10

Presence of Polycyclic Aromatic Hydrocarbons (PAHs) in Semi-Rural Environment in Mexico City

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1. Introduction

The quality of the environment in big cities depends on its population and their domestic, transport, and industrial activities. In some places agricultural land use coexists with urban areas and as a result of this urbanization and the presence of infrastructure for services like water, electricity, drainage, and the use of fossil fuels etc, contamination problems in the atmosphere, soil and water (Wilcke, 2000), that lately lead some ills on organisms such as respiratory malaises, liver-lung-skin cancer, irritation on eyes and others discomforts. The growth of urban environments presents a major challenge. However, Mexico City as center of economic growth, education, technological advancement, and culture, large city also offer opportunities to manage the growing population in a sustainable way.

These concentrations of people and activity are exerting increasing stress on the natural environment, with impacts at urban, regional and global levels. In the last few decades, air pollution has become one of the most important problems of megacities. The nitrogen and sulphur compounds are main air pollutants, photochemical smog-induced primarily from traffic, but also from industrial activities, power generation, and solvents-has become the main source of concem for air quality. Air pollution has serious impact on public health, causes urban and regional haze, and has the potential to contribute significantly to climate change (Molina & Molina, 2004).

Mexico City and metropolitan area (MCMA), often simply called Mexico City, consists of 16 delegations of the Federal District and 37 contiguous municipalities from the State of Mexico and one municipality from the State of Hidalgo, some with populations over 1 million, that make up the total population of above 20 million for this megacity (Escobedo et al., 2000).

Polycyclic aromatic hydrocarbons (PAHs) are compounds with two or more aromatic rings (benzene) produced by both natural and anthropogenic pathways although anthropogenic activities generally release much greater amounts to the environment (Eom et al., 2007). They originate from combustion, coke production, oil derivates and high temperature industrial processes. PAHs are considered as persistent organic pollutants (POPs) according to the Stockholm Convention. In many studies of contamination, they have been found in air, water, food and soil. There is evidence that some PAHs are carcinogenic, mutagenic and toxic. Monitoring of the PAHs in the environment is important in the evaluation of risk to the health of organisms.

With this problematic situation, the food production may be contaminated with different classes of organic and inorganic residues and contaminants (García-Alonso et al., 2003). For Mexico City case, the presence of contaminants in rural environment highlights persistent organic pollutants (POPs), for example polycyclic aromatic hydrocarbons (PAHs). The sources of these compounds are variable, for example vegetation and fossil fuel combustion, heating (Finizio et al., 1998). PAHs with high persistent in the environment are benze(a)pyrene, anthracene, crysene and others with molecular high weight (> 4 rings aromatics). The occurrence of PAHs is widespread in environmental compartments as air, water, soil and food.

Soils are large reservoirs of hazardous contaminants derived from anthropogenic activities. Some studies of wet and dry atmospheric deposition of PAHs have found values of >10 mg/kg, mainly in urban soils and tropical areas, for example in Brazil (Krauss et al., 2000; Wilcke, 2000). Soils are contaminated with PAHs mainly from atmospheric deposition from stationary sources (gas burning, industrial and municipal organic residues incineration, forest fires) and mobile sources (mainly from fuel fossil combustion for terrestrial transportation) (Mastral & Callen, 2000).

The presence of PAHs in soils has been found to be increasing in industrial and urban developments over the last few decades. Some studies have indicated that vehicle exhausts are major sources of PAHs in soils along with increased use of wastewater for irrigation of crops. Soil contamination by PAHs is considered to be a good indicator of the level of environmental pollution by human activities (Chung et al., 2008). PAHs from soil and water are possibly dangerous to human health because plant root uptake can result in bioconcentration (Samsoe et al., 2002).

The quality of air, water and soil are important for the production of vegetables and animals, and of course for humans as well. The occurrence of contaminants in the environment above certain levels may entail multiple negative consequences in the ecosystems as well as for the human food chain (Liu & Korenaga, 2001).

Our objectives were to investigate the occurrence of PAHs on semi rural terrains within Mexico City and identify the sources of these organic contaminants in crops, water for irrigation and soil in two areas (Tlahuac and Milpa Alta), which are considered important as aquifer recharge zones.

2. Material and methods

The Metropolitan Zone of Mexico Valley (MZMV), comprises Mexico City which is considered a Megacity (Molina & Molina, 2004) located in a basin on the central Mexican plateau with a population around 20 million, 4 million vehicles, and 35,000 industries

(Figure 1). It is situated at a tropical latitude, has an urban area of about 3500 km^2, is at 2240 m altitude, and is surrounded by high mountains on three sides, all of which contribute to poor air quality (Fast et al., 2007).

We collected a composite sample (2 kg) of apple for each location from an area of approximately 1500 m^2 during both dry and wet months and steam cactus stem in Milpa Alta in 2008-2009. For irrigation water we took 1 L during 2008 from each location with glass previously cleaned with solvents. Finally, we collected a composite sample (1 kg) of soil from each location during both dry and wet months in 2009. The samples were conserved according to standard methods of conservation.

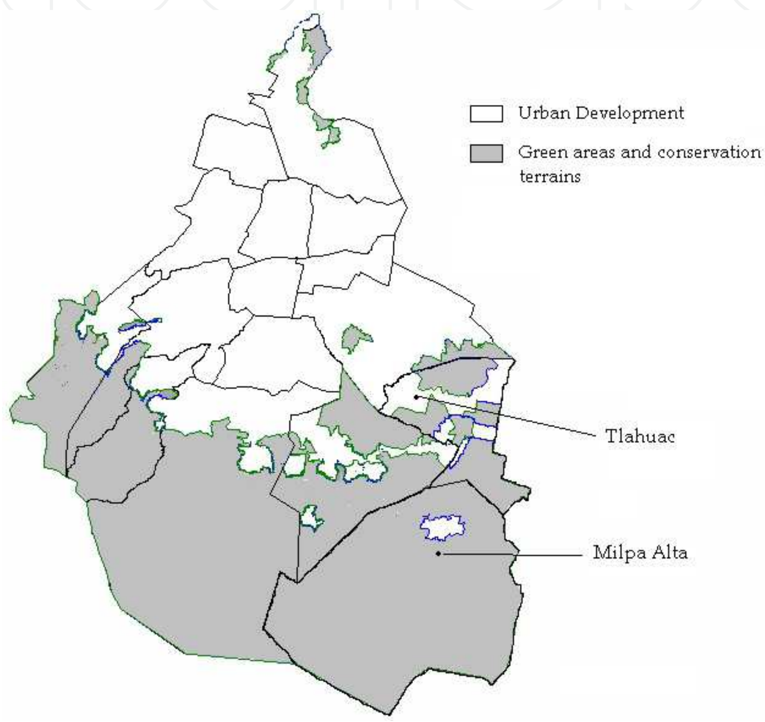

Fig. 1. Distribution of urban and green-conservation terrains in Mexico City (From GDF, 2003).

Soxhlet extraction was used for fruits and soil to extract 10 g of sample mixed with anhydrous sodium sulfate, using a solvent mix of hexane-dichloromethane (1:1) according to the method of Samsoe et al. (2002). For water samples liquid-liquid extraction was used with a mix of hexane-acetone. Chromatographic columns were prepared with chromatographic absorbents to obtain PAH extracts. The organic extract was concentrated in a rotary evaporator to 1 mL and transferred to a vial for gas chromatographic analysis according to EPA method 8100. The concentrations and profiles of PAH compounds were analyzed using a Perkin Elmer AutoSystem gas chromatograph with capillary column HP-5. The oven temperature was initially set at 90°C and the final temperature was 300ºC. Detector and injector temperature were 320ºC. The carrier gas was high purity helium (99.99%). A sample of 1 µL was injected in splitless mode.

Identification of PAH compounds was based on matching their retention time with a mixture of PAH standards (Chem Service). The 16 PAH compounds were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)fluorene (BaF), benzo(a) anthracene (BaA), chrysene (Cry), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), indeno(1,2,3-cd)pyrene (Ind), dibenzo(ah+ac)anthracene (DaA), and benzo(ghi)perylene (Bghi). In general the detection limits were 0.01 mg/kg.

Quality control was carried out by analysis of fortified blanks and samples together with the performance of the GC. Recoveries were 80-95% except for naphthalene for which a value of 50% was obtained. Quantification of individual PAHs was made by an external standard method.

3. Results and discussion

3.1 Water

The occurrence of low weight molecular compounds in water is due to wet and dry deposition of particles from the atmospheric that contain adsorbed PAHs such as naphthalene and phenanthrene. The probable source of these compounds is organic matter combustion to low temperatures (Nagy et al., 2007); relatively high concentrations in comparison to high molecular weight compounds can be explained by the relative solubility of the PAHs. This pattern of concentrations has been seen before (Bishnoi et al., 2005; Ma et al., 2005; Chung et al., 2008)

The mean value of total PAHs in Tlahuac and Milpa Alta water samples for 2008 were both 0.04 μg/L. This did not exceed the permissible value of 1.0 μg/L proposed by European Union for irrigation of crops.

In 2009, the values were lower than detection limits. The PAHs were concentrated in suspended particles or in sediment particles that accumulated in the reservoirs with high content of fine sediments and organic matter.

Within results in water samples, we observed that values changed according to the wet and dry season. In the dry season, concentration and number of PAHs were higher than in the wet season, probably due to a dissolution effect where concentration reduced. There is a great interaction of contaminants between atmospheric, water superficial bodies and soils. The scarcity of water in some months of year for crops is limiting in these rural terrains

The use of wastewater for this zone does not present a problem of contamination for crops and soils, as there is no association between the PAHs and type of water. In some areas of China there a direct association between residual water and contamination and degradation of arable soils and an associated drop in quality of crops over the medium to long term (Cai et al., 2007).

In the figure 2 we appreciated the distribution of PAHs according number of aromatic rings, where in Tlahuac and Milpa has similar percentage of 3, 4 and 6 aromatic rings, the high values were in 3 (33% in both sites) and 4 (35% approximately in both sites). Similar studies have determined that those compounds are derived of combustion of organic matter (vegetation and fuels), so PAHs occurrence in water in both zones is by combustion mainly via deposition for case of Mexico City.

The occurrence of PAHs in water generally is associated by suspended particles or sediments due the high affinity to organic carbon further low solubility of many aromatic compounds. The main source of contamination of PAHs in water is by deposition of airborne and urban storm water runoff. Many PAHs found in water are derived of combustion process such as anthracene, benzo(a)pyrene and others compounds. Some investigations have suggested a monitoring of wastewater a long term domestic wastewater irrigation to evaluate risks about this resource for agricultural terrains (Chung et al., 2008)

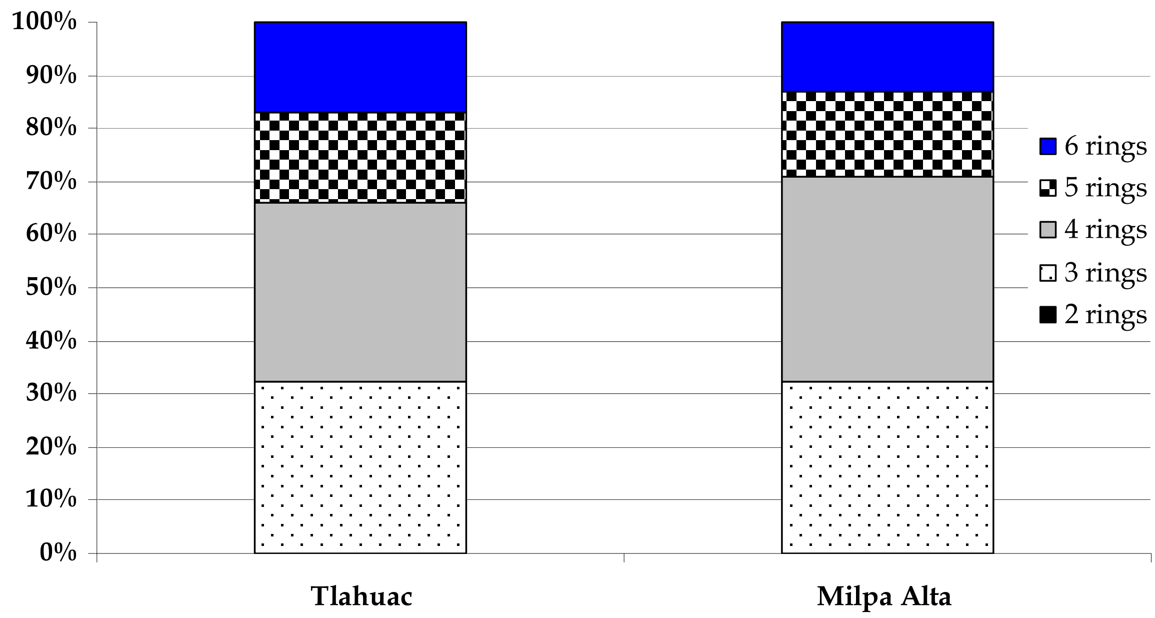

Fig. 2. Distribution of PAHs in water for irrigation in crops semi-rural terrains in Mexico City.

Finally, these areas are considered areas of recharge for aquifers but the PAHs found in the water do not represent a risk for crops (toxicity by translocation) and soils (degradation). Despite the high contamination in Mexico City, wastewater use is adequate for crops although some work has shown that wastewater is a potential source of PAHs contamination (Escobedo et al., 2000; Chung et al., 2008).

3.2 Crops

Our study focus in two crops of economical importance for Tlahuac and Milpa further the government has impulse with economical, technical and material resources for development of farmer. Cactus stem has high acceptation in population because is traditional food from prehispanic to present time while apple crop recently is accepted as attractive and rentable crop. Although there are several agriculture products that grow in these areas and around such as spinach, broccoli, amaranth, olive, ornamental flowers and etc (Grupo Produce, 2006).

Human exposure to PAHs is 88–98% connected with food (meat, seed, vegetable, fruit and others). PAHs can penetrate food indirectly (from air or water) and directly, e.g. during smoking. Once these compounds are released into the atmosphere they can be transported away from their emission sources over long distances and/or deposited to the terrestrial and aquatic environment through dry and wet deposition. A major issue associated with the emission of these compounds is the zone of influence, which determines whether the possible source has predominately local impacts or contributes to regional or global background levels (Rey-Salgueiro et al., 2008).

According to Rey-Salgueiro et al. (2008) the form of vegetable or fruit influenced the PAH concentration over the surface as they found that leaves and quasispherical fruits (grapes and tomatoes) had greater concentrations of PAHs (4 and 5 aromatic rings) than quasi-conical fruits (pepper). Some authors have suggested that lower molecular weight PAHs which dominate in the atmosphere can easily penetrate the cuticle surface of the foliage, while the higher molecular weight PAHs, mainly associated with the atmospheric particulates, are only superficially deposited on plant foliage and are thus more easily washed away by rain.

Kluska (2003) established that the content of PAH in fruits and vegetables depends on pollution in the environment (mainly air pollution) and on area of contact: Apples usually contain 200–500 ng/kg, tomatoes 200 ng/ kg, spinach 6600 ng/kg, and cabbage (savoy) 20,400 ng/kg; this provides a basis for estimating a low potential biological impact associated with the levels found. García-Falcón et al. (2006) screened for the presence of PAHs in soil of rural areas and found thattotal PAHs were always lower than 13,000 ng/kg. As a conclusion, the selected plant foods will probably not cause adverse biological effects to take place. In Tianjin (China), at a PAH contaminated site, total PAHs of rice leaves from various growth stages ranged from 58,900 to 548,000 ng/kg with a mean value of 216,000 ng/kg (Tao et al., 2006).

In Table 1 we compared our results with other vegetables where individual concentrations of PAHs in high molecular weight were highest; we believe that these differences were due at the type of skin (waxes) and morphological structure of crop further there aren`t values for apples and cactus stem. Although our concentrations were variables in 2008 and 2009 probable to time and amount of rain, winds and dust storm, mainly.

Vegetation is reportedly an effective media for the entrapment of these and other compounds, mainly through atmospheric deposition. The green parts of vegetables or skin of fruits are provided with an epicuticular wax which acts as a sorbent for lipophylic contaminants (Ratola et al., 2011). It is necessary evaluate crops from semi-rural zones of Mexico City by periodically to assess good quality of products of organic contaminants such as aromatic hydrocarbons. Due some compounds has described as carcinogens at benzo(a)anthracene BaA, chrysene Cry, benzo(b)fluoranthene BbF, benzo(k)fluoranthene BkF, benzo(a)pyrene BaP, indeno(1,2,3-cd)pyrene Ind, dibenzo(ah)anthracene DaA and benzo(ghi)perylene Bghi.

In figure 3 shows dominant individual PAHs in apple were Ant, Fla, Pyr, BaP and BaA mainly in dry season and BaA, BkF, BaP, DaA in wet season. For cactus stem were DaA, Bghi, Pyr, Cry, BaA, Fla, BaP, Ind, Ant and Phe in dry season and BaA, Fla, DaA, Pyr, Bghi and Ant in wet season. In wet season in both crops were high concentrations of PAHs we supposed a diminished by effect of washing but the irregular rains in Mexico City (low content of water and spread out) only causes drop of suspended particles in atmosphere in long time of wet season

It is recognized that the low molecular weight PAHs (two and some three rings) are common in fresh fuels, but also in combustion activities and in some industrial emissions, indicating mostly petrogenic origins, four-ring PAHs (and also some three-ring) are linked with motorized traffic in general and diesel consumption in particular and the high molecular weight PAHs (five and six rings) denote the existence of heavy machine or industrial activities (Yin et al., 2008; Wang et al., 2009)

Compounds	Vegetable samples										
	Apple[1] (mg/ kg)	Cactus stem[1] (mg/ kg)	Apple[2] (mg/ kg)	Cactus stem (mg/ kg)	Rye rootso[3] (mg/ kg)	Potato skin[4] (g/ kg)	Carrot skin (g/ kg)	Cabbage (g/ kg)	Spinach[5] (g/ kg)	Fruits[6] (g/ kg)	Aerial leafs (g/ kg)
Nap (2)*	---	---	0.33	---	---	0.73	0.28	90	41	16.4	589.8
Acy (3)	0.32	0.69	---	---	---	0.42	0.40	63	1.8	2.0	2.3
Ace (3)	1.11	0.58	---	---	---	---	---	---	---	0.4	16.2
Flu (3)	1.11	1.27	---	---	---	---	---	7.0	4.0	4.0	41.5
Phe (3)	1.73	2.77	0.89	0.26	0.6-43.5	3.32	1.34	55	9.2	63.6	100.6
Ant (3)	3.49	2.89	2.04	6.40	---	1.47	1.41	---	22	8.4	85.4
Fla (4)	3.56	3.68	0.01	4.97	---	2.65	10.59	152	746	49.2	66.4
Pyr (4)	3.06	5.04	---	2.89	0.8-272.1	1.63	1.23	56	256	38	8.7
BaA (4)	4.35	4.30	8.46	13.35	---	0.52	0.61	---	13	---	8.0
Cry (4)	1.17	5.23	3.15	2.21	---	---	---	15	45	17.2	12.5
BbF (5)	2.14	2.39	---	0.41	---	0.05	0.66	---	---	1.6	3.1
BkF (5)	4.09	1.99	0.98	2.10	---	0.05	0.62	---	---	1.2	4.8
BaP (5)	3.80	3.79	1.42	0.63	---	0.32	0.91	---	---	2.0	42.4
Ind (6)	0.84	4.95	2.18	2.04	---	0.17	0.40	---	---	---	---
DaA (5)	2.29	10.14	4.28	8.73	---	0.25	0.57	---	---	10	1.1
Bghi (6)	2.78	4.64	0.47	8.71	---	0.42	0.48	---	---	12	0.9

Table 1. Comparison of PAH concentrations in vegetable samples. Note: * Number of aromatic rings; --- No detected; 1. This survey, 2008; 2. This survey, 2009; 3. Zohair et al., 2006; 4. Mo et al., 2008; 5. Li et al., 2008; 6. Tao et al., 2004

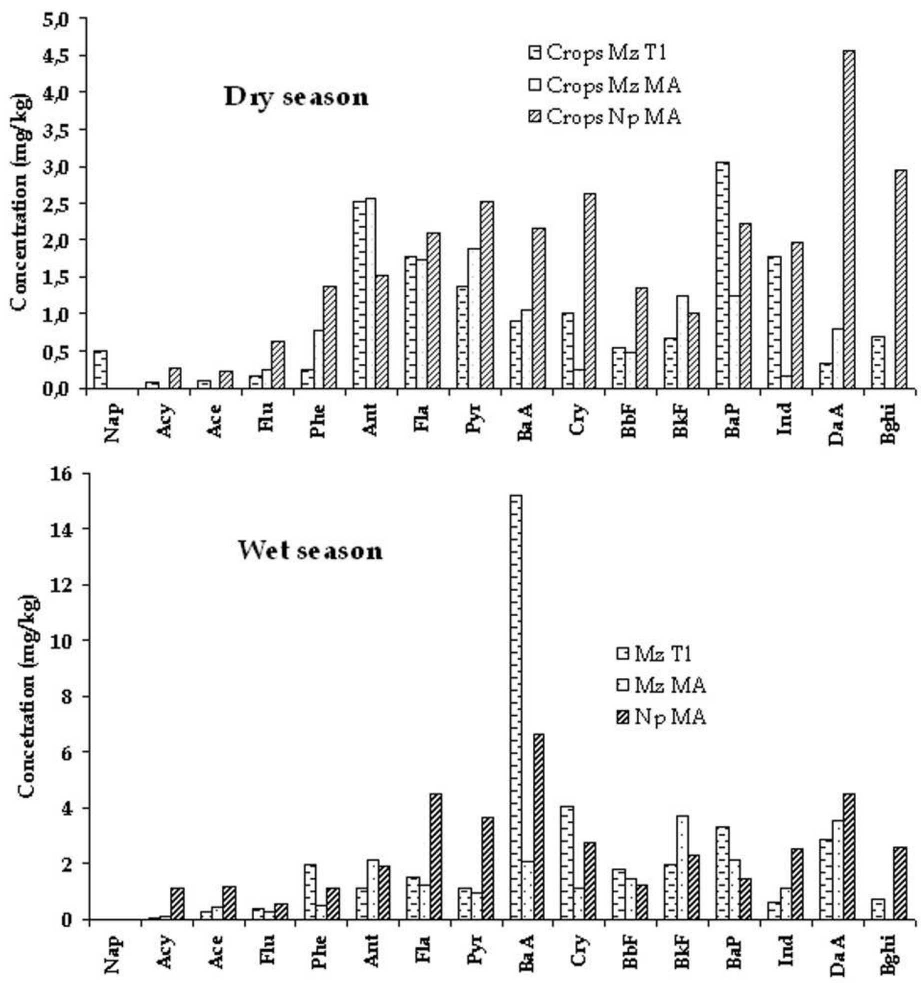

Fig. 3. Values of PAHs for semi-rural terrains from Mexico City (Tlahuac and Milpa Alta).

There routes of PAHs in plants such as take up from soil via the roots or from air via the foliage; uptake rates are dependent on the concentration, solubility, and molecular weight of the PAH and on the plant species (ATSDR, 1995). Some plants have been used to monitor atmospheric deposition of PAHs, example, mosses, lichens and vegetables. In some studies, the atmospheric PAHs such as indeno(l,2,3-c,d)pyrene, fluoranthene, and benzo(a)pyrene are deposited on foliage (leaves and flowers). In general, the atmospheric deposition on leaves often greatly exceeds uptake from soil by roots as a route of PAH accumulation.

In figure 4 we appreciated the average of compounds for 2008-2009 for apple and cactus stem where aromatic compounds were variable in both season. In general dominant compounds for crops were four and five aromatic rings follow by three and six aromatic rings. These occurrence of compounds coincide with before describe by similar studies.

The differences of aromatic compounds are influenced by particularly conditions of each area; in Tlahuac (Tl) coexist mines of construction materials as sand and gravel with diesel machinery and transit of gasoline vehicles, garbage and weed combustion. While Milpa Alta (MA) there gas station, transit of gasoline vehicle, garbage and weed combustion. These sources and particular environmental conditions can explain occurrence of PAHs. For case of apple crop in dry season only Tlahuac has naphthalene and high proportion (~15 %) of compound of six aromatic rings than Milpa Alta (~5 %) while Milpa has high proportion of three, four and five aromatic rings (~30 %, 50 % and 25 % respectively) than Tlahuac; in wet season Tlahuac showed high proportion of four aromatic rings (~60 %) than Milpa Alta (~25 %) and Milpa Alta showed high proportion of three, five and six aromatic rings (~18 %, 52 % and 9 % respectively) than Tlahuac (~ 10 %, 25 % and 5 %). For cactus stem showed differences in four, five and six aromatic rings in dry (~35 %, 30 % and 18 %) and wet season (~45%, 22 % and 10 % respectively).

The differences among crops were due waxes composition of skin where cactus stem has a high concentration of PAHs than in apple. In cactus stem has elevated waxes than apple skin and favour accumulation of particles or contaminants due PAHs are affinity a fat and waxes.

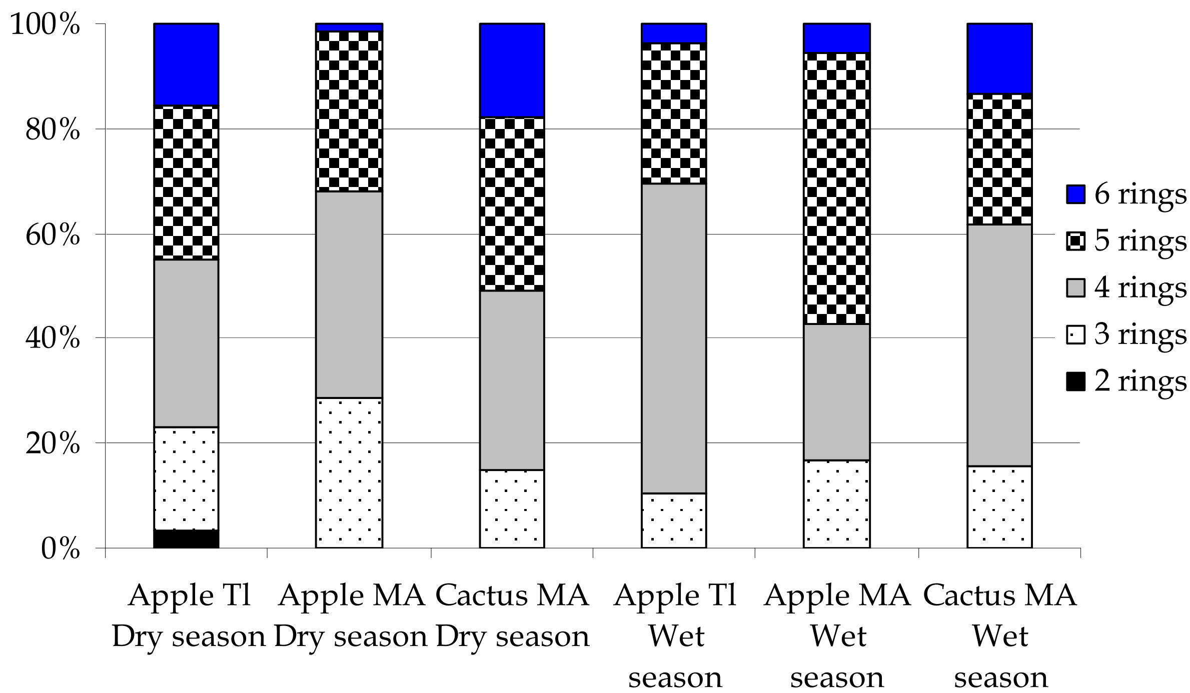

Fig. 4. Distribution of PAHs in crops according number of aromatic rings in Tlahuac (Tl) and Milpa Alta (MA).

Finally vegetables and fruits obtained from a polluted environment may contain higher PAH concentrations than those obtained from nonpolluted environments. According to ATSDR (1995) the PAH content of plants and animals living on the land or in water can be many times higher than the content of PAHs in soil or water.

3.3 Soils

According to the results we found higher values of PAHs in crops than soil. For the case of crops, the individual PAHs were slightly lower in wet than dry season; in the rainy season the irregular intensity and duration of rainfall cleans the atmospheric of suspended particles. In figure 4 the results show greater values in apple from Tlahuac and cactus stem from Milpa Alta in the wet season. In general, the compounds > 3 aromatic rings were present in crops and soil in both season such as BaA, Cry, Fla, Pyr, DaA, BaP and BkF are dominant in apple while cactus stem. According García-Alonso et al. (2003) the presence of Fla and Bghi in the two areas may indicate a common vehicular emission source.

There are many factors influencing the distribution of different PAHs in the environment, such as physicochemical properties of PAHs, physicochemical properties of soil, sources of emission of PAHs, and photochemical degradation of atmospheric PAHs. Two to three ring PAHs are subject to atmospheric transport to remote areas and are considered ''multi-hop'' chemicals, while higher ring PAHs are associated with particles and undergo ''single hop'' transport behavior, and higher ring PAHs are prone to rapid deposition and retention close to source regions. So, PAHs may become fractionated from source regions to remote regions during atmospheric transport (Wang et al., 2010).

The concentrations of BaP in the soils is an indication of both pyrogenic and petrogenic sources of PAH pollution on the environment (Essumang et al., 2010) for both seasons. BaP is considered within permissible limits (2 mg/kg) for agricultural and residential land use according to Mexican regulation NOM 138-SEMARNAT/SS-2003. However, the levels of BaP surpassed the limit established by the Danish Environmental Protection Agency (0.1 mg/kg) and Canadian Council of Ministers of the Environment (0.26 mg/kg; Essumang et al., 2010). The BaP concentrations are considered to be a risk to human health due to its potential exposure to carcinogenic PAHs for those living in those areas. According other international regulations our soils has severe problems of contamination, where some prevent measurements have applied such as strict control of emissions of industries, vehicular park and matter combustion.

Within polycyclic aromatic hydrocarbons considered in Mexican regulation, the concentrations of DaA, BaA, BbF, BkF and Ind were lower than the permissible limit for agricultural land use according NOM-138-SEMARNAT/SS-2003 (2 mg/kg). These compounds do not represent a risk for human health in comparison to BaP.

In figure 5 we appreciated the distribution of PAHs in dry and wet season found it a relative high concentration of chrysene in wet season in both sites. In general dominant PAHs for dry season were BaA, Cry, BaP, Fla, Ind and BkF with range of 0.5 to 3.5 mg/kg; Milpa Alta has slightly high BaA, BaP and Fla and Tlahuac were Cry and DaA. In wet season dominant PAHs were Cry and BaP mainly, with range of 1 to 9.5 mg/kg; Tlahuac has high concentration of Cry and BaA and Milpa Alta were Fla, BaP, Bghi, BbF, BkF, Ind and DaA. The variability of individual PAHs is key to recognize the possible source of contamination in the semi-rural area further the environmental condition defines distribution and concentration of contaminants in the soil and other media.

The presence of 4-6 aromatic rings compounds in soils in Mexico City was similar to results from a survey in soil described by Wang et al. (2010) in urban soils from North China. In semirural soil of Mexico the compounds predominant were Cry, BaP and BaA different at found it in North of China. For dry season we found similar percent of four (50 % approximately); five (25 % approximately) and six (10 %) ring aromatic compounds in Tlahuac and Milpa Alta (Figure 6). In wet season, there are significant changes over aromatic compounds, in Tlahuac has 90 % of four ring aromatic compounds while others compounds diminished to 8 % (5 rings compounds) and 2 % (6 ring compounds). So, Milpa Alta shows similar percent of aromatic compounds than dry season.

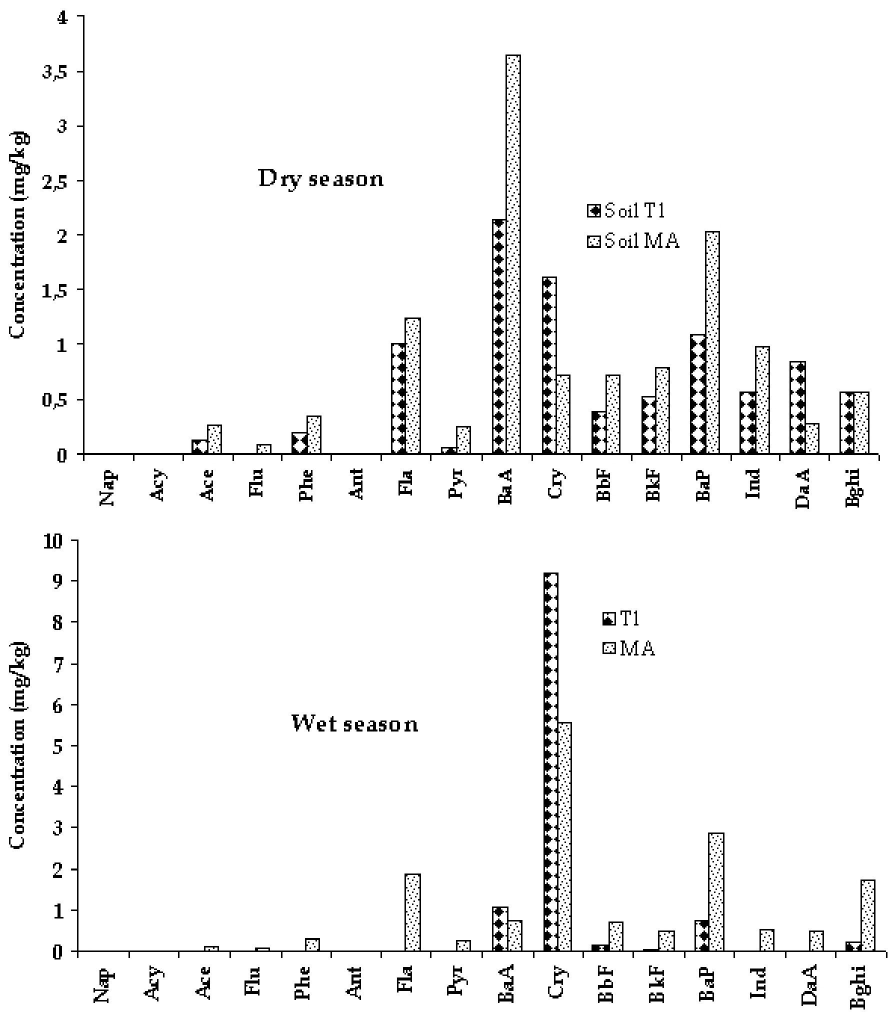

Fig. 5. Values of PAHs in soils from semi-rural terrains from Mexico City.

Nap not found in our analysis we supposed a loss in handling of sample due that is high volatile compound.

The most prominent source of PAHs in the urban environment is the incomplete combustion of biomass (such as vegetation) and fossil fuels (petroleum). Vehicular traffic (mainly diesel-powered) is considered to be the most significant contributor to the atmospheric PAH load within urban areas (Marr et al., 2004). Atmospheric deposition is the most common source of pollution in soil and it is expected that most combustion derived PAHs will be restricted to the top layer of the soil. Urban areas generally have high traffic density which results in heavy contamination of surface soils (Agarwal, 2009). For our study areas there are several asphalt ways that communicate with population areas, it considering as a source of contamination.

According Cram et al (2008), the high concentration of these contaminants in atmospheric is concentrate in South of Mexico City, mainly due to the direction of wind from North to South. As appreciate in figure 1 Tlahuac and Milpa are located in Southeast. These soils are considering as conservation, recharge of aquifer and recreational areas further gives other environmental services as retention, regulation and alleviates the deposition of contaminants derived of fossil fuels combustion that origins heavy metals and ethers, hydrocarbons, etc.

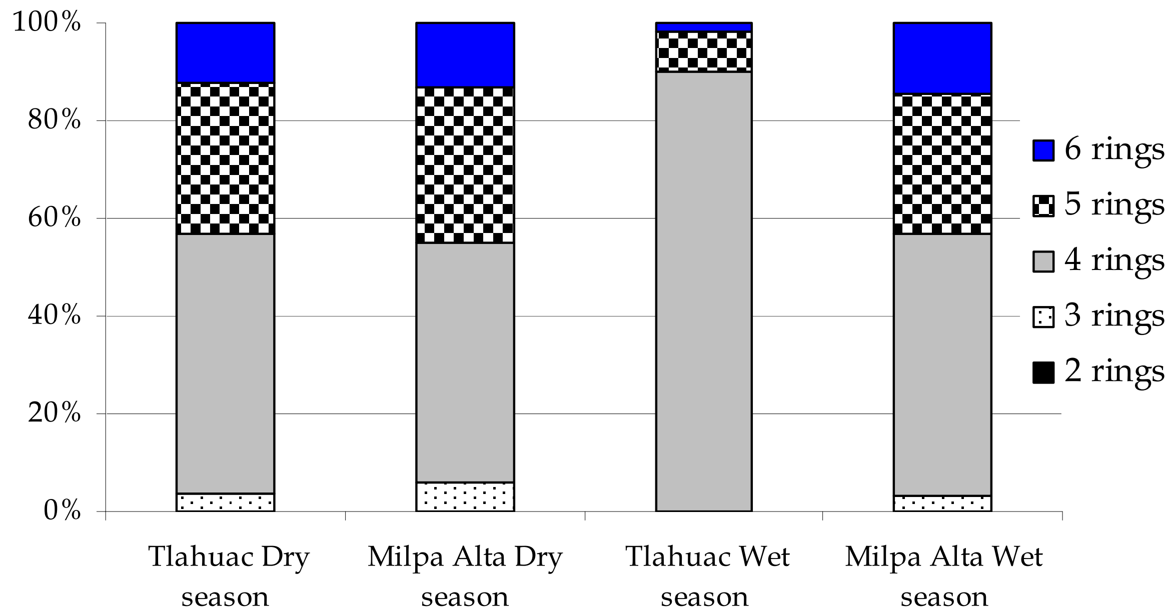

Fig. 6. Distribution of PAHs in soils according to its number of aromatic rings in Tlahuac and Milpa Alta.

Important aspect for these soils in Tlahuac and Milpa are addition of farmyard manure and compost where we appreciated low values of PAHs in comparison crops (Cai et al., 2007). The organic matter plays a role to catch contaminants where can be stabilized within its structure. A long term, organic matter is long reservoirs of several contaminants which must be practice good management of this parameter of soil.

The presence of low molecular weight PAHs (2-3 aromatic rings) is indicative of petroleum (fossil fuel combustion) while high molecular weight PAHs (> 4 aromatic rings) are more likely to be derived from organic material combustion (Ma et al., 2005). There are likely to be multiple contamination sources in vegetables and garbage from these conservation terrains.

The contamination in Mexico City is high due to the environmental conditions, for example high population density and geography (such as altitude and temperature), where atmospheric deposition (diffuse and point sources) leads to high concentrations of PAHs. Similar contamination situations have been reported in Chinese soils (Ping et al., 2007).

In table 2, we appreciated high values of individual PAHs than others areas where compounds with high molecular weight surpass values of others studies of different countries. We supposed that high concentrations are due to pull of contaminants to South of City together certain activities of specific areas as possible explication.

Maliszewska-Kordybach (1996) suggested a soil contamination classification system based on ΣPAH16 as follows: noncontaminated soil (<200 ng/g), weakly contaminated soil (200–600 ng/g), contaminated soil (600–1000 ng/g) and heavily contaminated soil (>1000 ng/g). According to this classification system, all samples in this study were heavily contaminated. This discrepancy among European and Mexican regulations are based in diverse criteria of analytical techniques mainly.

Studies made in past years for Mexico City has showed differences in abundance, type and distribution of PAHs according landscape type and territories of intensive urbanisation/

industrialisation (Marr et al, 2004; Maliszewska-Kordybach et al., 2009). The spatial distribution of soils contaminated with PAHs reflected that rural/forested/ recreation areas decreasing along the South to North of Mexico City. Due in North there high concentration of industries and urban areas while in South of City the soils are considered conservation and recharge of aquifers with low density of population.

Compounds	Soils (µg/kg)						
	Mexico, D.F.[1]		China[2]	India[3], Delhi		Korea[4]	Francia
	Tláhuac	Milpa Alta	Fangcun	Rural zone.	Highway	Rural zone	Park
Nap	---	---		131	---	78.5	
Acy	---	---	50	120	317	41.5	
Ace	60	180	9	198	298	33.7	36.0
Flu	---	90	40	48	152	37.6	9.3
Phe	150	330	281	39	259	141	254
Ant	---	---	34	25	135	33.7	9.8
Fla	500	740	583	101	599	353	8.3
Pyr	30	250	492	45	363	317	581
BaA	1620	2180	232	47	521	284	244
Cry	5400	3150	693	23	332	267	319
BbF	270	720	267	36	540	431	313
BkF	270	630	101	37	661	138	139
BaP	920	2030	136	35	461	294	249
Ind	250	750	47	---	621	248	145
DaA	420	380	42	---	623	120	21
Bghi	380	1150	70	---	1618	221	239
Total	10270	12580	3077	885	7501	2834	3390

Table 2. Comparison of PAH concentrations in rural soils near to urban areas. Note: 1. This study, 2009; 2. Chen et al., 2005; 3. Agarwal, 2009; 4. Nam et al, 2003.

The importance of contamination of soil is due serious risks on population health due:

- Inhalation of smallest particles
- Ingestion of particles or food on contaminate soils
- Direct contact with skin in workers of field or direct markets of commercialization (Sabroso & Pastor, 2004).

Further the contamination of water resource in form superficial or underground that are employ for irrigation for crops or human and animal consumption

Government hopes that in medium time the contaminants reduce significantly in favour the environment and health population of Mexico by programs of improvement of quality air.

3.4 Sources of PAHs in semirural sites

We used the Flu/(Flu+Pyr), Ant/(Ant+Phe), Ind/(Ind+Bghi), BaP/(BaP+Cry), BkF/Bghi and BaP/Bghi ratios and the majority of samples fell into the section identifying pyrogenic sources (fossil fuel, grass and garbage combustion) (Table 3). This is logical considering the presence of heavy machinery (Tlahuac) and traffic jam (Tlahuac and Milpa Alta) and the vegetation combustion (which for example is sometimes used to remove weeds) in the city. Further our results are consistent with reports in Mexico City of the influence of vehicular traffic and industrial activities on atmospheric contamination and contamination of other environmental compartments such as water, soil, crops and organisms (Marr et al., 2004).

Diagnostic ratios	Tlahuac (Tl)		Milpa Alta (MA)		Probable source
	Dry season	Wet season	Dry season	Wet season	
Fla/(Fla+Pyr)	0.94	0.86	---	0.88	Tl: Pyrogenic MA: Pyrogenic
Ant/(Ant+Phe)	---	---	---	---	Tl: Not detected MA: Not detected
Ind/(Ind+Bghi)	0.50	---	0.68	0.23	Tl: Vegetation combustion MA: Vegetation combustion and petrogenic
BaA/(BaA+Cry)	0.57	0.11	0.88	0.03	Tl: Pyrogenic and petrogenic MA: Pyrogenic and petrogenic
BkF/Bghi	0.92	0.09	1.45	0.27	Tl: pyrogenic MA: pyrogenic and petrogenic
BaP/Bghi	1.93	3.55	3.36	1.63	Tl: Traffic and vegetation combustion MA: Traffic and vegetation combustion

Table 3. Diagnostic ratios for identification of contamination source in rural sites from Mexico City.

Further, we employed some statistic tools such as principle components analysis (PCA) and extraction with different factor loadings indicated correlations of each pollutant species with each PC. Each PC was further evaluated and recognized by source markers or profiles as reasonable pollution sources according to Agarwal (2009), Wang et al., (2009) and Zhang et al. (2011).

In this investigation, PCA was performed for PAHs founded in soil samples using Statistica 16.0 software. Within principal components with values greater than 0.7 were retained. Two PCs were finally extracted and explained 58.3% of the total variance for apple case, 93.4% for cactus stem and 71.8% for irrigation water for 2008 (Table 4).

In 2008 for apple, PC 1 explained 31.8% of the total variance and had heavier loadings on Ace, Fla, BaA, Cry and BkF. The presence of Fla, BaA and Cry are typical tracers of traffic emission. Bkf and Bbf are also largely released by both gasoline and diesel engines (Wang et al., 2010). Thus, PC 1 can represent contribution from traffic emission. PC 2 explained 26.4% of the total variance and had heavier loading on Flu, Ind and DaA. As Ind and DaA are considered as predominant emissions of industrial and diesel combustion; PC 2 was deduced to represent industrial combustion (Agarwal, 2009). In cactus stem, PC 1 defined 54.5% and had heavier loadings on Ace, Flu, Phe, Pyr, BbF, BaP, Ind and DaA. The presence of 2 and 6 aromatic rings showed a vegetation and fossil fuel combustion, so PC1 represented a mixed combustion. PC 2 explained 38.8% of total variance and had heavier loading on BaA and Cry, indicators of fuel combustion (Table 4).

For irrigation water, PC 1 explained 52.4% of total variance and had heavier loadings Acy, Ace, Flu, Ant, Cry, BbF, BaP, Ind, DaA and Bghi. These compounds are from vegetation, fuels and industrial combustion. PC1 is classified as mixture combustion. PC 2 explained with 19.3% of total variance and had only Phe, as derived of vegetation combustion. Thus, PC 2 is vegetation combustion.

Compounds	Apple		Cactus stem		Irrigation water	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Nap	---	---	---	---	---	---
Acy	0,621	-0,596	-0,687	-0,697	**-0,715**	0,446
Ace	**0,773**	-0,483	**-0,701**	-0,697	**-0,795**	0,572
Flu	0,283	**-0,803**	**0,829**	-0,520	**-0,882**	-0,434
Phe	-0,330	-0,536	**0,924**	-0,381	-0,309	**-0,810**
Ant	-0,384	-0,382	-0,682	-0,697	**-0,773**	-0,516
Fla	**0,855**	-0,002	0,347	-0,622	-0,593	-0,608
Pyr	0,550	0,143	**0,765**	-0,633	-0,531	0,404
BaA	**0,881**	0,169	0,624	**-0,724**	-0,535	0,299
Cry	**0,808**	-0,104	-0,643	**-0,758**	**-0,715**	0,121
BbF	0,596	0,346	**0,901**	0,371	**-0,891**	-0,327
BkF	**0,722**	0,368	0,687	-0,621	-0,541	0,170
BaP	0,146	-0,471	**0,775**	-0,618	**-0,855**	-0,288
Ind	-0,095	**-0,858**	**-0,734**	-0,673	**-0,718**	0,470
DaA	0,123	**-0,889**	**-0,713**	-0,695	**-0,809**	0,433
Bghi	-0,264	-0,489	**0,875**	-0,473	**-0,909**	-0,094
Explain Variance (%)	31.83	26.47	54.50	38.84	52.42	19.37
Accumulative Variance (%)	31.83	**58.30**	54.50	**93.34**	52.42	**71.79**

Table 4. Principal component analysis on apple, cactus stem and irrigation water in rural areas of Tlahuac y Milpa Alta (2008, first step). Note: --- Not detected

For 2009, second step of sampling we analyze apple and cactus stem as one matrix while Tlahuac and Milpa Alta soil samples with same criteria with intention to corroborate the sources of contamination founded in 2008 sampling in others matrix and to understand the movement of PAHs in soil. In crops we employ three PC that explained 73.4% of the total variance. For soil samples we employed four PC that explained 68.9% of total variance for soils in semirural areas (Table 5).

In crops, PC 1 explained 48.7% of the total variance and had heavier loadings on Acy, Ace, Flu, Ant, Fla, BbF and Bghi. The aromatic compounds are associated with vegetation and fuels combustion. Thus, PC 1 can represent contribution from mixed combustion. PC 2 explained 13.6% of the total variance and had heavier loading on BaA, derived of fuel combustion; PC 2 was deduced to represent fuel combustion. And PC 3 explained 10.9% of the total variance and had heavier loading on Phe and Cry, these derived of fuel combustion. In soils, PC 1 explained 35.8% of total variance and had principal compounds on Ace, Ant, Fla, Pyr, BaA, BbF, BaP and Bghi. These ranges of compounds are representative of vegetation, fossil fuel and industrial combustion (Agarwal, 2009). PC 2 explained 15% with BkF derived of diesel combustion, PC 3 explained with 9.5% on Cry derived fuel combustion and PC 4 explained 8.4% with DaA associated with industrial combustion (Zhang et al., 2011).

Compounds	Apple and Cactus stem			Soils			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4
Nap	0,095	-0,519	0,152	0	0	0	0
Acy	**-0,980**	-0,115	0,023	0	0	0	0
Ace	**-0,972**	-0,125	0,024	**0,947**	-0,047	0,203	-0,026
Flu	**-0,915**	-0,154	0,026	0	0,511	-0,028	0,365
Phe	-0,109	-0,134	**-0,884**	0,682	0	0	0
Ant	**-0,824**	0,435	0,233	**0,970**	-0,211	0,008	-0,000
Fla	**-0,966**	-0,070	0,020	**0,912**	0,337	0,045	0,060
Pyr	-0,302	0,651	0,286	**0,849**	0,407	0,033	0,257
BaA	-0,390	**0,729**	-0,177	**0,736**	-0,323	0,363	-0,236
Cry	-0,382	-0,037	**-0,833**	0,123	0,246	**-0,814**	-0,467
BbF	**-0,981**	-0,112	0,022	**0,975**	-0,066	-0,182	-0,069
BkF	**-0,890**	-0,197	0,102	0,675	**-0,696**	-0,046	-0,065
BaP	-0,127	0,381	-0,214	**0,717**	-0,474	-0,395	-0,044
Ind	-0,664	-0,390	0,094	0,584	-0,022	0,327	-0,316
DaA	-0,102	0,580	-0,133	0,080	-0,496	-0,306	**0,715**
Bghi	**-0,903**	0,022	-0,003	**0,763**	0,499	-0,122	0,004
Varianza explicada (%)	48.77	13.61	10.95	35.86	15.07	9.58	8.46
Varianza acumulativa (%)	48.77	62.48	**73.43**	35.86	50.93	60.51	**68.97**

Table 5. Principal component analysis on crops (apple and cactus stem), and irrigation water in rural zones of Tláhuac y Milpa Alta (Step second).

Biomass burning and wildfire are important sources of organic contaminants (PAHs) at a global level. Motor vehicle emission in urban areas where population densities are much higher were found to be high, contribution of PAHs from motor vehicles going to air, dust, water, crops and human exposure; the risk is much higher than in rural areas (Shen et al., 2011). Although recent decades have shown a trend in some big cities of decreasing PAH concentrations due to emission control measures introduced in some countries.

The urban area comprises a wide range of different land uses such as traffic, industry, business, residence, garden and public green space, implying different patterns of human activities and their possible impacts on soil quality. Some work has demonstrated that specific land uses in the urban environment always showed higher PAH concentrations than other land uses. For example, soils collected at the roadside or in busy streets in Shanghai, Dalian and New Orleans all showed much higher levels of PAHs than those collected from parks and residential areas. Haugland et al. (2008) and Jiao et al. (2009) studied PAHs in urban soils from Bergen, Norway and Tianjin, China, respectively, and soils from both cities showed much higher PAHs in the industrial area than other areas.

Although these studies have indicated different levels of PAHs in some land uses of urban areas, research about PAH composition and sources in different land uses of urban environment is scarce; it is thus highly desired to have a better understanding about how different land uses affect PAH distribution in urban soils (Liu et al., 2010).

According to Amador-Muñoz et al (2011) the principal sources were diesel, natural gas and fuel combustion, biogenic emissions and organic matter pyrolysis where PAHs are associated with airborne particles in atmospheric media. Generally, between 80% and almost 100 % of PAHs with 5 rings or more (which are predominately particle-bound in the atmosphere) can be found associated with particles with an aerodynamic diameter of less than 2.5 μm (European Communities, 2001).

The presence of heavy machinery (Tlahuac) and vehicle traffic (Tlahuac and Milpa Alta) with vegetation combustion (which for example is sometimes used to remove weeds) are the sources of PAHs in the city. Further, our results are consistent with reports in Mexico City of the influence of vehicular traffic and industrial activities on atmospheric contamination and contamination of other environmental compartments such as water, soil, crops and organisms.

The presence of low molecular weight PAHs (2-3 aromatic rings) is indicative of petroleum (fossil fuel combustion) while high molecular weight PAHs (> 4 aromatic rings) are more likely to be derived from organic material combustion (Ma et al., 2005). There are likely to be multiple contamination sources in vegetables and garbage from these conservation terrains.

Lastly, recent studies indicate that POPs atmospheric depositions are main source of contamination in big cities derived fossil fuels (diesel, gasoline and natural gas), garbage and vegetation combustion (Rossini et al., 2005). For this reason, the atmospheric compartment must be constantly monitored by supervisory authority and considered by Mexican regulation which, until now, has provided limits for some pollutants such as suspended particles, ozone, carbon monoxide and dioxide, nitrogen oxides and sulphur oxides especially considering the high vehicular units, industrial zones and landfills.

According geography and meteorology conditions play critical roles in the dilution and dispersion of air pollution from source locations, through vertical mixing and horizontal transport in Mexico City (Figure 7). Vertical mixing is facilitated by upward motion of warm air near the surface, to cold air above. In cases where this temperature profile is reversed and warm air lies above colder air at the surface, vertical motion is restricted. This sets up a temperature inversion, which is characterised by stable atmospheric conditions, and results in the accumulation of air pollution (November to March, mainly). Horizontal wind speeds are also reduced, limiting transport of pollutants downwind. The resulting poor air quality and concentrate of organic contaminants may lead to health problems in susceptible populations (Wallace et al., 2010).

Many studies highlight a distinct increase in concentrations of pollution during temperature inversions in Los Angeles, London, Tokyo and others important cities. This seasonal variation also coincides with that of temperature inversions, which are also most frequent in the winter and spring and lead to the accumulation of not just air pollutants, but also allergens and viruses (Wallace et al., 2010).

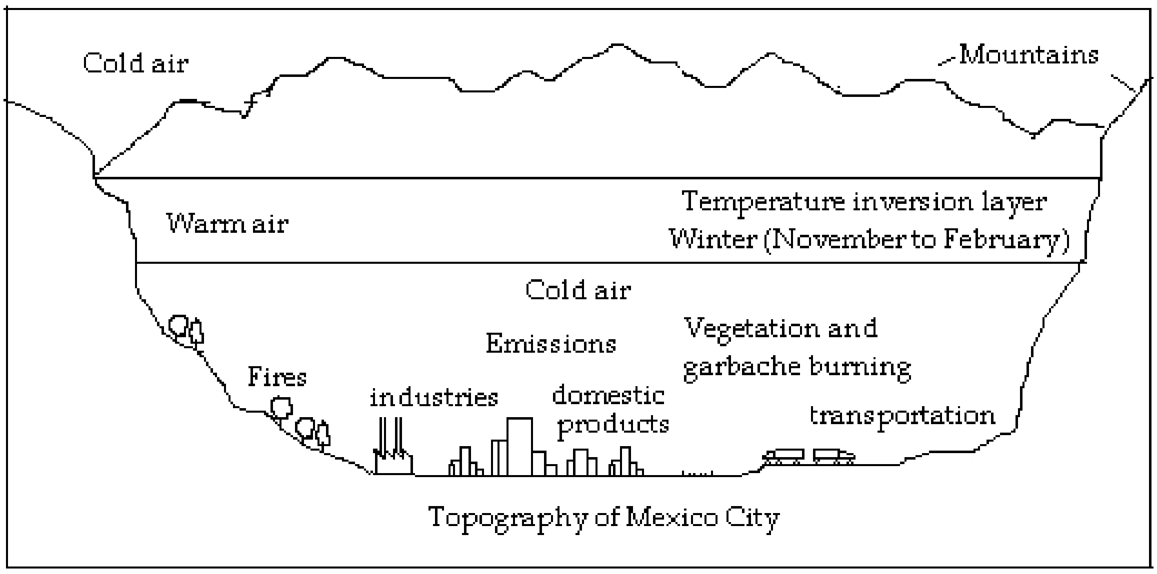

Fig. 7. Scheme contamination for PAHs in Mexico City, while in spring, summer and autumn the behaviour of contaminants change according to environmental conditions.

Thus we found a good description of contamination sources for our studied matrix and the movement of PAHs in the semirural environment for Mexico City. With better data, the Mexican authorities can take more informed decisions in the management of natural resources, legislation and politics, for better control of contaminants and pollution in general.

4. Conclusion

PAH concentrations were variable through the study due to environmental conditions of season, wet (rain) and dry (dust) deposition mainly for crops and soil. The quality of atmospheric conditions defines the contamination in these zones, both for wet and dry deposition. For the case of crops (apple and cactus stem) the values were high over the skins for high and intermediate molecular weights, but values declines with adequate washing or peeling. In soils the values found were within permissible limits of individual PAHs such as benzo(a)pyrene. Organic matter has a high affinity to catch organic contaminants in soils; it is a crucial environmental parameter that regulates the availability of inorganic and organic contaminants in the environment.

This type of study is important to evaluate the degree of contamination in specific environments, considering environmental variables to know the movement the organic contaminants. This will also help guarantee the quality of food produced in semi rural zones nearest to high density population and/or industrial areas such as Mexico City.

Nowadays, the new technologies employ in fuels, gasoline and diesel engines and programs of industrial-vehicular control has improvement the air quality in Mexico City. These actions have the goal to reduce many organic contaminants in favour of human and environment health. In the last years.

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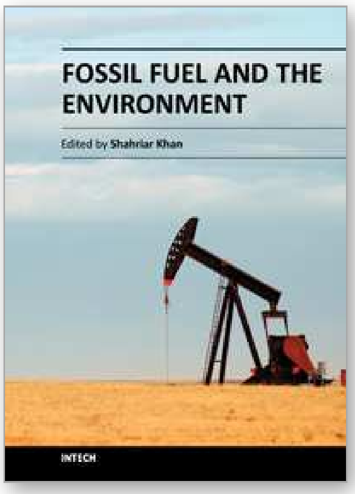

Fossil Fuel and the Environment

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The world today is at crossroads in terms of energy, as fossil fuel continues to shape global geopolitics. Alternative energy has become rapidly feasible, with thousands of wind-turbines emerging in the landscapes of the US and Europe. Solar energy and bio-fuels have found similarly wide applications. This book is a compilation of 13 chapters. The topics move mostly seamlessly from fuel combustion and coexistencewith renewable energy, to the environment, and finally to the economics of energy, and food security. The research and vision defines much of the range of our scientific knowledge on the subject and is a driving force for the future. Whether feasible or futuristic, this book is a great read for researchers, practitioners, or just about anyone with an enquiring mind on this subject.