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Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere of Mexico City

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1. Introduction

Mexico City faces a severe atmospheric pollution problem, which directly affects the population's health. This problem is engraved by the geographic conditions of the city. Recent studies around the world have demonstrated an association between the presence of airborne particles and adverse effects to health (Brauer et al, 2001; de Koc et al., 2006). Significant differences exist in the chemical composition and size distribution of PM based on the wide range of sources, meteorological conditions, atmospheric chemistry, diurnal and seasonal factors. Also PM aerodynamic size has become a relevant element when studying PM toxicity due to its variable ability to penetrate the respiratory system; fine particles can reach the deep regions of the lungs, whereas coarse PM may be deposited early within the nasal-pharyngeal passages of the airways. Nevertheless, still remains an uncertainty about the physic and chemical mechanisms of these effects. Particles are composed by many different organic and inorganic species and some of these could be the main responsible of such adverse effects.

The chemical composition of the airborne particles includes inorganic species such as heavy metals and elemental and organic carbon compounds. Among these compounds, the polycyclic aromatic hydrocarbons (PAHs) are semivolatile species formed trough the fusion of two or more benzene rings by a pyrolitic process during the incomplete combustion of carbonaceous materials. PAHs can be found also in the atmosphere in the vapor phase, especially those species with low molecular weight and when temperature is high.

The main anthropogenic sources of PAHs are gasoline and diesel vehicle exhaust gases, use of natural gas, LP gas and carbon, oil combustion, petroleum refining and waste incineration. Anthropogenic combustion of wood and forest fires is also important sources of PAHs (Freeman & Catell 1996). Some of these PAHs have a significant role on the mutagenic activity of airborne particles and some of them have been classified as carcinogenics for humans (IARC, 1984; Sanderson et al., 2000, NPT, 2005): benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k[fuoranthene, chrysene, dibenzo[a]anthracene and indeno[1,2,3-cd]pyrene. PAH derivatives such as nitroPAHs, chlorinated PAHs and oxyPAHS, which can be emitted directly from anthropogenic sources

or formed in the atmosphere by secondary reactions of PAHs usually present higher mutagenic activity than their PAH parents due probably to their higher polarity (Ohura, 2007). The human health risk associate to PAHs and their derivates is higher in the urban atmospheres considering the high population's density (Harrison et al., 1996).

Mexico City lies on an elevated plateau at 2200 meters above mean sea level, with mountains on three sides, as consequence, has complex mountain and surface-driven wind flows with predominant winds from the north-northeast; in this sense, it must be remarked that most of its industries are located precisely within the northern zone (GDF, 2005). These winds transport significantly large amounts of air pollutants emitted by industries, such as uncharacterized gaseous emissions from ferrous and non-ferrous smelting and heat-treating facilities, glass manufacturers, bricks and ceramic factories, and thermoelectric power plants. Also at the north, close to Mexico City Area, there is a large oil-refining facility located in the Hidalgo State. More than four million of vehicles. The urban area of Mexico City has more than twenty millions of inhabitants, which are exposed to the emissions from 4,000,000 of vehicles and around 30,000 industries.

In the last decade, several studies have been carried out to determine the presence of PAHs in the atmosphere of Mexico City. Velasco et al. (2004), measured real time total particles' PAHs concentrations, and Marr et al. (2004, 2006) conducted studies to determine the total PAH emission factors associated to vehicles, and to understand the atmospheric PAHs transformations; nevertheless the authors did not report detailed information on individual PAHs characterization. Villalobos-Petrini et al (2006, 2007) related the mutagenic activity with atmospheric PAH´s concentrations in PM_{10} and Amador-Muñoz (2010) studied the PM size distribution of PAHs at the Southwest of Mexico City. Considering the importance of PAHs individual speciation, Mugica et al. (2010) conducted a whole year study to characterize and evaluate the seasonal behavior of PAHs in the gas phase and PM_{10}.

The main objective of this chapter is dedicated to the review of the campaigns and studies realized in Mexico City during the last years related with the quantification and speciation of PAHs, by the group dedicated to atmospheric chemistry at the Universidad Autónoma Metropolitana-Azcapotzalco. Sampling and analysis methodologies, as well as new findings and unpublished material have been included to enrich this review.

2. Methodology

The U.S. Environmental Protection Agency (USEPA, 1985) has identified 16 unsubstituted PAH as priority pollutants (Figure 1).

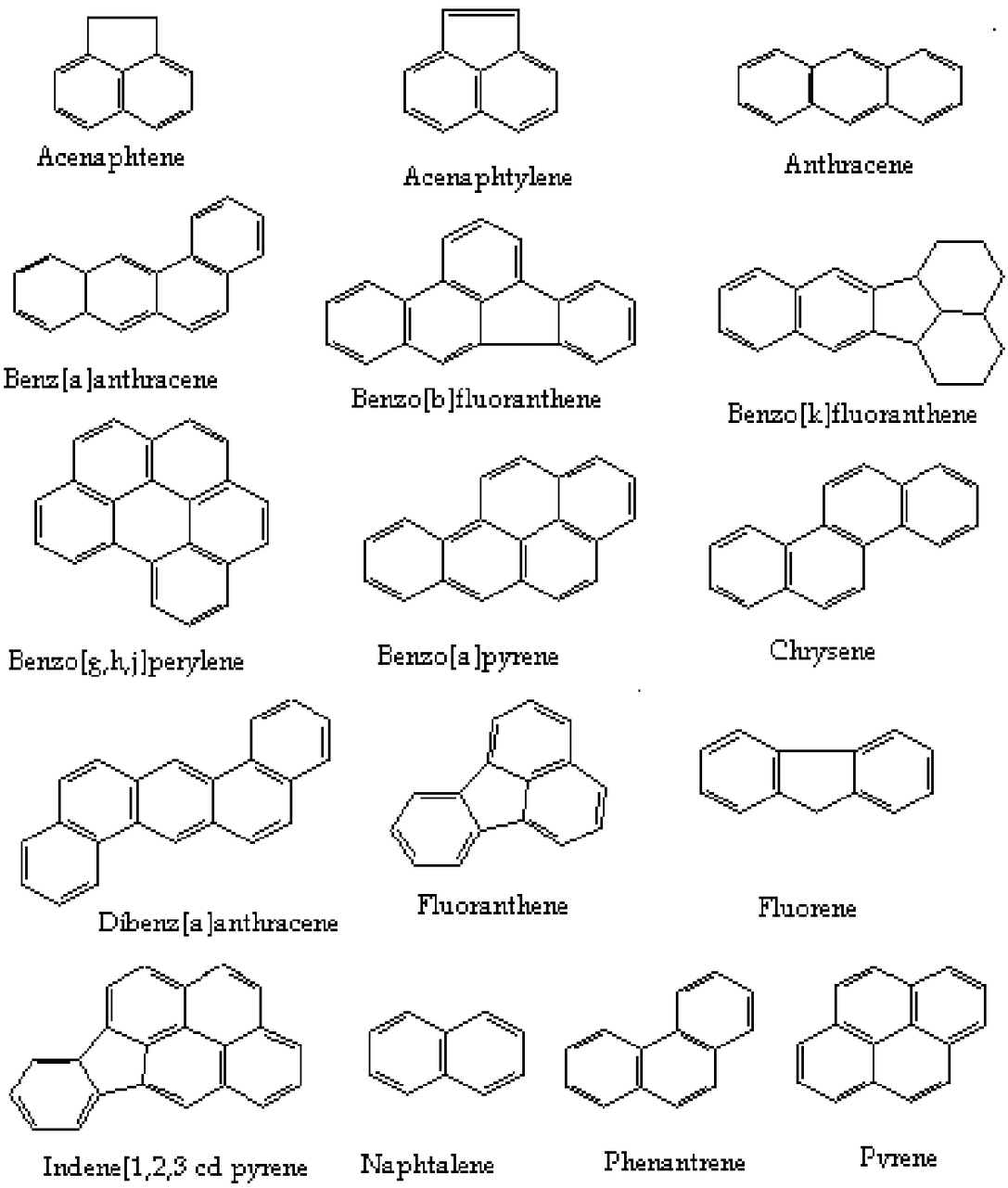

Fig. 1. Priority PAHs according to USEPA.

2.1 Sampling

The 2003 and 2005 sampling campaigns were carried out at the monitoring station of the Metropolitan Autonomous University, Campus Azcapotzalco (UAM-A), located at the North of the city, where the surrounding urbanization displays a mixed land occupation composed by housing and industrial areas. High volume samplers were located around six m above ground level and 230 m away from an avenue.

On the other hand, during the 2005 field campaign other three sites were selected for monitoring in order to have more information about the variation of PAHs contained in PM_{10}. These sites were the monitoring stations of Xalostoc at the Northeastern located in a huge industrial area, Merced is located close to downtown of Mexico City with many avenues with heavy and light traffic and Pedregal is located at the Southwest in a commercial and residential area. These three stations belong to the Monitoring Network of Mexico City. These places were selected since they have been representatives of other monitoring campaigns realized in Mexico City (De Vizcaya et al, 2005).

The 2006-2007 campaign was carried out from April 2006 to March 2007 within Centro de Investigación y de Estudios Avanzados (CINVESTAV, from its Spanish initials), in northern Mexico City. This site is neighboring some important state municipalities bearing intense industrial activities, and it is also surrounded by important main roads with large transit volumes, connecting northern and central regions of the metropolitan area.

In general, Mexico City climate is temperate with little humidity, namely an annual rainfall of 651.8 mm, average annual temperature of 17 °C, 3.1 $m \cdot s^{-1}$ average wind velocities with prevailing northerly winds. Three seasons are recognized in Mexico City by the Monitoring System of Air Quality in Mexico City (GDF, 2005): the warm-dry season (from February to May), the rainy Season (From June to September) and the cold-dry season (from October to February).

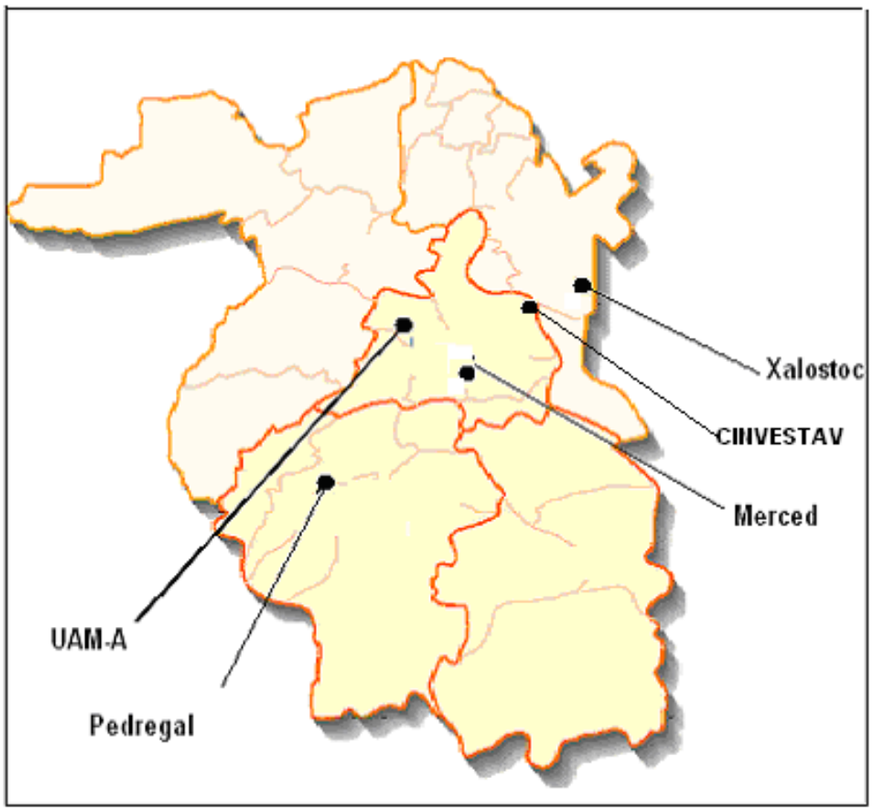

Fig. 2. Sampling Sites in the Mexico City Metropolitan Area.

Figure 2 shows the different sites where field campaigns have been performed with the aim to determine the levels of PAHs in the atmosphere of Mexico City.
The integrated 24 hr samples of PM_{10} and $PM_{2.5}$ were collected every six days with the aid of Andersen and Tisch high volume samplers, using 20 x 25 cm Whatman quartz fiber filters, previously stabilized at 550°C during 24 h to remove organic matter. The vapor phase PAHs was collected into sorbent polyurethane tubes containing 50 g of XAD-4 resin located between two polyurethane foams (PUF) using a Tisch-PUF sampler. PUFs were cleaned and compress-cleaned three times using a hexane: methanol: methylene chloride (5:3:2v/v) mix, whereas the XAD-4 resin was cleaned with sonication plus water, methanol and methylene chloride rinsing. The Temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD) were obtained from the nearest monitoring station located at 2 Km of the monitoring site (Tlalnepantla) of the Automatic Monitoring Net in Mexico City (*RAMA*, for its Spanish initials). (http://148.243.232.103/imecaweb/base datos.htm).

2.2 Extraction and analysis

PAHs were extracted from the filters and XAD4/PUFF by immersing them in an ultrasonic bath using acetonitrile/dichloromethane 1/1 v/v, for three 10 min periods. The extracts were concentrated down to 5 mL with a rotavapor followed by evaporation under purified nitrogen to near dryness and reconstituted with acetonitrile. The resulting solution was filtered to clear impurities. Finally the extracts were transferred to small amber glass vials that were sealed and stored in darkness at -18 °C until analysis.

PAH	Code	MW
Naphtalene	NAP	128
Acenaphtylene	ACY	152
Acenaphtene	ACE	154
FluorenE	FLU	166
Phenantrene	PHE	178
Amthracene	ANT	178
Fluoranthene	FLT	202
Pyrene	PYR	202
Benz[a]anthracene	BAA	228
Chrysene	BKF	228
Benzo[b]fluoranthene	BBF	252
Benzo[k]fluoranthene	CRY	252
Benzo[a]pyrene	BAP	252
Indene [1,2,3-cd] pyrene	DBA	276
Dibenz [a,h] anthracene	IND	278
Benzo [ghi] perylene	BGP	276

Table 1. Identification of quantified PAHs.

Identification and quantification was performed through GC/MS (GC model HP 6890, MS model 5973 equipped with a quadrupole mass filter and autosampler) using a 60-m 0.25 mm diameter HP-1701 capillary column (0.25 m film thickness HP). The temperature program applied was 65°C for 2 min, then 8°C/min to 320°C, held for 10 min. Fluoranthene d10 was added as internal standard according to Method TO-13A. A standard PAHs mixture was used for quantification PAHs (Table 1).

For quality control, filters and sorbent tubes were wrapped with aluminum foil and stored in the dark with refrigeration down to -18° C until sampling was to be carried out. All of the filter and PUF samples were transported to and from the field in a cooler and kept refrigerated until analysis. To address artifact contamination, a field blank for both quartz filters and PUF cartridges was collected and analyzed. As a quality control, the urban dust standard reference material (SRM 1649a) from the National Institute of Standards and Technology (NIST) was used to evaluate all PAHs mean recovery efficiency; this varied from 76% to 87.5% (ACY and BGP) from the extracted 100 ng of urban dust, subtracting of course, the field blanks filters from the sample values.
The precision and bias of the PAHs analyses were determined from quality control check samples prepared in the laboratory with fluoranthene d10 (FLUd10). Each PAH measurement was replicate eight times.
Mid-range standards (0.5 ng/L) were also run during each day of the sample analysis to verify the initial calibrations.

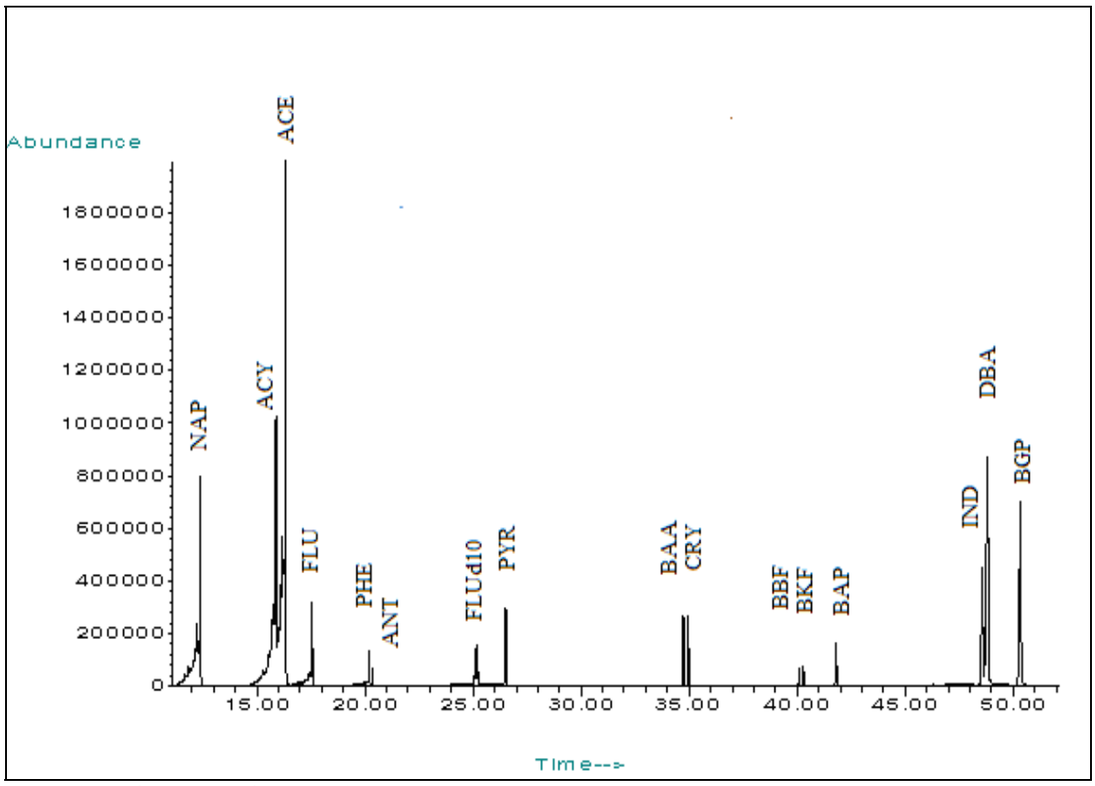

Fig. 3. Identification of PAHs by GC-MS

Precision values in percent relative standard deviation (%RSD) were: NAP (5.4), ACY (4.6), PHE (4.4), BAP (3.8), BBF (5.1), BAA (4.7), FLU (6.1), FLT (6.3), PYR (4.4), CRY (4.3), BKF (5.1), DBA (4.9), IND (4.3), and BGP (3.7). The biases in the same order were: 0.23, 2.39, -2.3, 3.4, 2.5, 2.4, -3, 0.56, 0.22, -1.24, -0.72, 1.6, -2.3, and 0.11 percent.
Figure 3 shows a typical chromatogram for individual PAH identification and quantification.

3. PAHs in Mexico City

In this section the most important results of the different campaigns carried out for the group of Atmospheric Chemistry of the Universidad Autónoma Metropolitana are presented and discussed.

3.1 First Findings of PAH in Mexico City

The first study related to PAHs conducted at the Universidad Autónoma Metropolitana-Azcapotzalco, was carried out with the aim to standardize the sampling and PAH quantification techniques. Hi-Vol equipments (Metal Works) with fiber glass precalcinated filters were used to collect atmospheric particles, during November and December of 2003.
The results of this study showed that the average of the total sum of the 12 quantified PAHs was 15.91±4.22 ng/m^3, with a maximum and a minimum of 20.77 and 11.04 ng/m^3 respectively (Figure 4); these concentrations were similar to those reported in Birmingham at the United Kingdom (Harrison et al 1996), in Naples, Italy (Caricchia et al, 1999), and Oporto and Vienna (Rocha et al, 1999).
Although naphthalene, acenaphtene, acenaphtylene and anthracene were quantified, they are not presented since during the sample manipulation, these compounds could be evaporated.

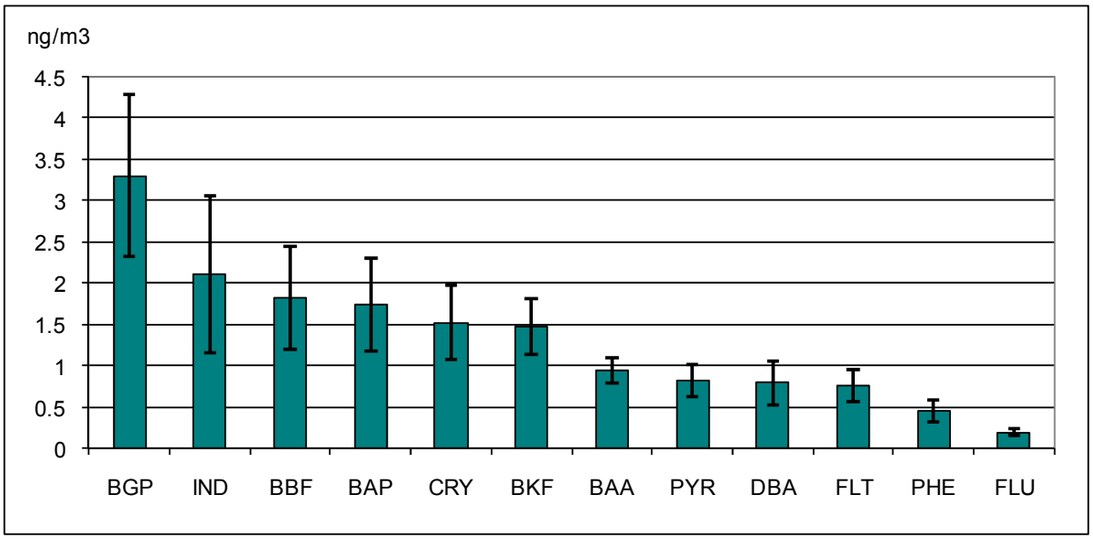

Fig. 4. PAH concentrations in PST (November and December 2003).

High molecular PAH were the most abundant species in PM. The highest concentration was presented by BGP followed by IND, BBF and BAP, which have been associated with vehicle emissions (Dichut et al, 2000). Most abundant compounds have low vapor pressures. The percentage of the seven potential carcinogenic PAHs ranged between 54 and 65% of the total PAH mixture.

It has been reported that FLT/FLT+PYR ratios below 0.40 imply the contribution of unburned petroleum and ratios between 0.40 to 0.50 suggest their emissions from the combustion of liquid fossil fuels (vehicle and crude oil), and ratios larger than 0.50 are characteristic of wood, or coal combustion (Yunker, 2002). The averge ratio (0.48) obtained in this campaign is indicative of combustion of liquid fuels, such as gasoline and diesel. On the other hand, when the ratio of IND/IND+BGP is lower than 0.2 imply petroleum emissions, if the ratio ranges 0.20-0.50 imply liquid fossil fuel combustion (Yunker, 2002), as is the case again since the obtained ratio is 0.30.

3.2 Temporal and spatial variations of PAHs associated with particles in Mexico City

A big field campaign was performed from February 2005 to January 2006 collecting 50 integrate samples at the UAM-A in Mexico City to determine the seasonal variation of PAHs contained in the vapor phase and in PM_{10} (Mugica et al, 2010). On the other hand, nine samples were collected at each of the other three monitoring sites: Xalostoc, Merced and Pedregal (three samples every season) in order to know the spatial variation of PAHs associated to PM_{10}.

The particle phase contributed with only less than 0.01 % of the total mass of PAH. High molecular PAH such as BBF, BKF, IND, DBA and BGP were found predominantly in the particle phase, whereas, as expected, light PAH of two, three and four rings, NAP, ACY, FLU and PHE were mostly in the vapor phase. Semivolatile PAH, PYR, BAA, CRY and BAP were observed in both phases.

Marr et al (2006) have reported that concentrations at different sites of the city are very variable, and this is the situation of the results found at the different locations. Figures 5, 6 and 7 show the average levels of the individual PAHs measured in PM_{10} in the different campaigns carried out during 2003. Highest concentrations were measured at Xalostoc that is the most important industrial area in the metropolitan area of Mexico City. In this site the sum of the 12 PAHs reached up to 105 ng/m^3 during the dry-cold season. The lowest values were found at UAM-A, although this could be due to more samples were collected and more holidays and different meteorological conditions occurred during the campaign, in addition the University has many trees and big green areas which can capture an important proportion of atmospheric particles.

In the dry-cold season the levels of total measured PAHs were up to three fold greater than in the other seasons, and the smallest PAHs measured concentrations were in the dry-warm season. These results may be explained by the fact that during the dry-cold season, temperature inversions and calm winds, occurring very often during the fall and winter, which favors air pollutants´ increase in Mexico City´s atmosphere. Further, during this season the main winds come from the North where the most important industrial area is located. The highest temperature and solar radiation values occurred during the warm-dry season and the lowest values in the cold-dry season, when the solar zenith angle is around 43^o. It is expected a PAHs' maximum evaporation as well as photochemical activity from PAHs to oxydated PAHs and nitro-PAHs in the months with greater actinic fluxes, which

happen at the end of winter through spring; this fact could explain the lower PAHs levels in the warm-dry season in comparison with the other seasons. The seasonal variability of PAH concentration in the atmosphere has been reported for other cities such as Los Angeles (Eiguren, 2004).

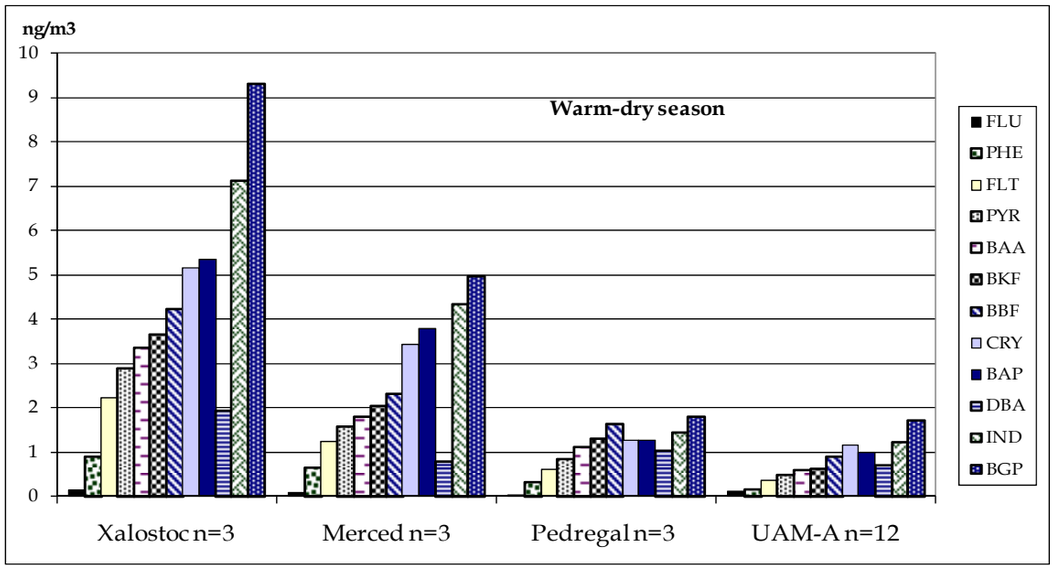

Fig. 5. Concentrations of PAHs at different locations in the warm-dry season.

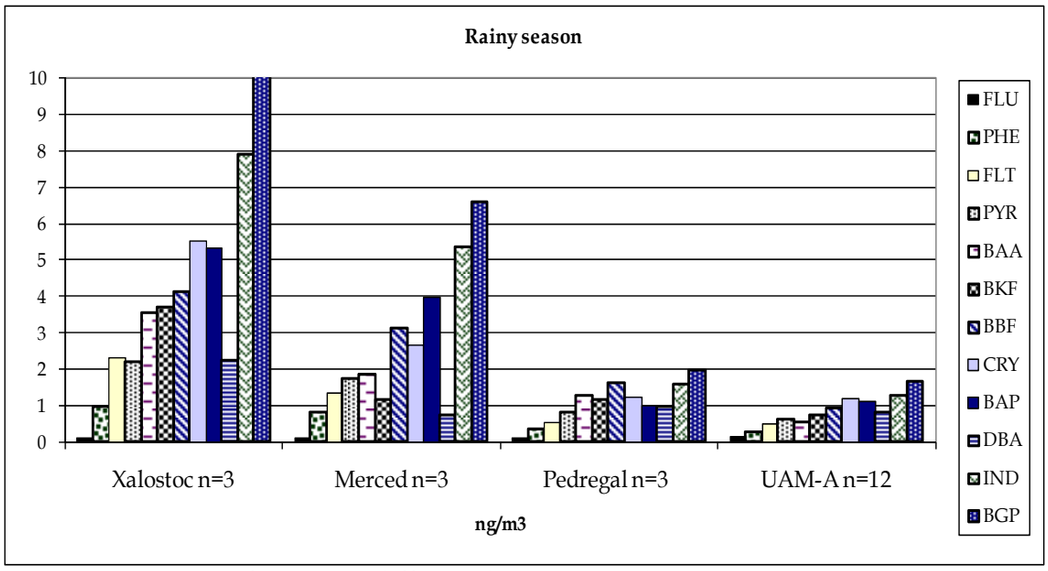

Fig. 6. Concentrations of PAHs at different locations in the rainy season.

Amador-Muñoz et al (2010) quantified in 1999 the PAH concentration at the National University of Mexico, which is located pretty close from the Pedregal site. The concentrations found in this study are a little higher to those found by these researchers although the University area has many green areas which can diminish the PM concentrations. Besides, this study is in agreement with the results reported by Guzmán-

Torres et al. (2009), where PAHs associated with PM_{10} were determined in 2003 at two of the sites sampled in this study: Merced considered as a source site and Pedregal considered as a receptor site. In that study, was determined that higher PAH concentrations are observed during the morning from 5:00 to 13:00h, whereas the lowest concentrations were found from 13:00 to 21:00, at the two sites.

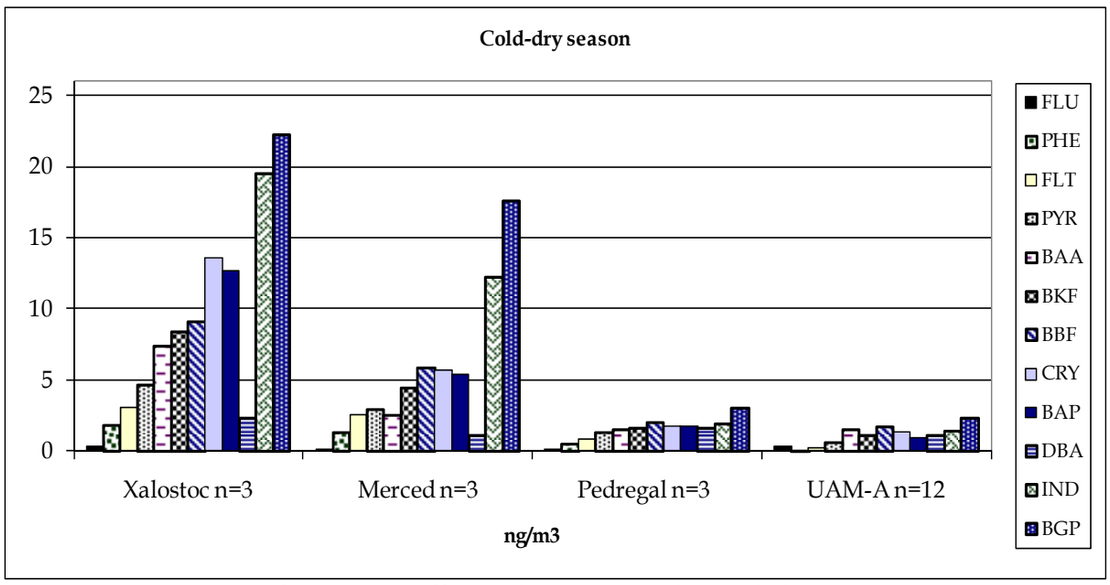

Fig. 7. Concentrations of PAHs at different locations in the cold-dry season.

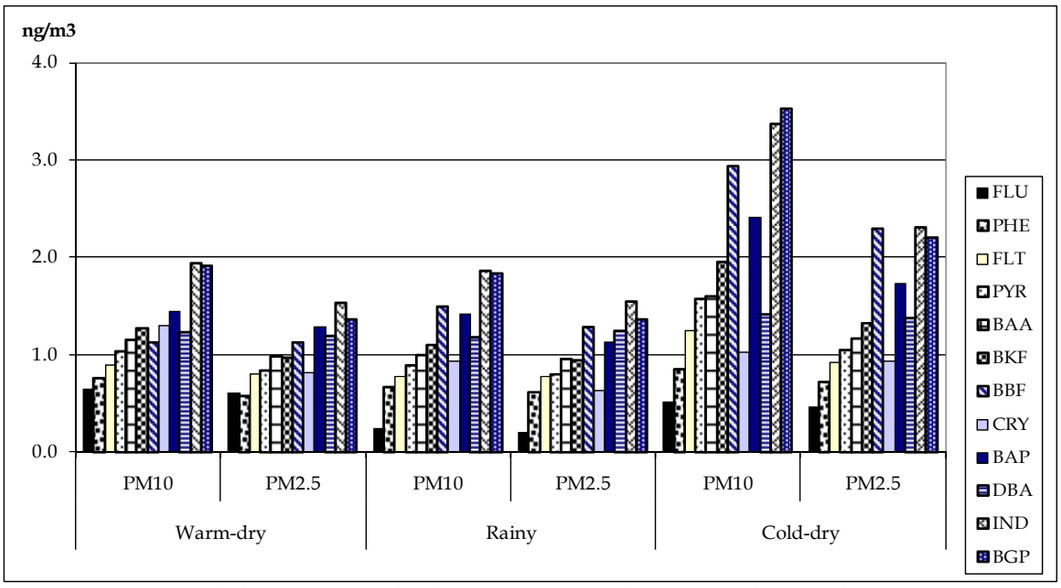

Fig. 8. Comparison of the content of PAHs in PM_{10} and $PM_{2.5}$ at CINVESTAV site.

The last campaign was conducted from April 2006 to March 2007 at the CINVESTAV. In this campaign, not only were determined the PAHs contained in PM_{10} but also in $PM_{2.5}$. Figure 8 shows the comparison of the content of PAHs in both sizes of airborne particles. The

average ratio between $PM_{2.5}/PM_{10}$ was 0.82, 0.86 and 0.74 for the warm-dry, rainy and cold-dry seasons respectively. In general, low molecular PAHs had a higher ratio than high molecular PAHs.

3.3 Temporal variations of PAHs in the vapour phase in Mexico City

Table 2 shows the average temperatures and relative humidity observed during 2005 in the UAM-A site. These values explain the concentrations of PAH in the vapor phase presented in the Figure 9. Due to its high abundance, naphthalene was eliminated from the graph, but its average concentrations were 149±89, 28±5 and 78±28 ng/m^3, for warm-dry, rainy and cold-dry seasons respectively.

	TEMPERATURE °C				RELATIVE HUMIDITY			
	Mean	**S.D**	**Max**	**Min**	**Mean**	**S:D**	**Max**	**Min**
Warm-dry	18.5	5.1	29.9	8.0	51.0	16.9	82.9	19.9
Rainy	17.6	3.8	27.3	11.4	72.0	13.7	93.4	40.9
Cold-dry	13.2	3.9	23.2	4.7	55.9	16.3	92.5	23.3

Table 2. Temperature and Relative Humidity in Mexico City in the three seasons

Two and three-ringed PAHs (naphtalene through anthracene), were found almost exclusively in the vapor phase. The four, five and six-ringed PAHs FLT to BGP) were distributed in both phases.

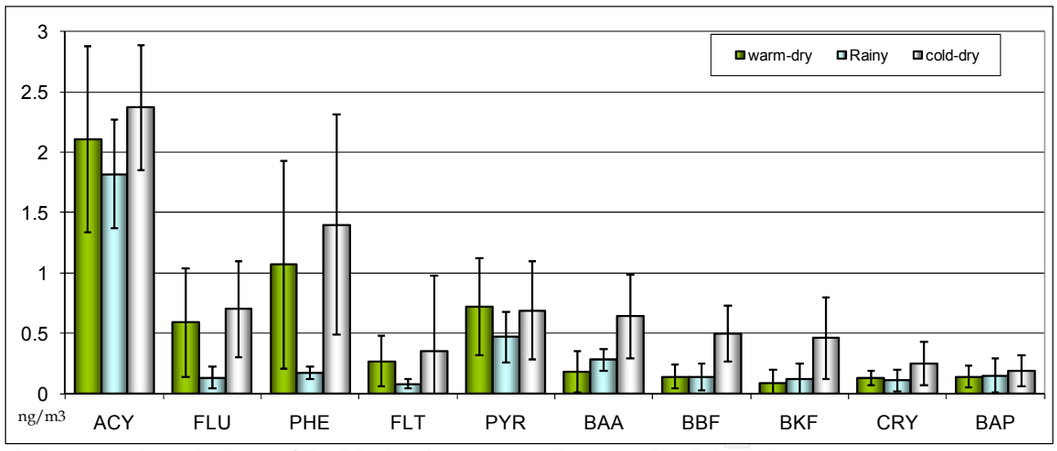

Fig. 9. Seasonal variation of PAHs in the vapor phase at UAM-A site.

The gas/particle partitioning of these compounds is affected by the physicochemical characteristics of the aerosol (chemical composition, particle size, surface area) and the ambient conditions (temperature, pressure). Table 3 shows the seasonal variability of the gas-particle partitioning through 2005 as well as their vapor pressure (USEPA, 1997). As expected, due to the elevated temperatures, the highest gas/particle ratio was attained during the dry-warm season, although the gas-partitioning ratio of most of the PAH considered was lower for the rainy season than for the dry-cold season, despite of minor

temperature during the latter, showing that other factors different from temperature have an influence on the gas-particle partitioning, such as the relative humidity and vapor pressure of PAH, among other factors as reported previously (Bae et al, 2002).

PAH	Vapor pressure KPa	Dry-warm	Rainy	Dry-cold
FLU	$8.7x10^{-5}$	5.9	1.7	2.3
PHE	$2.3\ x10^{-5}$	13.52	3.12	5.45
PYR	$3.1x10^{-6}$	2.07	1.85	1.19
FLT	$6.5x10^{-7}$	2.28	0.77	1.4
BBF	$6.7x10^{-8}$	1.01	0.52	0.41
BKF	$2.1x10^{-8}$	0.79	0.57	0.43
BAA	$1.5X10^{-8}$	1.06	0.63	0.40
CRY	$5.7X10^{-10}$	0.54	0.41	0.18
BAP	$7.3x10^{-10}$	0.58	0.53	0.24

Table 3. Gas-particle partitioning of semivolatile PAH ng/m^3vapor/ng/m^3PM. (Mugica et al, 2010)

4. Back trajectory analysis

This study was performed for the 2005 campaign although there are many similarities with the other years. Meteorological conditions varied along the year, the dry season runs from the middle of October to the beginning of May and is characterized by almost daily temperature inversions and high speed winds, producing an increase in air pollutants in the boundary layer. As often is the case, during the dry-warm season some fires were reported and the predominant high speed winds that originate from the south-east of 5.5-10.8 m s^{-1}, favored the pollutant's dispersion; consequently the PM concentrations in 2005 were lower than those registered other years, incidentally lower than in the rainy season, where winds originated mainly from the east with WS of 1.6 a 5.5 m s^{-1}. Finally, during the dry-cold months the predominant winds came from the north and northeast, with 0.3 to 1.6 m s^{-1}, compared with the spring and summer months, the high stability of the air mass reduced the rates of pollutant dispersion. With the aim to know the relationship between the average concentrations and wind directions, PAH were associated with the corresponding air mass back trajectories calculated by the NOAA HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) (Draxler and Rolph, 2003). Air mass back trajectories were estimated for 1000 and 3000 meters above ground level. NOAA trajectories were calculated for year 2005. The 1000 MAGL (Meters above Ground Level) level was used because storm cloud bases frequently lie around 1000 MAGL. The 3000 MAGL level is about 1200 m higher than the highest mountain summit lying Mexico City; It is also close to the height of the 500 millibar (mb) isobaric surface (one of the mandatory levels in meteorological analysis).

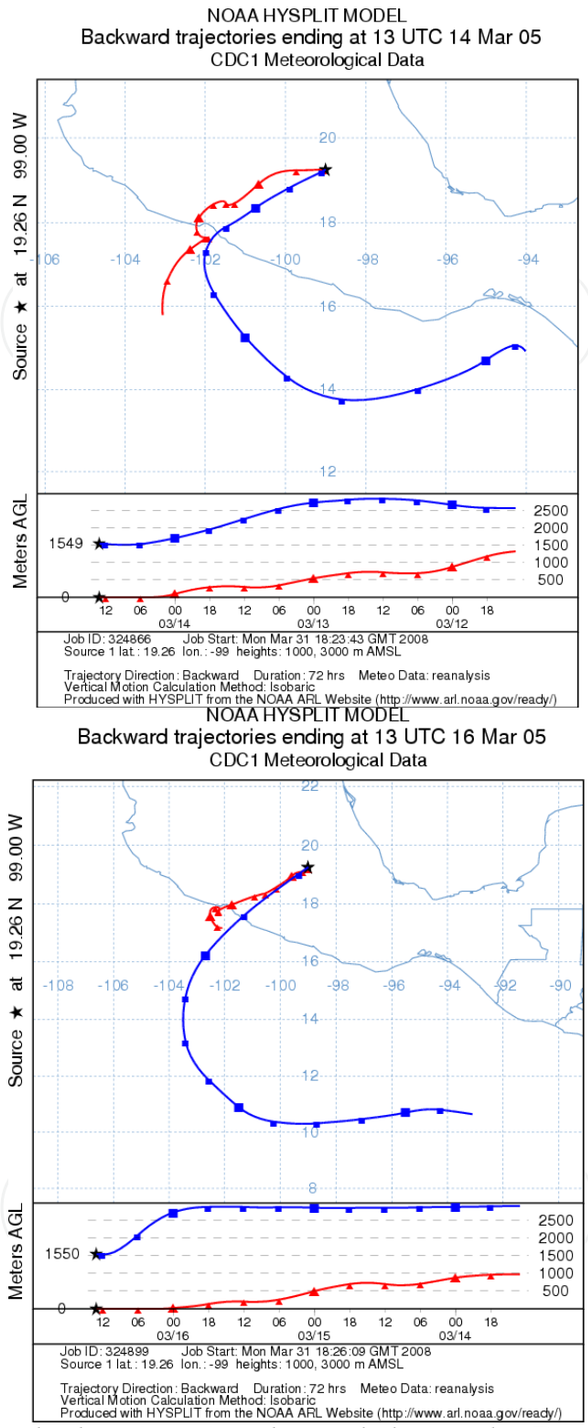

Fig. 10. Some air-mass back trajectories observed during the Dry-warm season in 2005 corresponding to 1000 and 3000 MAGL.

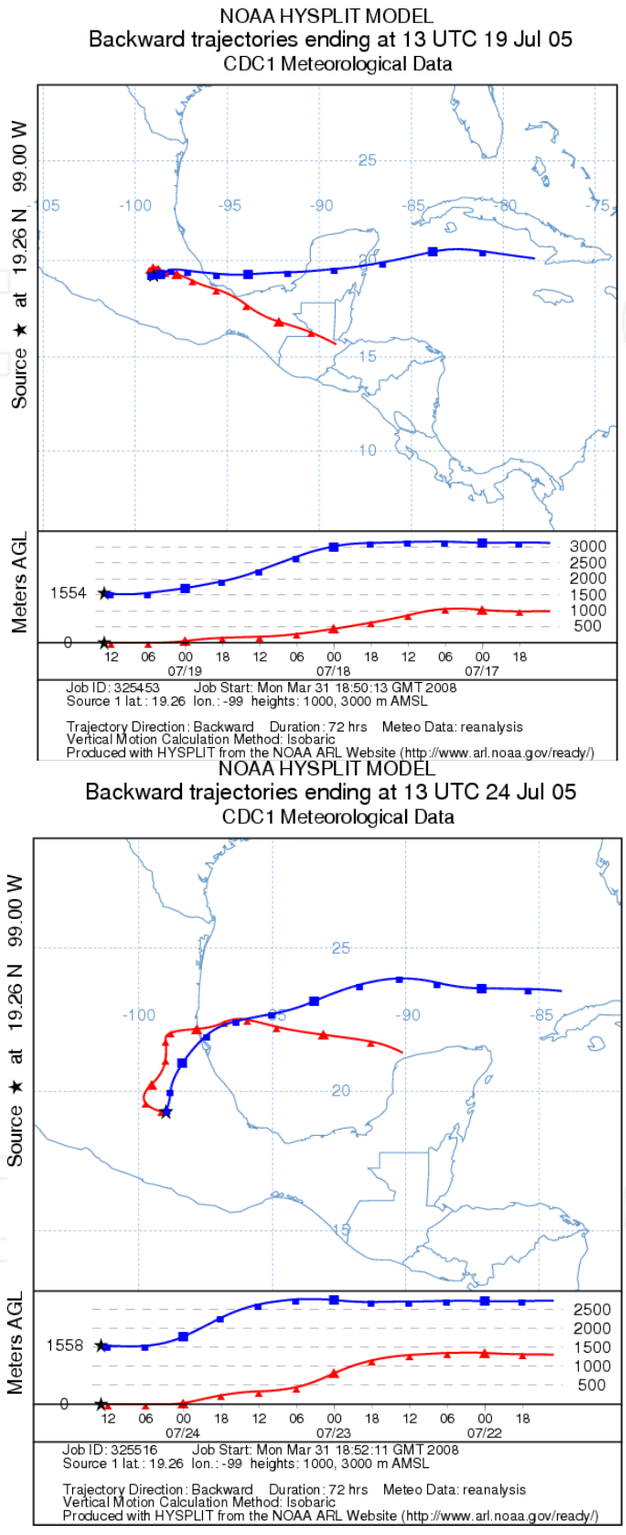

Fig. 11. Some air-mass back trajectories observed during the rainy season in 2005 corresponding to 1000 and 3000 MAGL.

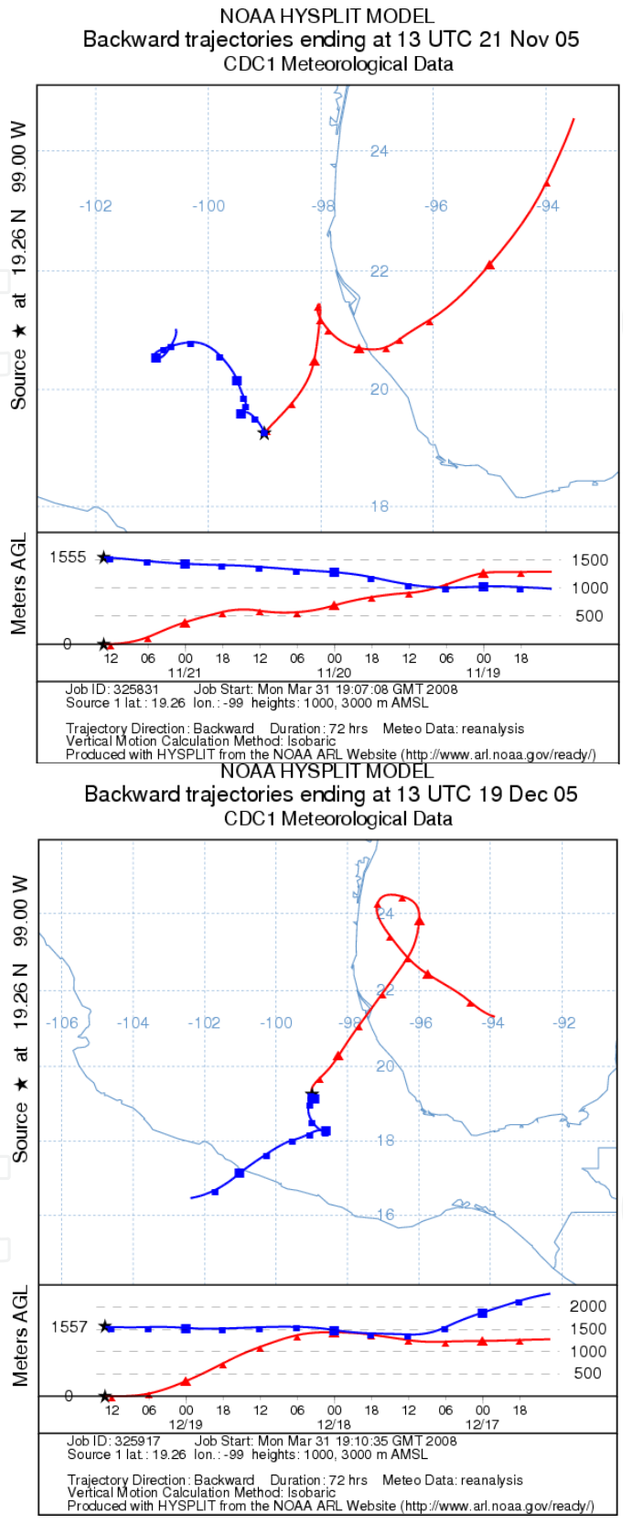

Fig. 12. Some air-mass back trajectories observed during the Dry-cold season in 2005 corresponding to 1000 and 3000 MAGL.

Figures 10, 11 and 12 show an example of six trajectories chosen at random because it would be excessive to show all the trajectories. Since Mexico City is the subject of intense anthropogenic emission sources. Figure 10 shows the air mass back trajectory analysis during the dry-warm season along 2005. Trade winds have a consistent component from the west and during this season the winds blow mostly along south and southeast. There was also a reasonably good correspondence with the physical characteristics on the sampling site. Since the University site is surrounded by intense anthropogenic emission sources, Figure 11 shows some examples of air mass back trajectories randomly selected during the rainy season when winds bear eastern directions. The average of PAH decreased in the order NAP, ACY, FLU, PYR, FLT, BAA, BAP and BGP at 1000 and 3000 MAGL.

Figure 12 shows the analysis at 3000 MAGL for the dry-cold season, where large extensions of barren soils lie. An attempt was made to associate these PAH concentrations with surface wind.

The concentration of major PAHs in PM_{10} were presented when back trajectories indicated winds from the North and Northeast where most of the industrial areas are situated, and this, in addition to the atmospheric stability of this season explain the high concentrations of particles and total PAH found. This agree with the synoptic meteorological conditions that prevail in Central Mexico (MC) during the dry-cold; trade winds have a consistent component from the East, that is, winds blow between North and Northeast most of the time during this season.

5. Source identification applying statistical analysis

StatSoft 6.4 program was used to calculate Principal Component Analysis (PCA). With this analysis is possible to identify possible sources of pollutants and to validate the method applied, following the criteria described by other authors. Table 4 shows the factor loadings normalized with the VARIMAX rotation, which maximizes the variances of the squared normalized factor loadings across variables for each factor. The greater the loading of a variable the more that variable contributes to the variation accounted for the particular Factor or Principal Component (PC). In general only loadings greater than 50% are selected for PC interpretation[25]. This is one of the methods mostly used for source identification.

The PCA applied to PAHs, revealed three factors that explained the 72.76% of the total variance. These factors indicate their major role on the total variance, when PCA is applied through the linear combination of twelve PAHs and represent the source categories. The first factor is the most important, given the explained variance of 34.91%. The main tracers of this factor are mostly associated to low molecular weight PAHs, namely, ACY, FLU, PHE and FLT, which could be associated mainly with diesel source emissions, since Wang et al., (2007) indicated the dominance of diesel combustion with the presence of three and four ring PAHs (such as FLT and PHE), as well as with oil combustion. Large emissions from diesel could be related also with the high concentrations of CRY which has been suggested as a diesel tracer (Simcik et al. 1999; Fujita et al. 2007).

The second factor was mostly associated with high molecular weight PAHs accounting 23.66% of the total variance. CRY,BAP, BBF, BKF, IND and BGP can be related to gasoline vehicles. Some researchers have found that IND and BGP are gasoline tracers (Harrison et al, 1995; Miguel et al., 2004).

The third factor was characterized by CRY and BAP which has been related with wood burning, diesel and meat cooking (Rogge et al., 1991, Kulkani and Venkataraman, 2000).

Variable	2005, 2006, 2007. PM_{10}		
	Factor 1	Factor 2	Factor 3
mass	0.143	**0.60**3	0.304
NAP	0.352	0.143	**0.832**
ACY	**0.967**	0.212	0.165
FLU	**0.847**	0.009	0.048
PHE	**0.798**	0.142	0.054
FLT	**0.843**	0.251	0.077
PYR	0.217	0.187	0.316
BAA	0.233	0.393	0.088
CRY	**0.579**	**0.754**	**0.922**
BAP	**0.749**	**0.648**	**0.634**
BBF	0.025	**0.792**	0.212
BKF	0.043	**0.748**	0.137
IND	0.085	**0.572**	**0.738**
DBA	0.239	0.217	**0.823**
BGP	0.154	**0.881**	0.250
% Total Variance	34.912	23.662	14.183
% Accumulated Variance	35.381	58-574	72.757

Table 4. Principal Component Analysis for PM_{10} in Mexico City. Bold numbers are significant at > 0.5.

6. Health implications by the presence of PAHs in Mexico City

The percentage of the seven potential carcinogenic PAHs found in the TSP collected in 2003, ranged between 54 and 65% of the total PAH mixture, whereas in the campaigns conducted in 2005 the seven carcinogenic PAHs represented between 61 and 73% of the total mixture of PAHs in PM_{10}. The carcinogenic PAHs contained in $PM_{2.5}$ ranged between 65 and 68% with higher percentages in the cold dry-season during 2006-2007. If we estimate the daily potential dose of carcinogenic PAHs considering an intake of 20 m^3 of polluted air, the average results to be between 123 ng/m^3 and 1460 ng/m^3 as can be appreciated in Table 35. These high values show that the population of Mexico City is exposed to high concentrations of potential carcinogenic species, especially those who live at the Northeast close to Xalostoc.

The European Union has proposed for the PM_{10} fraction, a maximum permissible risk level of 1000 pg/m^3 of BAPeq calculated for one year calendar, to be achieved in 2010 (European directive, 2004). To calculate the inhalation unit risk for excess lung cancer over the risk posed by BAP for each of the other carcinogenic PAHs in the polluted atmosphere, the particular PAHs risk is divided by the risk of BAP to obtain their individual toxic equivalence factor /TEFs). Thus, the TEF for BAP is for definition 1.0. These TEFs can be used to estimate the relative carcinogenicity of the PAH mixture when concentrations of individual PAHs are known. The concentrations of each individual PAH are multiplied by the TEF to obtain the BAPeq values. Table 6 presents the estimated BAPeq values by site using the factors proposed by Nisbet & Lagoy factors (1992), where is evident that in all the

sites the annual average of BAPeq, which represents the carcinogenic potential of inhaled PAHs, is exceeded, especially in Xalostoc and Merced locations where the values are almost eleven and six folds higher than the proposed standard respectively. BAP alone contributes to carcinogenic potency in PM_{10} with 63 to 71%, underlying the importance of this compound. These results suggest that the inhabitants of those municipalities could be in a high-risk category for developing cancer. Taking in account this information the policy makers could review the airborne particles regulation and consider the recommendation of a similar standard than the European Community.

STUDY/SEASON	DRY-WARM SEASON NG/DAY	RAINY SEASON NG/DAY	COLD-DRY SEASON NG/DAY
PST, 2003. UAM-A			208
PM_{10}, 2005. UAM-A	123	131	184
PM_{10}, 2005. Pedregal	180	175	250
PM_{10}, 2005. Merced	369	377	748
PM_{10}, 2005. Xalostoc	616	647	1460
PM_{10}, 2006-2007. CINVESTAV	190	180	295
$PM_{2.5}$, 2006-2007 CINVESTAV	159	156	223

Table 5. Daily potential intake of carcinogenic PAHs at different sites and seasons in Mexico City

PAH	**Nisbet & Lagoy TEF**	**BAPeq in pg/m³**				
		XAL 2005	MER 2005	PED 2005	UAM-A 2005	CINVESTAV 2006-2007
FLU	0.001	0.199	0.131	0.097	0.183	0.465
PHE	0.001	1.225	0.947	0.399	0.223	0.771
FLT	0.001	2.527	1.728	0.652	0.367	0.978
PYR	0.001	3.247	2.089	0.978	0.553	1.176
BAA	0.100	476.733	207.267	131.567	90.000	125.682
BKF	0.100	523.633	254.633	137.033	83.333	145.104
BBF	0.100	582.533	375.967	177.267	117.333	186.32
CRY	0.010	81.000	39.303	14.297	12.433	10.896
BAP	1.000	7774.333	4381.000	1332.667	1000.000	1752.595
DBA	0.100	216.567	87.500	122.633	86.667	128.355
IND	0.100	1151.033	731.833	165.133	128.000	239.426
BGP	0.01	139.637	97.173	22.693	19.033	24.317
		10953	**6180**	**2105**	**1538**	**2615.897**

Table 6. Toxic equivalency factors (TEFs) and calculated BAPeq from measured concentrations.

7. Comparison of the level of PAHs in other countries

The data for PAH concentrations in PST and PM_{10} are lower than those measured in Shijiazhuang, China (Feng et al, 2007) and New Delhi, India (Dhruv, 2003), they are similar to those found in Seoul, Korea, Jakarta, Xiamen, China and Bangkok, Thailand (Panther et al 1999; Hong et al., 2007, Thongsanit et al., 2003), but are significantly higher than those observed in Italy (Menichini et al., 1999), London (Kendall et al., 2001), Gran Canaria (2003), Greece (Kalaitzoglou et al., 2004) and California, USA (Miguel et al., 2004).
Table 7 presents a comparison of the PAHs associated to $PM_{2.5}$ at different cities in the world, where it is possible observe that concentrations of PAHs in Mexico City at the CINVESTAV site are similar to those of the other Latin America city of Sao Paulo, but higher than cities in the United States and Spain.

	Mexico	**USA[a]**	**USA[a]**	**Brasil[b]**	**Spain[c]**
[ng/m³]	CINVESTAV	Lompoc/LA	Riverside/LA	Sao Paulo	Valencia
NAP	0.629	0.015	0.007	0.020	0.13
ACY	0.644	N.D.	N.D.	0.090	0.5
ACE	0.488	0.003	0.001	0.350	N.D.
FLU	0.293	0.008	0.008	N.D.	0.17
PHE	0.739	0.001	0.027	0.180	0.33
ANT	0.667	0.002	0.002	N.D.	0.03
FLT	0.858	0.005	0.024	0.680	0.37
PYR	0.962	0.006	0.038	0.520	0.23
BAA	1.081	0.006	0.020	0.460	0.29
CRY	1.180	0.008	0.032	0.510	0.33
BBF	1.831	0.012	0.056	1.230	0.48
BKF	0.811	0.006	0.027	0.760	0.27
BAP	1.483	0.009	0.047	0.520	0.32
IND	1.899	0.012	0.052	2.470	0.41
DBA	1.297	0.002	0.006	N.D.	0.49
BGP	1.862	0.023	0.112	2.360	0.41

a Eiguren Fernández et al., 2004, b Bourotte et al., 2005., c Viana et al, 2008.

Table 7. Comparison of PAH associated to $PM_{2.5}$ in the CINVESTAV study at Mexico City with other countries.

8. Summary

Several studies have been carried out in Mexico City related with the presence of airborne PAHs in vapor and particle-phase. The concentration of PAHs observed are higher than those found in the Unites States and Europe, but lower than in the most polluted cities of China and India, and showed a great variability at different sites of the city. The most polluted locations are close to the industrial areas at the Northeast of the city where

dominant winds prevail. Most of PAHs are present in the fine fraction ($PM_{2.5}$) contributing with 75 to 85% of the total mass. Seasonal variations in PAH concentrations were also observed as well as the highest concentrations in both size of particles and in the phase vapor were during the cold-dry season. High concentrations of BAP, BGP and IND indicate that the city is impacted by vehicular emissions. The levels of PAHs in the atmosphere of Mexico City are such as that constitutes a high health risk to its inhabitants. Long-term studies at several locations should be conducted to determine with a higher certainty the exposure of the population and should be considered the proposal of a standard just like in the European Union. On the other hand, results obtained showed that this is an important issue for the management of Mexico City air quality, since inhabitants of Mexico City spends more than an hour near to the roadsides.

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