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Exploratory study of particle-bound polycyclic aromatic hydrocarbons in different environments of Mexico City

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Abstract

Several studies regarding particulate matter in air pollution have been performed in Mexico City, but none have focused on environment exposure to particle-bound polycyclic aromatic hydrocarbons (PPAH), which are related to the occurrence of cardiopulmonary diseases and mortality. On this account, this study presents measurements of personal exposure to PPAH in different outdoor and indoor environments, as well as along roadways in Mexico City. The measurements were done with portable sensors based on photoelectric charging and diffusion charging to determine the PPAH concentrations and the joint active surface of all particles, respectively. The use of these two sensors in parallel is a useful tool to qualitatively identify the major sources and to describe the physical and chemical characteristics of the particles. The highest exposures were found in ambient air near traffic sources, mainly at sites with great influence of diesel vehicles, such as urban transfer bus stations. Roadway measurements showed that Mexican PPAH pollution levels are between those in large cities in Europe and USA. For indoor environments such as residences, shopping centers, restaurants and hospitality venues, it was found that secondhand smoke is the major contributor, however badly calibrated pilot stoves, inefficient ventilation and faulty air-conditioning systems can be additional sources of PPAH.

Keywords: Particulate matter; Polycyclic aromatic hydrocarbons; Personal monitor; Photoelectric charging; Mexican pollution

1. Introduction

Consistent evidence has been found that long and short term exposure to particulate matter in ambient air is contributing to thousands of premature deaths caused by cardiovascular and respiratory illnesses (Colburn and Johnson, 2003; Dominici et al., 2003; Pope et al., 2002; Pekkanen et al., 2002; Samet et al., 2000). Presently it is not well known which characteristic of particulate air pollution determine its health effects, however the dominant hypotheses concern the chemical composition, the surface properties and the large number of fine particles (particles $<2.5\,\mu m$ in diameter). Fine particles can be inhaled and retained deep into the lungs, becoming carriers of most of the mutagenic and carcinogenic organic components in humans, such as the polycyclic aromatic hydrocarbons (PAH).

PAH are associated with the incomplete burning of fossil fuels, wood, garbage, tobacco, or other organic materials (Finlayson-Pitts and Pitts, 1997). Particle bound-PAH (PPAH) are formed by combustion and noncombustion processes through gas to particle

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condensation and accumulation mechanisms. Automobile exhaust has been recognized as the major PAH contributor in urban areas (Kittelson et al., 2004; Vera Castellano et al., 2003; Manoli et al., 2002; Sheu et al., 1997; Nielsen, 1996; Lee et al., 1995). The emission profiles of PAH vary among engine type; diesel engines are the major source of low-molecular weight PAH, whereas light-duty gasoline engines are the principal source of high-molecular weight PAH such as benzo(a)-pyrene and dibenzo(a,h)anthracene (Miguel, 1998).

Miguel (1998) suggested that the PPAH from traffic sources follow two formation mechanisms: a combustion process that leads to the formation of gasoline- and diesel-derived PAH primarily in the ultrafine mode (particles $< 0.10\,\mu m$ in diameter) and a noncombustion process associated with diesel-derived PAH that is found mainly in the accumulation mode (particles with diameter between 0.10 and $2\,\mu m$). Most of the PPAH mass is found in the accumulation mode. Recent laboratory investigations suggest that the nuclei mode (particles with diameter between 0.005 and $0.05\,\mu m$) from diesel engines are formed by condensation after combustion (Ziemann et al., 2001).

Mexico City is a megacity known for its air pollution problems, with a population over 18 million, a density of 12 000 inhabitants per km^2, and more than 3.5 million cars with an average age of 10 years. Mexico City is at an elevation of 2240 m above sea level, which makes combustion processes less efficient, and therefore, produces a larger amount of pollutants, including PPAH. The health effects related to particles pollution in Mexico have been well documented in several studies (Sanchez-Carrillo et al., 2003; Rosas et al., 2000; Loomis et al., 1999; Borja-Aburto et al., 1998; Villalobos-Pietrini et al., 1995), but few studies have focused on the micro-environmental and personal exposure to fine particles (Garcia-Gutierrez et al., 2000), and none on PPAH.

To perform risk assessment it is necessary not only to measure the concentration of the PPAH, in addition the total active surface area must be measured, since it is the critical characteristic in many processes in which the particles are involved and because PPAH are mainly formed by molecules located in the external layer, making the active surface more important for cell interaction and health effects than the particles' core (Moshammer and Neuberger, 2003; Höhr et al., 2002; Tran et al., 2000).

In this context, this paper presents near-real time measurements of personal exposure to PPAH in different outdoor and indoor environments of Mexico City. The objectives of this study were to determine the PPAH concentration and the joint active surface area to which citizens are exposed, and to identify in a qualitative way the possible emission sources. The results will help to perform risk assessments in Mexico that consider the toxicity of ambient particles.

2. Methodology

The measurements were done with portable sensors based on photoelectric charging (PC) and diffusion charging (DC) to determine the PPAH concentration in $ng\,m^{-3}$ of particles with a diameter below $1\,\mu m$ and the joint active surface area of all particles in $mm^2\,m^{-3}$, respectively. Storage time intervals were 10 s. These two sensors have been evaluated through laboratory studies and used in previous investigations for monitoring exhaust particles, and health and environmental issues (Sakai et al., 2002; Bukowiecki et al., 2002; Tang et al., 2001; Siegmann and Siegmann, 2000; Matter et al. 1999; Siegmann et al., 1999; Ramamurthi and Chuang, 1997; Niessner et al., 1989). A brief description and advantages of these instruments are provided below and Table 1 shows their characteristics.

2.1. The photoelectric aerosol sensor (measurement of PPAH concentration)

Conventionally, PPAH are sampled by mechanical instruments and collected on a filter over a finite period of time (for example 8 h). The filter is weighted and the PAH are extracted by solvent extraction, followed by a pre-concentration, clean up and reconcentration before they can be analyzed by gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS). In theory these techniques are highly reliable, however in practice they are complicated, time consuming, expensive and their results can be hampered by a number of artifacts due to the minute

Table 1
Instrument information

Parameter	Instrument	Detection limit	Lower threshold	Response time	Model	Manufacturer
Total PPAH concentration (particles $<1\,\mu m$)	PAS-PC	$1\,ng\,m^{-3}$	$\pm 15\%$ of reading $\pm 3\,ng\,m^{-3}$	10 seg	PAS 2000CE	EcoChem analytics
Total active surface area	PAS-DC	$1\,mm^2\,m^{-3}$	$\pm 15\%$ of reading $\pm 2\,mm^2\,m^{-3}$	10 seg	DC 2000CE	EcoChem analytics

amount of material and the evaporation or condensation of species during the collection on the filter.

An alternative option for the detection of the total PPAH is the use of a photoelectric aerosol sensor based PC (PAS-PC). The operational principle of the PAS-PC is described in detail by Burtscher (1992). Briefly, the PAS-PC employs pulsed UV light (207 nm) to ionize the PPAH, while gas molecules and other aerosols remain neutral. Following ionization, each photoelectron attaches to an oxygen molecule to form a negative ion in the carrier gas. The negative ion diffuses back to the particle if the particle is about 1 μm or larger in size (Siegmann et al., 1999). However, particles of smaller size remain positively charged, while the negative ions diffuse to the walls or are removed by an alternating electric field. The positively charged particles are collected on a filter element and the electric current generated is monitored by an electrometer. The electrometer provides an output signal that is proportional to the PAH mass adsorbed on particles with a diameter $<1\,\mu m$ collected by the filter. Note that the PC instrument can measure only total PPAH and can not provide PAH speciation, which requires techniques such as GC-MS or LC-MS.

At ambient temperature, the PAH detected by the PAS-PC are those with four and more rings, since PAH with less rings are not condensed at the particle surface. The detected PAH include pyrene, benzo(g,h,i)fluoranthene, benzo(a)anthracene, chrysene, triphenylene, perylene, coronene, benzo(c)phenanthrene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and dibenzo(a,h)anthracene. PAH with a molecular weight higher than 200 amu will be preferentially detected, since PAH with lower molecular weight have the potential to repartition onto particles with a diameter greater than 1 μm. Allen et al. (1997) measured oxygenated PAH associated with urban aerosols, and found that they were initially associated with fine particles after formation by either combustion or gas phase photooxidation and then partitioned to larger particles by vaporization and sorption.

2.2. The diffusion charging sensor (measurement of active surface area)

Particles have cavities, as well as internal and external surfaces. The latter are known as the active surface area, which is the location where energy and momentum are transferred to the carrier gas in collisions with its molecules, determining the rate of particle growth by surface condensation, the ultimate speed of chemical reaction involving the carrier gas and the catalytic activity and the deposition of particles by impaction and by diffusion in filters. The surface area enclosed in the interior of the particle or located in bays or cracks is known as the passive surface, and does not contribute to the instantaneous exchange of momentum and energy with the carrier gas, yet it may shield reactive species from, e.g., oxygen and contribute to particle changes on a longer time scale (Keller et al., 2001).

To investigate the active surface area of the PPAH, particles must remain in the carrier gas. If they are brought into a vacuum in order to image them with an electron microscope, many of the surface compounds can evaporate or may even transform under the impact of the imaging electron beam. Hence, while the electron microscope is an excellent tool to image nanostructures, it merely reveals the graphitic skeletons or other non-volatile nuclei of the combustion generated particles (Keller et al., 2001). Instead, the active surface can be measured by a PAS based on unipolar diffusion charging (PAS-DC), where ions are produced in the carrier gas by a corona discharge. The ions attach to the surface of the particles which are collected in an electrically insulated particle filter. The electric charge is converted to a voltage signal. The number of attached ions over a wide size range of particles depends linearly on the active surface which can be interpreted as that fraction of the geometrical surface of the particles which is directly accessible from outside (Keller et al., 2001).

2.3. PC/DC ratio

The ratio between the PPAH concentration and the total active surface area (PC/DC) obtained from simultaneous measurement with the PAS-PC and the PAS-DC, has been described as a fingerprint for individual types of combustion particles (Bukowiecki et al., 2002; Matter et al., 1999). A plot of the PC versus the DC has been found to yield a linear relationship for any type of combustion. Since both instrument responses are a function of the particles surface area concentration, the slope of PC/DC plots can be considered as the capability of the surface to undergo photoelectric charging, which depends on the surface material. Siegmann et al. (1999) measured a slope of $4.00\,ng\,mm^{-2}$ for candle soot, 0.36 for cigarette smoke, 0.6 for paper fire, and between 1.28 and $1.83\,ng\,mm^{-2}$ for vehicular particles from a roadway in Switzerland. It should be noted that particles from other than combustion sources can generally not be charged photoelectrically because of the absence of PAH. Hence, such particles will produce a signal only in diffusion charging, with a $PC/DC \approx 0$.

The amount of PAH from a combustion source varies widely depending on the fuel and the conditions of the combustion. Hence, ambient measurements can exhibit a characteristic PC/DC ratio according to the major emission source of each specific site with an associated variability due to the contribution of other sources.

2.4. PC/DC ratio of a diesel engine as a control level

The exhaust emission of a diesel truck was measured to obtain a control level for the PC/DC ratio to be compared with the subsequent measurements. The measurement was performed in an open air workshop with a well maintained 20 years old dump truck. The sensors were located close to the truck, but not exactly in the exhaust, in a similar distance as when the roadway monitors were performed. The expected linear relationship between the PPAH concentration and the total active surface area was corroborated through this experiment (Fig. 1), observing a good correlation coefficient of 0.93. The slope equals $1.18\,ng\,mm^{-2}$, indicating a high PC, since the PPAH background was $\sim 1\,ng\,m^{-3}$ and the active surface area during the experiment yielded values over $200\,mm^2\,m^{-3}$, which correspond to typical values of fresh diesel accumulation mode particles without coexisting nuclei particles, as Bukowiecki et al. (2002) have documented.

2.5. Field measurements

Both sensors were operated in representative sites of Mexico City during December 2001, coinciding with Christmas festivities, which are related with more congested traffic, and more visits to shopping and entertainment centers, as well as an increase in pollutant emissions. Six outdoor sites were selected, including three bus stations and a public market. Thirteen sites, including residences, restaurants, department stores and two subway lines were chosen for indoor environment measurements. Additionally, measurements were conducted in seven roadways with different fleet composition. Tables 2 and 3 list the sites and roadways, and provide a brief description of each.

For all outdoor and some indoor measurements, such as in shopping centers and in the subway, both sensors were carried in a personal bag sharing the same inlet sampling located close to the height at which people breathe. For the other indoor measurements the sensors were located in a common place, for example, on a table in the middle of a restaurant, or in the living room of a residence. During the roadway measurements the sensors were placed on the dashboard of a car with the windows opened.

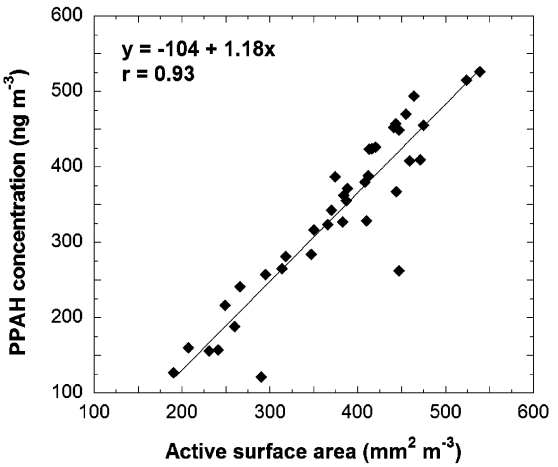

Fig. 1. PC/DC plot for the exhaust emissions of a diesel dump truck.

3. Results

Figs. 2 and 3 show the means of the PPAH concentration and the total active surface area for the measurements conducted in indoor and outdoor environments, as well as on roadways, using the codes for each site established in Tables 2 and 3. Limits for the 95% of confidence levels obtained from 2 times their standard deviation are also shown. The variability of the measurements was higher than the lower threshold for both, the PAS-PC and the PAS-DC.

The observed levels of PPAH are discussed in the following sections. The possible sources for each monitored environment are identified through the PC/DC ratio and the diesel control level. The physical and chemical characteristics of PPAH are described comparing our results to recent references. Finally, the exposure to PPAH is presented in terms of the cigarette exposure equivalent to provide a qualitative idea of the adverse effects imposed by PPAH.

3.1. Outdoor environments

The highest PPAH concentrations were observed in outdoor environments, with the exception of one from an underground parking lot. The means of the outdoor PPAH ranged from 17 to $582\,ng\,m^{-3}$, and the means of the active surface areas from 122 to $702\,mm^2\,m^{-3}$. The two monitored bus stations of urban transport (IV and Toreo) had concentrations up to 71% higher than the diesel engine used as control level, and differences lower than 18% of the total active surface area. The elevated concentration of PPAH represents a large emission of fresh particles in the accumulation mode due to the abrupt acceleration, chaotic and slow movement of the old buses in these stations. These results are in contrast to the concentrations measured in a coach bus station (CCN), which was 74% lower than the control level, illustrating the use of technologies with emission controls and a better driving organization.

Table 2
Outdoor and indoor sites monitored in this study

Code	Site	Characteristics
Outdoor environments		
Dow	Downtown Mexico City (12:15–12:35 h)	1 and 2 lanes streets with congested traffic Passenger cars, taxi cabs and microbuses (buses with capacity for 25 passengers) Meanly commercial area High density population
MS	Mexico City Main Square (Plaza Mayor) (11:47–12:15 h)	Open area Passenger cars and taxi cabs High density population
Prg	Downtown Progreso de Obregon City, Hidalgo State (17:34–18:00 h)	Small city in the north of Mexico City Diesel trucks Sub-rural area surrounded by agriculture fields Emissions influence from a power plant and a petroleum refinery
CA	Central de Abastos (18:20–18: 40 h)	Biggest market in Mexico City Diesel trucks High density population
IV	Indios Verdes bus station (15:36–14:01 h)	Ending line subway station Diesel buses, microbuses, public vans and taxi cabs, almost all of them with a poor maintenance Bad traffic High density population Influence from industrial emissions
Toreo	Toreo bus station (17:30–17:51 h)	Ending line subway station Diesel buses, microbuses, public vans and taxi cabs, almost all of them with a poor maintenance Bad traffic High density population Influence from industrial emissions Station bigger than *Indios Verdes*
CCN	Central Camionera del Norte coach station (14:28–15:06 h)	Diesel coach buses of recent model and relatively good maintenance High density population.
Indoor environment		
R1, R2, R3	Residences (diverse)	Medium class neighborhoods (Taxqueña, Narvarte and Progreso, respectively) No smoking residences
Cin	Cinema theatre (21:30–22:50 h)	Medium size theatre (Cineteca Nacional) No smoking site
Off	Office (13:34–14:52 h)	Southeast of the city (CENICA) No smoking site
Rest	Restaurant (18:30–19:38 h)	Restaurant (Samborns Universidad) Smoking site
SM	Supermarket	Big supermarket (Commercial Mexicana Pilares)
M1	Mall 1 (13:45–14:00 h)	Department stores, boutiques, banks and restaurants Southwest of the City (Perisur)
DS	Department Store (13:10–13:40 h)	One of the biggest department stores in Mexico City Inside of Mall 1
M2	Mall 2 (17:03–18:27 h)	Department stores, boutiques, banks and restaurants South of the City (Plaza Universidad)
PL	Underground parking lot at Mall 2 (18:11–18:20 h)	Medium size parking lot Poor ventilation Mainly new passenger cars with emissions control equipment
SGL, SBL	Subway (16:50–17:25 h line 2) (16:08–16:30 h line 3)	Underground subway Two of the most busy lines

Monitored time interval is shown in parenthesis.

In the old district center of the city and the Main Square, PPAH concentrations and total active surface areas were similar to levels observed in indoor environments, specifically residences and crowded sites as supermarkets or the subway. Although these two places are influenced by a large number of potential sources, the diesel vehicles are scarce, because no public buses and trucks are allowed to circulate in the narrow streets of this area of the city.

3.2. Indoor environments

The highest PPAH concentration was measured in an underground parking lot of a department store (PL); it

Table 3
Roadways monitored in this study

Code	Roadway	Characteristics
TSA-T (bad traffic), TSA-NT (low traffic)	Tlalpan Sur Avenue (11:17–11:48 h)	6 lanes roadway Passenger cars, diesel trucks, diesel buses, microbuses, taxi cabs and an electrical train Continuous traffic lights
MAQA	Miguel Angel de Quevedo Avenue (14:10–14:30 h)	6 lanes roadway Passenger cars, diesel buses, microbuses and taxi cabs Continuous traffic lights and intersections
UA	Universidad Avenue (11:13–11:25 h)	4 lanes roadways Passenger cars, diesel buses, microbuses and taxi cabs Bad traffic Continuous traffic lights
ChA	Churubusco Highway (Centenario-Ermita) (10:55–11:11 h)	6 lanes roadway Only passenger cars and taxi cabs No traffic lights and intersections Smoothly running traffic
GMA	Gabriel Mancera Avenue (18:50–19:00 h)	3 lanes roadways Passenger cars, diesel buses, microbuses and taxi cabs Bad traffic Continuous traffic lights and intersections
E5SA	Eje 5 Sur Avenue (18:40–18:50 h)	4 lanes roadway Passenger cars, diesel trucks, diesel buses, microbuses and taxi cabs Relatively bad traffic Continuous traffic lights and intersections
Col-R	Colonia Roma Streets (19:00–19:20 h)	1 and 2 lane streets Passenger cars, taxi cabs and few microbuses

Monitored time interval is shown in parenthesis.

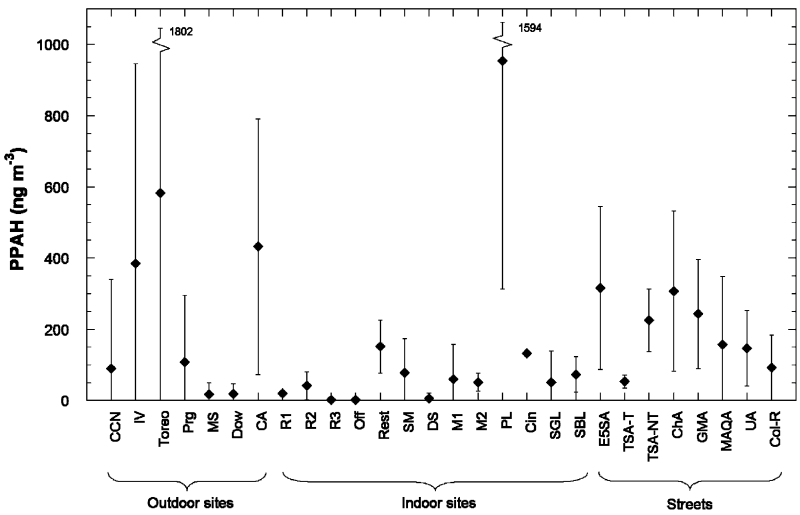

Fig. 2. Means of the outdoor, indoor and roadways concentrations of PPAH. The confidence bars (2 times the standard deviation) represent the natural variations.

was 280% higher than the diesel engine control level, and it showed a PC/DC ratio of 3 ng mm^{-2}, which was much higher than the typical ratio for diesel vehicles and roadways, but close to that produced by the combustion of a candle. The parking lot was poorly ventilated, completely full with a number of passenger cars entering and leaving from it at a low speed. Although most of the cars were new models with catalytic converters, their combustion was inefficient, coinciding with a high PC/DC ratio that can be related to combustion processes

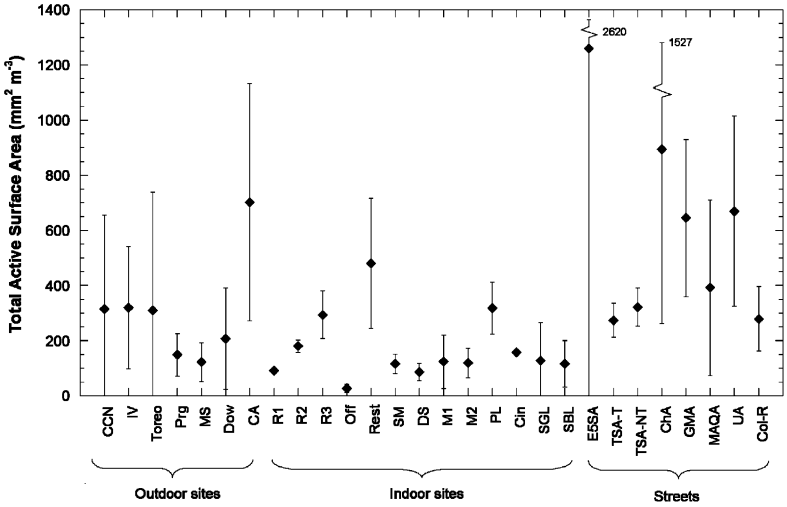

Fig. 3. Means of the outdoor, indoor and roadways areas of the total active surface. The confidence bars (2 times the standard deviation) represent the natural variations.

with poor oxygen (Siegmann et al., 1999). The existence of a malfunctioning boiler burning heavy oil, petroleum or other cheap fossil fuel for the air-conditioning system of the own department store can not be rejected in the contribution of the large amount of PPAH detected.

However, in general the lowest PPAH concentrations were found in indoor environments, showing PC/DC ratios similar to the measured ratio burning paper in a laboratory experiment (Siegmann et al., 1999). These results show that indoor PPAH come from combustion processes of organic materials others than fossil fuels, producing in most of the cases particles composed of non-photoemitting material, as nitrate, sulfate, water and hydrocarbons. Cigarette smokers were found to be the major source in indoor environments. Repace (2003) found that 85–95% of PPAH in hospitality venues come from secondhand smoke. A comparison of the mean PPAH concentration and the active surface area measured in an office with no smoking people (Off) and in a restaurant (Rest) with presence of smokers showed that the exposure to PPAH was 76 times higher in the restaurant than in the office. The mean total active surface area reported by the cigarette smoke in the restaurant was $480\,mm^2\,m^{-3}$, the highest of the indoor environments and higher between most of the outdoor places. The high total active surface area is due to the fact that the cigarette particles are much larger than the other particles and grow with time to even larger ones, since they contain liquid matter that condenses the condensable material on the fresh particulate matter core. Other major sources of indoor PPAH were found to be food cooking, badly operated pilot stoves, insufficient ventilation and malfunctioning air-conditioning systems.

In two busy lines of the underground subway (SGL and SBL) no major PPAH sources were identified, the observed PPAH could be related to outside ambient concentrations. The exposure level to pollutants in the Mexican subway is relevant since everyday more than 5 million of people travel by it.

3.3. Roadways

Representative avenues of Mexico City with different characteristics and fleet composition were selected to monitor the air along roadways. As was expected, the highest roadway concentration of PPAH was observed in an avenue with smoothly running traffic with an average speed of $60\,km\,h^{-1}$, composed of passenger cars, taxi cabs and a large number of diesel buses and heavy-duty trucks (E5SA). Comparing the particulate matter level from this roadway with the proposed diesel engine as control level, the PPAH concentration was 7% lower, but the total active surface area was 3.8 times higher ($1260\,mm^2\,m^{-3}$), the highest area observed in this study. There are three possible explanations for the observed differences. It may result from aged accumulation mode particles, which typically are larger than freshly emitted diesel aerosol particles and coated with at least one layer of non-photoemitting material. This coating is due to the condensation of condensable material on the fresh particles' core and may occur on relatively short time scales (minutes to hours). Alternatively, it may result from engine conditions that give relatively high emissions of large accumulation mode particles that act as a sink for volatile species that suppress photoemission (Bukowiecki et al. 2002). A third explanation is the existence of other particles on the roadway in addition

to those produced by the vehicles, which do not produce a signal in the PAS-PC.

The characteristics of the roadway, such as the number of lanes, the frequency of intersections and traffic lights, the fleet composition, the prevailing style of driving and the average speed appear to be relevant for the PPAH emissions. However, the speed average seems to be one of the most important parameters in the production of fresh soot containing PAH. Fig. 4 shows a PC/DC plot for ambient air in a busy roadway compressing 6 lanes, 3 each way, during congested traffic (TSA-T) and smoothly running traffic (TSA-NT). The PPAH concentration was 4.3 times higher during low traffic than during bad traffic. High PPAH emission rates appear to be related to periods of rapid acceleration more than periods of congested traffic with slow speed. This is expected as PPAH are generally produced by incomplete combustion. Similar results were found by Tang et al. (2001) studying the PPAH emissions from heavy duty diesel trucks and buses in New York. This observation does not contradict the high PPAH concentration found in the underground parking lot, where the poor ventilation and the absence of solar radiation produce their accumulation. Of particular interest in Fig. 4, is the fact that emissions of standing vehicles in a roadway during a traffic jam were enough to produce concentrations up to 50 ng m^{-3} of PPAH. Although the difference in PPAH is significant, the total active surface area showed a small difference of 13% between both conditions, suggesting that emissions of particles of other compounds than PAH do not depend closely of the driving speed.

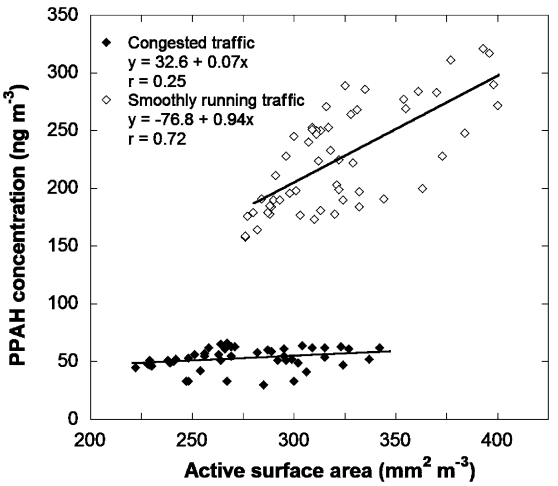

Fig. 4. PC/DC plot for ambient air in a roadway compressing 6 lanes during congested traffic (TSA-T) and during smoothly running traffic (TSA-NT).

Fig. 5 shows the concentration profile for PPAH and active surface area on a trip from the southwest to the center of the city on a sunny day. The means of the PPAH mass and the active surface area on the whole trip were 180 ng m^{-3} and 392 mm^2 m^{-3}, respectively, similar to the means observed in the other monitored roadways. The large active surface area is related to larger particles, which give to Mexico City the bad reputation with respect to particulate air pollution. For some periods of time, e.g. between 11:00 and 11:20 h, the PPAH concentration and the active surface area track each other quite closely, indicating that the photoemmiting and non-photoemitting particles were both emitted by motor vehicles. Several sharp peaks were observed, the highest one at 11:03 h was produced by a passenger gasoline car, likely because its engine was

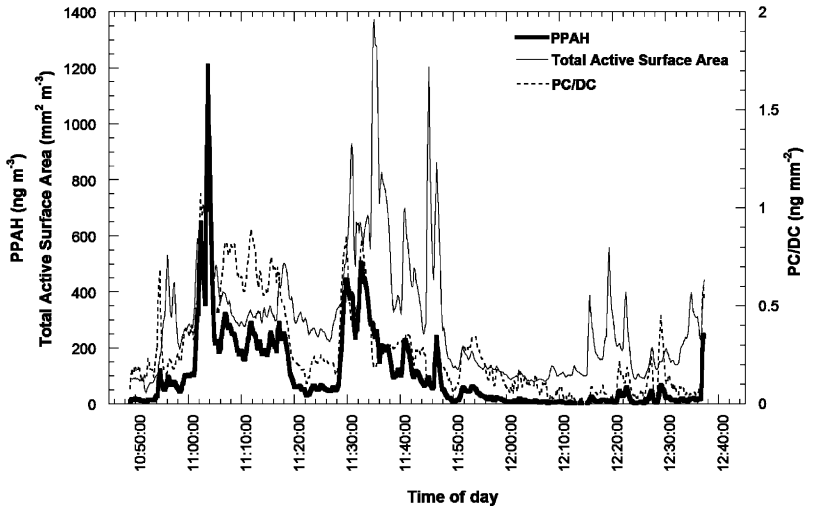

Fig. 5. PPAH concentration, total active surface area and PC/DC ratio for a trip from the southwest to the center of the city on a sunny day.

malfunctioning and/or had a defect catalyst. A traffic jam occurred between 11:20 and 11:38 h producing a visible decrease in the PPAH concentration, illustrating once more that large PPAH emissions are related to vehicles in movement and accelerating. The null PPAH mass detected from 11:50 to 12:15 h corresponded to the measurements performed around the Main Square of Mexico City, where there was little traffic. Between 12:15 and 12:37 h the measurements were conducted in different streets around downtown, which are characterized by slow vehicle's circulation, and hence a small presence of PPAH.

Following the characterization of particles in ambient combustion aerosols proposed by Bukowiecki et al. (2002), the PPAH concentration was plotted versus the total active surface area data collected during the return trip from the center to the southwest of the city. The plot shows two branches indicating a different relationship between the PAS-PC and the PAS-DC. It has been documented that in the absence of a nuclei mode, a highly positive slope results, indicating a high positive charge collected on the PAS-PC current filter. On the other hand, the presence of a large nuclei mode concentration prevents a large positive PAS-PC signal (Bukowiecki et al., 2002; Matter et al., 1999). It is important to note that a flat branch is not only caused by the presence of a nuclei mode, but also by situations in which the concentration of surface PAH and elemental carbon is low (Siegmann and Siegmann, 2000). This result clearly shows the existence of particles in both the nuclei and accumulation mode in Mexican roadways, as well as that the use in parallel of the PAS-PC and PAS-DC can be an useful tool for their identification in real time (Fig. 6).

The average of the PPAH concentrations monitored at the 7 roadways described in Table 1 was similar to those observed in the trips from the southwest to the center of the city discussed above. The difference was less than 22%, indicating that PPAH pollution is a problem of the entire city. The average of 173 ng m^{-3} from all the roadways is lower than observed in Madrid, Paris, Tokyo and Zurich, but higher than cities in the USA such as Boston and New York (Zhiqiang et al., 2000; Siegmann et al., 1999). The poorer air quality in Paris and Madrid compared to Mexico City can be attributed to the tax laws favoring the use of diesel vehicles. Since Mexico does not have diesel passenger cars, the PPAH must be due to cars with defective catalysts and old diesel trucks and buses.

3.4. Cigarette exposure equivalent

As the harmful health effects from smoking cigarettes have been well documented (Hoffmann and Hoffman, 1998), PPAH results can be presented in terms of the cigarette exposure equivalent proposed by Siegmann and Siegmann (1998), who assume an inhaled dose of 200 ng per cigarette to a smoker. The average minimum volume of air needed by humans in 24 h is 11 m^3. Hence the PPAH exposure concentration is equivalent to smoking n number of cigarette per hour as Eq. (1) indicates.

$$n = (\mathrm{PPAH}/200)(11/24). \quad (1)$$

As an example, the PPAH exposure in the monitored parking lot is equivalent to 2.2 cigarettes per hour. If a person works there 20 h per week, his equivalent exposure could reach in an extreme case up to 44 cigarettes per week. Applying the equivalent exposure to the roadway data, suggests that driving around Mexico City is equivalent to smoking 0.4 cigarettes per hour.

Obviously, the health risk from urban air pollution is not the same as from cigarette smoke. The cigarette exposure equivalent only tries to provide a qualitative idea of the adverse effects imposed by PPAH in different environments. However, some PAH have been identified in particles from both cigarette smoke and urban air, such as phenanthrene, anthracene, fluoranthene, pyerene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-c,d)pyrene, among others (Hoffmann and Hoffmann, 1998; Sheu et al., 1997; Gundel et al., 1995).

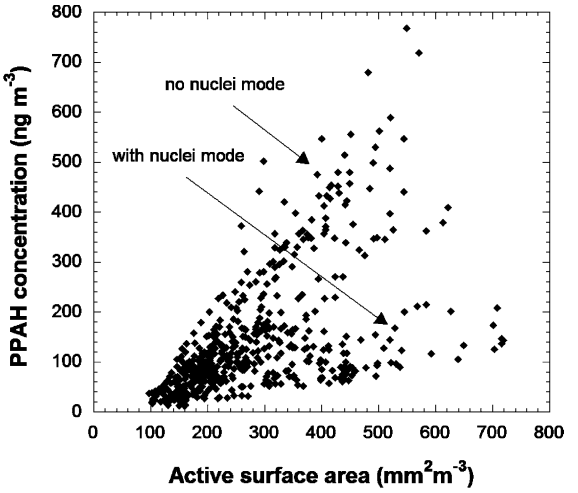

Fig. 6. PPAH concentrations versus active surface areas measured during a trip from the center to the southwest of the city. There is evidence of two branches indicating a different relationship between the two instrument responses.

4. Conclusions

PPAH concentration and total active surface area were measured for the first time in Mexico City at

different indoor and outdoor locations, and on roadways. Measurements were obtained using PC and DC photoionization monitors. The results show that most of the personal exposure in Mexico City to PPAH comes from cigarette smoke in indoor and diesel engines in outdoor environments.

The highest exposures were found in ambient air near traffic sources, mainly in sites with a large number of diesel vehicles such as urban transfer bus stations. However, high levels of exposure were also found on all the monitored roadways, indicating that PPAH pollution is a problem of the entire city. In addition, the roadway experiments showed that not only diesel exhausts, but poorly functioning gasoline or/and defective catalysts generate significant amounts of PPAH. On this account, the future introduction of secondhand vehicles from the United States, following the plans of action of the North American Free Treaty Agreement (NAFTA), must be strictly regulated in order to avoid a serious increase of super-pollutant cars in the streets of Mexico.

Simple measures such as removing the super-pollutants vehicles and arranging the chaotic movements of buses in transfer stations would be highly effective in improving air quality. Special attention must be taken in underground parking lots, as those in commercial centers, where ventilation is low and cars idle in long queues. In the same sense is necessary that diesel and heavy duty trucks also undergo periodical exhaust emissions and engine tests. These tests must be effective and focused in the particle traps on the diesel vehicles and in the exhaust catalysts on gasoline cars.

The observed concentration of PPAH in roadways is within the range found in large cities in Europe and USA. The bad air quality with respect to PPAH in cities such as Madrid is due to the tax laws favoring the use of diesel vehicles, and must be a good indicator for future environmental and energetic policies in Mexico and developing countries in similar situation.

As it was expected, PPAH exposure was lower in indoors than in outdoor environments. However, the presence of smokers, poorly adjusted pilot stoves, inefficient ventilation and badly functioning air-conditioning systems showed to be major PPAH sources in places as residences, restaurants, shopping and entertainment centers, among others. Some states in the USA and countries in Europe, for example California and Ireland, have implemented bans on smoking in workplaces and hospitality venues such as clubs and pubs in an attempt to protect the public from exposure to secondhand smoke (Repace, 2000). The respiratory health benefits that have been provided by these bans should encourage the Mexican health authorities to decree prohibitions on smoking in public places, since authorities have the obligation to protect the health of workers and citizens by ensuring clean indoor air.

In conclusion, personal monitors based on PC and DC techniques may be used as a rapid and economic tool for near-real-time and semi-quantitative estimation of the PPAH concentration and total active surface area, providing reliable information about the quality of the air measured, and helping to identify the major sources. These are features that could not be achieved by the conventional chemical analysis and may be very important for environmental risk assessment. Although results from this study are encouraging, more research on PC is needed, particularly regarding instrument calibration and potential response variability versus PAH composition. Since PAH speciation varies from one city to another due to the different combinations of emission sources, type and quality of fuels, and natural conditions such as weather, it is necessary to perform a comparison analysis between the photoelectric aerosol sensor and conventional chemical analysis for particles collected in different environments of a specific city. This analysis must also include size distribution measurements to identify the size mode in which particles attaching PAH can be expected at different locations and deliver more useful information on the characterization of urban aerosols.

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