml min<sup>-1</sup> at 1.5-hour intervals (day, midday and afternoon). Sampling was carried out using a Universal XR pump model PCXR4 (SKC), at three sampling periods: B1 (from 9:00 to 10:30 h), B2 (from 12:00 to 13:30 h) and B3 (from 15:00 to 16:30 h). During sampling, the Swagelok® fitting was removed from the marked end, and a diffusion cap was fitted to the end of the sampling tube. Prior to the main study, several pilot experiments were conducted to evaluate the suitability of the sampling procedure intended for use in the main study. This procedure included determining appropriate sampling times. Samplers tubes were protected from bad weather conditions by aluminium shelters. After the exposure time, the adsorption tubes were labeled and capped tightly with PTFE caps and transferred to the laboratory in cold boxes. This procedure was applied to both clean and sample tubes for storage prior to use or analysis. Field blanks were transported along with samplers to the field and stored in the laboratory during the sampling period. Samples were analyzed within three weeks after sample collection at the Environmental Sciences Laboratory in the Autonomous University of Carmen City (UNACAR).

### 2.2.2. Monitoring of meteorological parameters and criteria Pollutants

Wind conditions (direction and speed), relative humidity, temperature, solar radiation and barometric pressure were monitored from August 08 to September 23, 2011 (summer). A portable meteorological station Davis Vantage Pro II model was used in order to measure the meteorological parameters. Wind roses were constructed for each day using the software WRPLOT (from Lakes Environmental) [32]. 24 hr back air masses trajectories were calculated for the studied period using HYSPLIT model from the NOAA (National Oceanic Administration Agency, USA) [33] in order to identify the probable origin of the air masses. Criteria Air Pollutants (O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, CO and SO<sub>2</sub>) were obtained from the Integrated System of Environmental Monitoring of the MAM (SIMA), specifically from the Northeast Station. This station is located in the Laboral Unity District in San Nicolás de los Garza, N.L. at 25° 44' 42 "N and 100° 15' 17" W at 500 msnm, within an area with high density of population. All criteria pollutants were determined using automatic analyzers API Teledyne.

## 2.3. Analytical Method

Samples were extracted with 1 ml of CS<sub>2</sub> for each section of the samplers tubes, shaking during 30 s to assure a maximum desorption. Extracted samples were analyzed using a TRACE GC Ultra gas chromatograph (Thermoscientific) and one flame ionization detector (FID; Thermoscientific Technologies, Inc) (Method INSHT MTA/MA-030/A92) [31]. The analytical column used was a capillary column (57 m, 0.32 mm i.d., 0.25 µm film thickness). Operation of the instrument was controlled using a Trace Chemstation data system. The oven temperature program was initially set to 40 °C for 4 min, which was then increased at a rate of 5 °C/min up to 100 °C, and was finally maintained for 10 min at 100 °C. The FID temperature was set to 250 °C using a hydrogen/air flame with constant flows of 35 ml min<sup>-1</sup> and 350 ml min<sup>-1</sup> for ultra-pure hydrogen and extra-dried air, respectively. The ultra-pure nitrogen carrier (99.999%) gas flow rate was 1 ml min<sup>-1</sup>. Four VOCs that included benzene, p-xylene, ethyl benzene, and 1,2,4-tri-methylbenzene, were investigated. 1,2,4-tri-methylbenzene was under the detection limit for all the collected samples.

Five-point calibration was performed using 99.98% Sigma-Aldrich analytical reagents at a

concentration of 2 ppm for each VOC. The established calibration curves for the four investigated VOCs were found to have R-square-values of 0.999. Method detection limit (MDL) for each compound was calculated by multiplying the standard deviation obtained from seven replicate measurements of the first level of calibration by 3.14 (Student's t-value). The analytical results showed that the MDLs for the four VOC compounds of benzene, ethyl benzene, p-xylene, 1,2,4-trimethylbenzene, were 0.0517; 0.0566; 0.0600; 0.0293;  $\mu\text{g m}^{-3}$ , respectively. The amount of VOCs in blank samples was below the limit of detection (LOD) for all studied VOCs.

## 2.4 Correlation and Principal Compound Analysis

Pearson correlations were applied to all data collected at the sampling site. To assess the relationships between concentrations of the studied VOCs (AH), meteorological parameters and criteria air pollutants measured, a factor analysis (Principal Component Analysis) was applied using the software XLSTAT [34]. The multivariate analysis technique involves first normalizing the data that each variable  $i$  have an average of zero and a standard deviation of one [34]. This analysis was made using the following formula:

$$Z_{ik} = \frac{x_{ik} - \bar{x}_{ik}}{\sigma_i} \quad i = 1, \dots, m; \quad k = 1, \dots, n.$$

Where  $x_{ik}$  is a measured concentration for compound  $i$  in  $k^{\text{th}}$  observation;  $\bar{x}_{ik}$  is the arithmetic mean concentration and  $\sigma_i$  is the deviation standard [35, 36]. The correlation matrix of the normalized variables produces the resulting eigenvectors (identifying the factors) and the corresponding eigenvalues (identifying the fraction of total variance in the data set described by factor) [35]. Varimax orthogonal rotation is widely used in atmospheric data manipulation to identify the principal components with clear pattern of factor loadings. Time-series study is another option to understand the behavior of criteria pollutants in a given site and it has been used broadly [37].

## 3 Results and discussion

### 3.1. Diurnal Variation

In Table 1 is shown the comparison of the results of this study with ambient air concentrations found in other sites around the world. It can be observed that the AH diurnal levels found in this study are lower than those measured in Birmingham [44], Detroit [48], Ulsan [47], Shizuoka [45] and El Cairo [46].

During summer 2011 it was found a clear diurnal pattern for the three measured AH. The highest concentrations were found during the morning (B1), decreasing during the midday (B2) and showing the lowest values during the afternoon sampling period (B3) as it can be observed in Fig. 2.

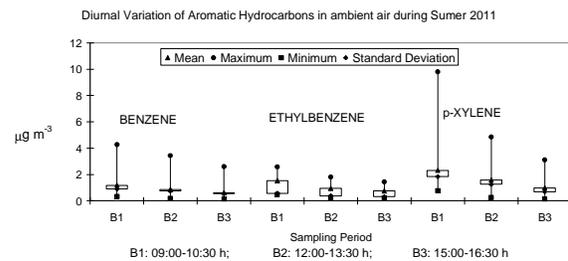


Fig. 2. Aromatic Hydrocarbons Diurnal variation in the study site.

### 3.2 Influence of the meteorological parameters on the AH levels

During summer mornings in 2011, winds blew from NNE (Apodaca, Nuevo Leon) in a 50% of the total period with speeds ranged from 0.4 to 2.2.  $\text{m s}^{-1}$ . In the afternoon, prevailing winds blew from ENE (Apodaca, Nuevo Leon) from 1.5 to 3.6  $\text{m s}^{-1}$  (Figs. 3-4). There were some episodes of pollution during the study: August 10, August 24 and September 23 (Fig 5 a, b y c) when winds blew from NNE and all the measured AH showed the highest concentrations. Whereas, p-xylene showed the highest concentrations when winds blew from NW in September 21.

In Figs. 6 a, 6 b and 6 c, wind roses are shown indicating the prevailing wind direction, frequency and wind speed for the different sampling periods (B1, B2 and B3, respectively).

### 3.3. Criteria Pollutants concentrations (CO, NO<sub>2</sub>, NO, NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>)

As it can be observed in Figs. 7- 11, CO, NO<sub>2</sub>, NO, NO<sub>x</sub> and SO<sub>2</sub> concentrations were below of maximum permissible values [14]- [18].

Table 1. Comparison of atmospheric concentrations of AH (µg m<sup>-3</sup>) found in this study with data of other studies around the world.

Location	B	EB	PX
This Study	0.9 ± 0.7	1.06 ± 0.43	1.63 ± 0.8
Mexico City. (Mexico) [38]	10.5	8.8	27.9
Mexico City. (Mexico) [39]	20.9	18.7	68.1
Rome (Italy) [40]	35.5	17.6	54.6
Berlin (Germany)[41]	2.2	1.2	3.2
Porto Allegre (Brazil)[42]	11.8	5.8	14.1
Seoul (Korea)[43]	3.2	3	2.3
Birmingham (England)[44]	7.3 ± 6.0	1.6 ± 1.4	5.2 ± 5.0
Shizuoka (Japan) [45]	0.2–1.6	0.2–11.1	0.3–10.0
El Cairo (Egypt)[46]	87.2 ± 10.0	43.3 ± 7.4	140.8± 21.8
Ulsan (Korea)[47]	5.9 ± 2.1	3.8 ± 1.4	6.6 ± 3.8
Nanjing (China)[25]	6.4 ± 3.8	2.9 ± 2.1	3.4 ± 2.8
Detroit (USA)[48]	4.5 ± 3.0	2.0 ± 1.4	6.8 ± 4.7
Baltimore (USA)[48]	7.2	5.3	16.1

Where: B.- Benzene; EB.- Ethyl benzene and PX.- p-Xylene.

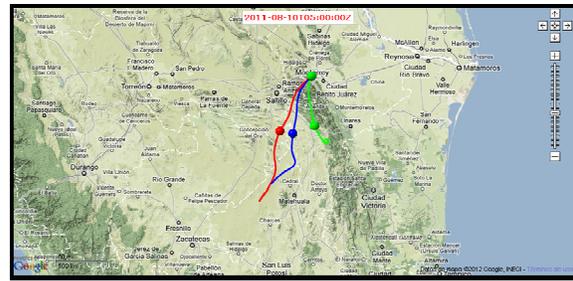
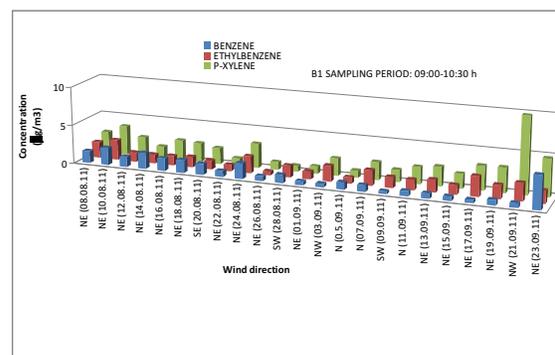


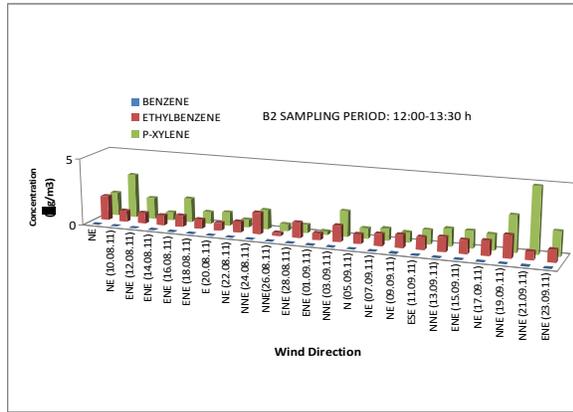
Fig. 3. 24 h Air backmass trajectory map for august 10 using HYSPLIT from NOAA (Maps from Google Copyright) [49] at 500, 700 and 1000 masl (green, blue and red lines, respectively).



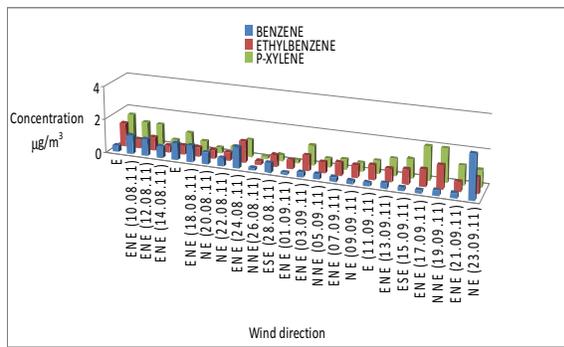
Fig. 4. 24 h Air backmass trajectory map for september 23 using HYSPLIT from NOAA (Maps from Google Copyright) [49] at 500, 700 and 1000 masl (green, blue and red lines, respectively).



a)

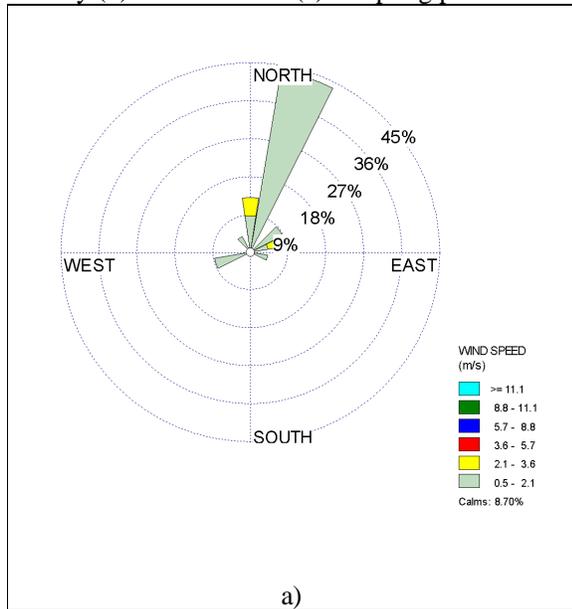


b)

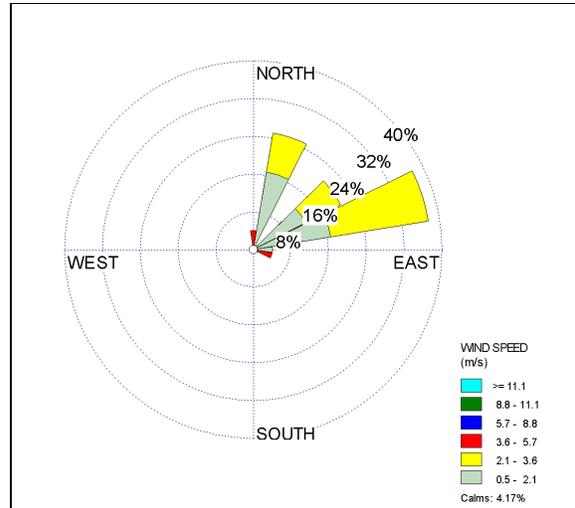


c)

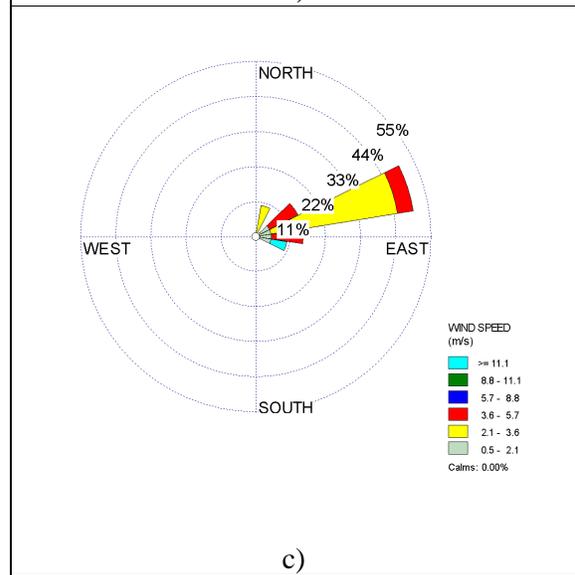
Fig. 5. Behaviour of AH concentrations according to the prevailing wind direction for the morning (a), midday (b) and afternoon (c) sampling periods.



a)



b)



c)

Fig. 6. Wind Roses indicating prevailing wind direction, freq for the morning (a), midday (b) and afternoon (c) sampling periods.

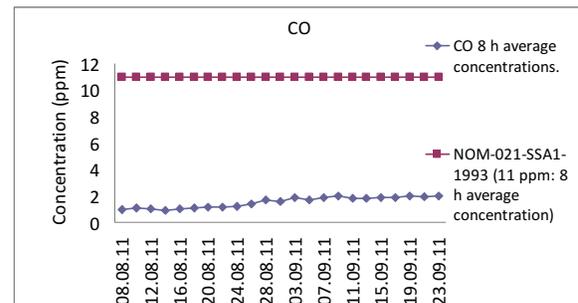


Fig. 7. Time-series for CO concentrations during the sampling period.

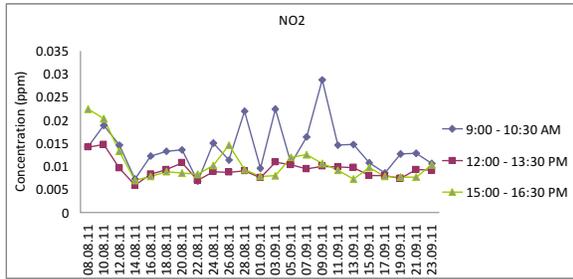


Fig. 8. Time-series for NO<sub>2</sub> concentrations during the sampling period.

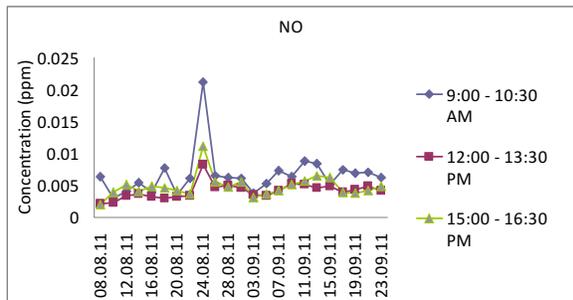


Fig. 9. Time-series for NO<sub>2</sub> concentrations during the sampling period.

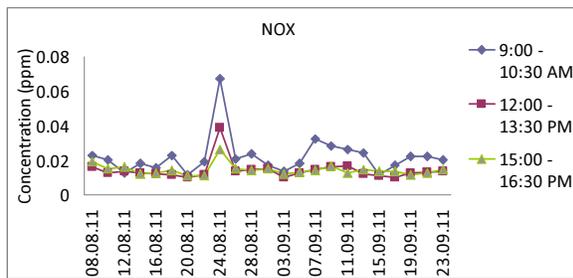


Fig. 10. Time-series for NO<sub>x</sub> concentrations during sampling period.

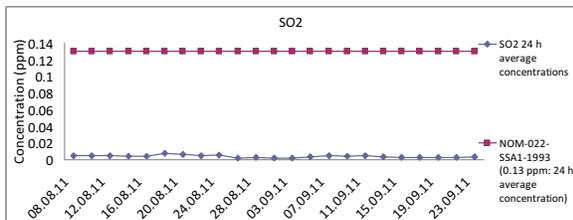


Fig. 11. Series time for SO<sub>2</sub> concentrations during sampling period.

Fig. 12 shows the behaviour of O<sub>3</sub> 1-h average concentrations during the sampling period. It can be observed that ozone concentrations were below the maximum permissible value established by the Mexican Air Quality Standard (0.11 ppm 1-h

average) [13]. These values are already approaching to the maximum permissible value, indicating that it is necessary to establish control policies in order to decrease ozone concentrations, otherwise MAM population health could be affected in a short time.

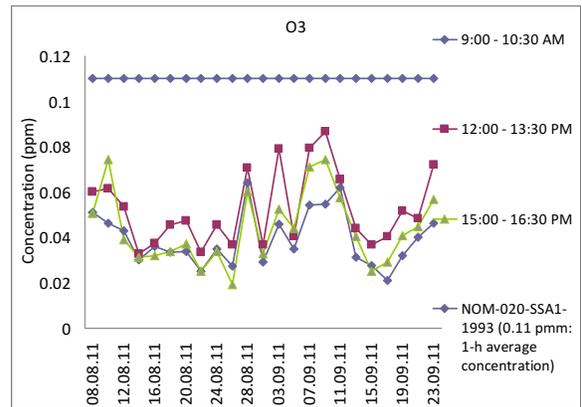


Fig. 12. Series time for O<sub>3</sub> concentrations during sampling period.

### 3.4. Benzene/VOCs ratios

The VOCs concentrations against benzene (Bz/VOCs) suggest a classifying of three groups of VOCs: those mainly are emitted from mobile emission sources, those mainly are emitted from stationary sources, and those comprising unstable compounds such as aldehydes and 1,3-butadiene. This technique constitutes a possibility of estimating emission sources using Bz /VOC ratios from environmental monitoring data, even when sufficient information on the emission sources are not available.

This is a common technique to infer the possible sources of VOCs [50], [25], [43], [47]. Bz/VOCs ratios higher than 1.0 indicate that the dominant sources in the study site are mobile sources and the vehicular traffic associated to them. As it can be observed in Table 2, only B/EB ratio for the midday sampling period showed values higher than 1.0, suggesting that the origin of the measured VOC's (AH) were possibly industrial sources and fugitive emissions.

Table 2. Benzene/VOCs ratios for each sampling period

SUMMER 2011					
B/EB	B/PX	B/EB	B/PX	B/EB	B/PX
B1	B1	B2	B2	B3	B3
0.85	0.57	1.01	0.78	0.87	0.83
B1: 09:00-10:30 h; B2: 12:00-13:30 h; B3: 15:00-16:30 h					
B: Benzene; EB: Ethyl benzene; PX: p-Xylene					

### 3.5. BTX/NO<sub>x</sub> ratios

Some studies have reported that these ratios are useful to determine if ozone formation is more sensitive to changes in VOCs emission than variations in NO<sub>x</sub> concentrations. Even this scale shows variations for different urban conditions and it must be carefully applied, it is broadly used to evaluate the importance of VOCs on tropospheric ozone formation [52]. Diurnal VOC's/ NO<sub>x</sub> ratios lower than 10.0 are representative of ozone formation sensitive to VOCs, whereas, values of this ratio higher than 20.0 correspond to ozone formation conditions sensitive to NO<sub>x</sub> [12].

Table 3 . BTX/NO<sub>x</sub> ratio for each sampling period.

B/ NO <sub>x</sub>	EB/ NO <sub>x</sub>	PX/ NO <sub>x</sub>	B/ NO <sub>x</sub>	EB/ NO <sub>x</sub>	PX/ NO <sub>x</sub>	B/ NO <sub>x</sub>	EB/ NO <sub>x</sub>	PX/ NO <sub>x</sub>
B1	B1	B1	B2	B2	B2	B3	B3	B3
1.03	1.30	2.12	1.06	1.17	1.66	0.67	0.88	1.42
B1: 09:00-10:30 h; B2: 12:00-13:30 h; B3: 15:00-16:30 h								
B: Benzene; EB: Ethyl benzene; PX: p-Xylene								

According to these ratios, the ozone formation in the study site seems to be more sensitive to VOCs variations than NO<sub>x</sub> changes. This rule does not consider the VOCs reactivity contribution, geographical variations or the severity of air pollution episodes. On the other hand, there is a geographical variation in the NO<sub>x</sub>-VOCs chemistry. It has been showed that rural areas are predominantly sensitive to NO<sub>x</sub> chemistry [12], and it is more probable that urban areas in big cities are more sensitive to VOC's chemistry related to local emissions. On the contrary, when there is air masses transport, the ozone formation chemistry tends to change toward "more sensitivity to NO<sub>x</sub>" [52].

### 3.6. Principal Component Analysis

Multivariate data analysis by Principal Components Analysis was used to study the variability pattern present in multivariate data set for the three sampling periods in the study site. Figs. 13-15 show the PCA loadings obtained for the morning, midday and afternoon sampling periods (B1, B2 and B3, respectively). In Fig. 13 it can be observed that there were some associations among compounds: a positive correlation between ozone and temperature was found, a relation among criteria pollutants and AH was identified, and a positive influence of the VOC's on ozone concentrations was found. All Aromatic hydrocarbons measured showed a positive correlation with temperature but this was not significant, indicating that maybe a little proportion of these compounds could be originated from evaporative emissions and that these compounds had mixed sources.

Relative humidity showed a negative correlation with ozone suggesting that this condition favours the atmospheric pollutants remotion by wet deposition or condensation [53-55]. Figure 14 shows a negative correlation between NO<sub>2</sub> with O<sub>3</sub>, suggesting that NO possibly react with O<sub>3</sub> to produce NO<sub>2</sub>. p-xylene and benzene had a marked positive correlation with temperature in the midday sampling period suggesting that as temperature increased VOCs concentrations increased too due possibly to volatilizations from oil stations.

VOCs showed a negative correlation with O<sub>3</sub> indicating that these AH suffered photochemical reactions to produce tropospheric ozone. It was found a close relation between CO and NO, suggesting that these compounds had common sources, probably vehicular emissions. It can be observed too a positive correlation among ethyl benzene, benzene and SO<sub>2</sub> indicating that these AH could be originated from industrial sources. Figure 15 shows the results of PCA for the afternoon sampling period. Ozone concentrations were positive correlated to relative humidity (RH), Temperature (T), NO<sub>x</sub>, NO, NO<sub>2</sub>, CO, SO<sub>2</sub>, p-xylene, and ethyl benzene. Benzene had a high correlation with temperature and a negative correlation with ozone. p-xylene probably contributed to ozone formation in a little proportion. Benzene possibly had mixed sources due to the fact that it showed a good relation with temperature, such as SO<sub>2</sub>. This indicates that this compound probably had its origin in fugitive emissions from evaporation process and industrial sources. Ethyl

benzene and p-xylene showed good correlations with NO and CO, suggesting that these compounds probably had their origin in vehicular sources. In this sampling period, a negative correlation between relative humidity and O<sub>3</sub> was found, suggesting that processes like wet deposition or condensation removed the air pollutants from the atmosphere. F1 and F2 factors showed a total variance of 61.83%, 47.46% and 55.58% on the measurements taken for B1, B2 and B3 sampling periods, respectively.

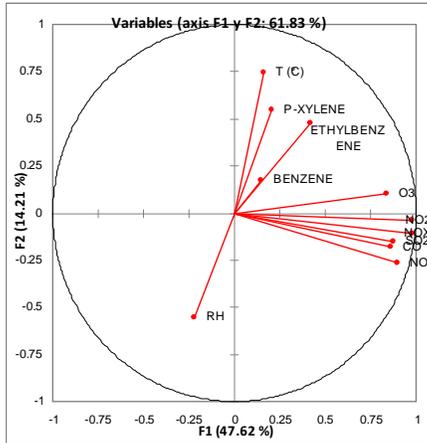


Figure 13. PCA for the morning sampling period (B1).

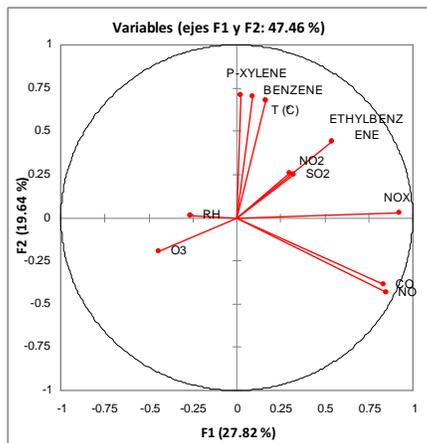


Figure 14. PCA for the midday sampling period (B2).

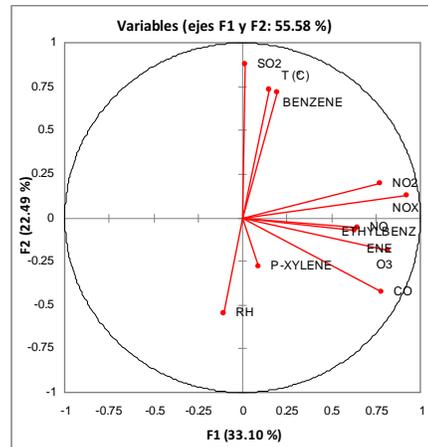


Figure 15. PCA for the afternoon sampling period (B3).

### 4 Conclusions

AH concentrations in this work showed values lower than those registered in other urban sites located in big cities around the world. There was a clear diurnal pattern in the AH concentrations showing the highest values during the morning and the lowest values during the afternoon.

From the meteorological analysis it was found that the prevailing winds blew from NNE, where Apodaca, Nuevo Leon municipality is located and where important companies and industries dedicated to produce lubricants, industrial additives, fertilizers, steel products, and so on are established. It can be suggested that all these industrial sources and the vehicular sources associated to the Apodaca-Dr. Gonzalez road could contribute to the AH concentrations found in this site during the sampling period. From the criteria pollutants time series, it can be concluded that population in MAM is not exposed to severe air pollution episodes since all the criteria pollutants showed values lower than the maximum permissible values requested by Mexican air quality standards. Benzene/VOCs ratios showed that in three sampling periods there was a contribution of mixed sources to the levels of AH (vehicular emissions, industrial sources and puntual sources) being more important the industrial activities one. VOCs/NO<sub>x</sub> ratios indicated that this site showed a greater sensitivity to VOCs changes than NO<sub>x</sub> variations in the potential to produce ozone. However, from the PCA it was found that during the morning ozone formation was more sensible to NO<sub>x</sub> concentrations, during the midday,

ozone formation showed greater sensitivitness to VOCs and during the afternoon, there was not a dominant pattern regards VOCs/NO<sub>x</sub> chemistry. Barletta et al. [52] have already reported uncertainties associated to the use of these relations in order to explain ozone formation mechanism. For this reason, it is necessary to propose additional criteria like the maximum incremental reactivity (MIR), the potential of ozone formation and other robust statistical methods to try to explain the ozone formation conditions in a specific site. We can therefore conclude that summertime monitoring of VOCs has special significance in the control of ozone precursors. However, in order to establish ozone control strategies, it is necessary to carry out intensive monitoring campaigns not only in this site and in the rest of the municipalities.

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