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FACULTAD DE QUÍMICA

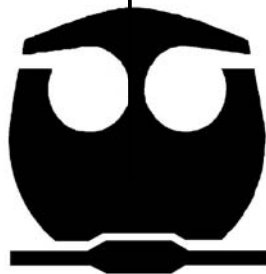
SOLVENT EXTRACTED ORGANIC MATTER AND POLYCYCLIC
AROMATIC HYDROCARBONS DISTRIBUTED IN SIZE-
SEGREGATED AIRBORNE PARTICLES IN A ZONE OF MEXICO
CITY: SEASONAL BEHAVIOR AND HUMAN EXPOSURE

ACTIVIDAD DE INVESTIGACIÓN

QUE PARA OBTENER EL TÍTULO DE
INGENIERA QUÍMICA

PRESENTA

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Título del protocolo de tesis

Comportamiento temporal de los hidrocarburos aromáticos policíclicos en partículas suspendidas con diferentes diámetros aerodinámicos en una zona de la Ciudad de México

1. ANTECEDENTES

Se tiene bien documentada la asociación entre los efectos adversos en la salud humana y las partículas atmosféricas gruesas ($>2.5 \mu\text{m}$) y finas ($<2.5 \mu\text{m}$) (de Kok et al., 2006). La magnitud de estos efectos generalmente depende del tamaño y de la composición química de las partículas, siendo su tamaño inversamente proporcional a la profundidad de depositación en el sistema respiratorio (Sugita et al., 2004). El riesgo a la salud humana se relaciona con diversos factores tales como el tipo de partícula, el comportamiento estacional, la fuente de emisión de las diferentes especies químicas atmosféricas y el tiempo de exposición, con mayor impacto en niños y ancianos. Las partículas atmosféricas pueden ser generadas a través de la resuspensión de la tierra debido al viento o a procesos naturales como la erosión. Pueden también ser producto de la combustión incompleta de materiales fósiles y no fósiles, así como el resultado de reacciones químicas y la condensación sobre partículas ya existentes (Solomon et al., 2001). Su composición química es una mezcla compleja que depende de varios factores como: la fuente de emisión, las condiciones geográficas y climáticas, y la reactividad atmosférica. Los hidrocarburos aromáticos policíclicos (HAP) están dentro de los compuestos orgánicos de mayor riesgo debido a sus propiedades carcinogénicas (IARC, 1983) y genotóxicas (Kawanaka et al., 2004; Villalobos- Pietrini et al. 2007), ya que se encuentran asociados a las partículas atmosféricas de menor diámetro (Venkataraman et al., 1994; Allen et al., 1996), lo que determina mayor y más profunda depositación en los pulmones. Los HAP surgen generalmente de una mezcla compleja emitida como resultado de un proceso de combustión incompleta. Son generados por fuentes naturales y fuentes antrópicas (ATSDR, 1995). La caracterización química de las muestras de partículas segregadas por tamaño se relaciona con el efecto tóxico de sus fuentes (Davidson et al., 2005). Los muestreadores de impactador en cascada de altos volúmenes permiten el uso de la misma muestra tanto para estudios toxicológicos como para los análisis químicos (Demokritou et al., 2002). En México existen algunos estudios

recientes que han reportado la presencia de HAP en las partículas del aire (Villalobos-Pietrini et al. 2006,2007, Marr et al. 2006, Saldarriaga et al. 2008, Stone et al. 2008, Guzmán-Torres et al. 2009). La abundancia y el comportamiento temporal de ellos justifican la evolución del riesgo que corre el ser humano ante su exposición atmosférica, por lo que este trabajo contribuirá con la escasa información que hay en lo referente a la caracterización de los HAP y de la materia orgánica en las partículas suspendidas inhalables.

2. HIPÓTESIS

Diversos estudios (Venkataraman et al 1994; Allen et al., 1996) han mostrado que la distribución de los HAP en las partículas es inversamente proporcional a su peso molecular (PM) y que la concentración tanto de las partículas, de la MOE y de los HAP en época de secas es mayor que en la de lluvias (Eiuguren-Fernandez et al. 2007, Guzmán-Torres et al. 2009). En este estudio se espera obtener la misma distribución de los HAP y similar comportamiento temporal al reportado en otros estudios. Por otra parte se espera que los HAP más abundantes sean aquellos considerados como marcadores de fuentes vehiculares dado que en la Ciudad de México circulan cerca de 4,000,000 de vehículos.

3. OBJETIVO GENERAL

Determinar el comportamiento temporal de los hidrocarburos aromáticos policíclicos en los diferentes diámetros aerodinámicos, al suroeste de la Ciudad de México.

4. OBJETIVOS ESPECÍFICOS

- Determinar la concentración de la masa de las partículas y de la MOE en ambas temporadas.
- Observar la distribución de la masa de las partículas y la MOE en función de los diferentes diámetros aerodinámicos.
- Determinar el tipo y la cantidad de HAP en los diferentes diámetros aerodinámicos.
- Observar la distribución de los HAP en los diferentes diámetros aerodinámicos en función de su peso molecular.
- Determinar las posibles fuentes de emisión de los HAP.

5. METODOLOGÍA

5.1 Muestreo de las aeropartículas

Las muestras se colectarán a 7 m del suelo en el Centro de Ciencias de la Atmósfera de la Universidad Nacional Autónoma de México (CCA-UNAM), ubicada al suroeste de la Ciudad de México, que es una zona con edificios, áreas verdes y calles aledañas a excepción de la parte sur que es ocupada por una reserva ecológica. Las aeropartículas se colectarán en filtros de fibra de vidrio (Gelman Science), después se calentaran a 180⁰C por 24 h para remover compuestos orgánicos absorbidos y posteriormente se colocarán en un humidificador con una humedad relativa < 40% a 20-23 ⁰C por otras 24 h. Para el muestreo se utilizará un impactador en cascada de 6 etapas con los siguientes rangos de diámetro (d):

1. $10 \geq d \geq 7.2 \mu\text{m}$ (etapa 1)
2. $7.2 \geq d \geq 3.0 \mu\text{m}$ (etapa 2)
3. $3.0 \geq d \geq 1.5 \mu\text{m}$ (etapa 3)
4. $1.5 \geq d \geq 0.95 \mu\text{m}$ (etapa 4)
5. $0.95 \geq d \geq 0.49 \mu\text{m}$ (etapa 5)
6. $d < 0.49 \mu\text{m}$ (etapa 6)

El impactador en cascada se acoplará a un muestreador de altos volúmenes con una entrada de partículas $\leq 10 \mu\text{m}$ (PM₁₀) (Andersen General Metal Works). Los muestreos se efectuarán a un flujo de $1.13 \text{ m}^3 \text{ min}^{-1} \pm 10\%$ cada 8 días (promedio) por 24 h , en 2 períodos de acuerdo con Jáuregui (2000), desde octubre 1998 a febrero de 1999 (temporada de secas) y de junio a octubre 1999 (temporada de lluvia). Después del muestreo, los filtros con partículas se estabilizarán en el humidificador por 24 h y se pesarán nuevamente. La concentración de partículas en $\mu\text{g m}^{-3}$ se calcularán en condiciones estándar (25 ⁰C y 1 atm).

5.2 Extracción y determinación de la materia orgánica extraída (MOE)

Cada cuarto se dividirá en pequeños trozos y se extraerá individualmente con cloruro de metileno (Burdick & Jackson) grado HPLC. La extracción se llevará a cabo en un baño de ultrasonido (Branson 3210). Los extractos se filtrarán a través de una membrana de teflón de 25mm de diámetro y 0.22 μm de poro, se concentrarán en un evaporador rotatorio, se colocarán en viales ámbar para evitar la fotodegradación y se refrigerarán hasta el momento del análisis.

Cada muestra se aforará y se tomará una alícuota que se colocará en un vial previamente pesado. Se llevará hasta sequedad bajo un flujo ligero de nitrógeno grado cromatográfico y se pesará nuevamente. La diferencia entre el peso final e inicial será la cantidad de MOE, que corregida al aforo final, representará la masa total de MOE. Dicha masa, dividida entre el volumen total de aire muestreado, representará la concentración de materia orgánica en el aire, expresada en $\mu\text{g m}^{-3}$.

5.3 Análisis cromatográfico

Las soluciones de referencia con los estándares y los extractos orgánicos de las muestras, serán analizadas en un cromatógrafo de gases (CG) Agilent Technologies 6890 acoplado a un espectrómetro de masas (EM) 5973N con cuadrupolo. Se utilizará una columna capilar de 30 m x 0.25 mm de diámetro interno recubierta internamente con una fase estacionaria de 5% fenil, 95% dimetil polisiloxano y un grosor de 0.25 µm. El EM será operado en el modo de impacto electrónico a 70 eV, con la temperatura de la fuente de iones en 230 °C y la del cuadrupolo en 150 °C.

El análisis cualitativo se basará en los tiempos de retención relativos a los 6 HAP-d, mientras que el cuantitativo, se llevará a cabo utilizando los factores de respuesta relativos a los estándares internos seleccionados, obtenidos de las curvas de calibración correspondiente a cada HAP.

5.4 Control de calidad

El equipo de muestreo será calibrado de acuerdo con las reglas establecidas en el Código de Referencia Federal de los EUA (40 CFR PART 50,1987). Las eficiencias para recuperar la MOE y los HAP se calcularán utilizando material de referencia certificado del Instituto Nacional de Estándares y Tecnología (NIST, en inglés). Los valores de HAP en las muestras serán sustraídas de los blancos de los filtros en el sitio de muestreo y del material utilizado en todo el procedimiento analítico. Las concentraciones en el aire de los HAP serán corregidas por los porcentajes de recuperación.

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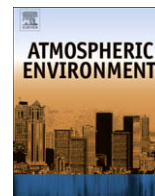
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Solvent extracted organic matter and polycyclic aromatic hydrocarbons distributed in size-segregated airborne particles in a zone of México City: Seasonal behavior and human exposure

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ABSTRACT

Airborne particulate mass was collected in a cascade impactor, and the mass concentration of solvent extracted organic matter (SEOM) and polycyclic aromatic hydrocarbons (PAH) were determined. A greater mass concentration of particles, SEOM and PAH were obtained in the dry season than in the rainy season for all impact stages; however, in the rainy season the proportion of SEOM/particles mass increased for all stages. There was an average decrease in particle mass concentration of $52.1 \pm 6.7\%$, a $33.6 \pm 12.3\%$ decrease in SEOM and a $43.9 \pm 16.9\%$ decrease in heavy PAH ($\geq 228 \text{ g mol}^{-1}$) in the rainy season. Heavy PAH were distributed in fine particles, while light PAH were more abundant in coarse particles. Estimations of SEOM and PAH inhaled daily by a person were made. Considering the carcinogenic PAH median mass (10th–90th percentiles) in 20 m^3 of air, and the sum of all stages that could be inhaled daily by a person, estimates of 137 ng day^{-1} (74–246) in the dry season and 57 ng day^{-1} (21–101) in the rainy season were determined. The toxic equivalent factors were calculated to more accurately characterize the carcinogenic properties of PAH mixtures. This was based on the contribution of the carcinogenic potency of benzo[a]pyrene. These estimations would need to be considered in establishing standards for Mexican air quality. Correlations were shown between other atmospheric pollutants and masses of particles, SEOM and PAH. Vehicles were suggested as an emission source for SEOM and PAH.

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1. Introduction

The association between atmospheric coarse ($>2.5 \mu\text{m}$) and fine ($\leq 2.5 \mu\text{m}$) particles with adverse effects on human health is substantially documented (de Kok et al., 2006). The magnitude of these effects generally depends upon the size and chemical composition of the particles, with the particle size being inversely proportional to the depth of the deposition area in the respiratory system (Sugita et al., 2004). The risk to human health is related to various factors, such as: particle type, particle size distribution, seasonal behavior, sources of different chemical atmospheric species and the length of exposure, which increases health effects in children and elderly people. Airborne particles can be generated through grinding activities, soil resuspension due to wind or from natural processes such as soil erosion. They can also be a product of

incomplete combustion of fossil and non-fossil materials, as well as result from chemical reactions and condensation onto preexisting particles (Solomon et al., 2001). The chemical composition is a complex mixture that depends upon several factors, such as: emission sources, geographic and climatic conditions and atmospheric reactivity. Polycyclic aromatic hydrocarbons (PAH) are among the most risky extracted organic compounds because of their carcinogenic (IARC, 1983) and genotoxic properties (Kawanaka et al., 2004; Villalobos-Pietrini et al., 2007), associated with atmospheric particles of different sizes (Venkataraman et al., 1994; Allen et al., 1996) which can influence their deposition on human lungs. PAH generally occur as complex mixtures emitted as a result of incomplete combustion processes. They are generated from both natural and anthropic sources (ATSDR, 1995). Chemical speciation of size-segregated particulate sampling links the toxic effects of the samples to their sources (Davidson et al., 2005). High volume cascade impactor samplers enable the use of the same sample for toxicological studies as well as for chemical analysis (Demokritou et al., 2002). In México there are a few recent studies which have

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reported the presence of specific PAH on airborne particles (Marr et al., 2006; Villalobos-Pietrini et al., 2006, 2007; Saldarriaga et al., 2008; Stone et al., 2008; Guzmán-Torres et al., 2009). Abundance and spatial behavior of PAH are of concern to assess the human risk from atmospheric exposure. In order to improve the scarce information of specific characterization of PAH and organic matter, four main objectives were established: 1) evaluate the seasonal behavior of particle mass, solvent extracted organic matter (SEOM) mass and PAH mass in dry and rainy seasons, 2) determinate the mass distribution of particles, SEOM and PAH in six different aerodynamic diameters, 3) determine the relationships between particles, SEOM and PAH with the atmospheric pollutants and the meteorological parameters, and 4) estimate the human health risk based on PAH using toxic equivalent factors.

2. Materials and methods

2.1. Airborne particles sampling

The samplings were carried out at 7 m above the ground in southwest Mexico City, at the Universidad Nacional Autónoma de México (UNAM), which is a zone with buildings, green areas and many surrounding streets, except on its southern side which is occupied by an ecological reserve. Most of México City lies from the northwest to the southeast with respect to the sampling site; high mountains lie toward the west and toward the south–southwest, and commercial and residential districts predominate. The airborne particles were collected on glass fiber filters (Gelman Science), baked at 180 °C for 24 h to remove organics adsorbed on them and then conditioned in a chamber with a relative humidity < 40% at 20–23 °C for another 24 h. For samplings, we used a cascade impactor (Sierra Andersen) with six stages with the following diameter (d) ranges: $10 \geq d \geq 7.2 \mu\text{m}$ (stage 1), $7.2 > d \geq 3.0 \mu\text{m}$ (stage 2), $3.0 > d \geq 1.5 \mu\text{m}$ (stage 3), $1.5 > d \geq 0.95 \mu\text{m}$ (stage 4), $0.95 > d \geq 0.49 \mu\text{m}$ (stage 5) and $d < 0.49 \mu\text{m}$ (stage 6). The impactor was coupled with a high volume sampler with an inlet for particles $\leq 10 \mu\text{m}$ (PM₁₀) (Andersen General Metal Works). Samplings were carried out at a flow rate of $1.13 \text{ m}^3 \text{ min}^{-1} \pm 10\%$, every 8th day (as an average) for 24 h, in two periods according to Jáuregui (2000), from October 1998 to February 1999 (dry season, $N = 18$) and from June to October 1999 (rainy season, $N = 24$). After sampling, the filters with particles were stabilized in the chamber for an additional 24 h and weighed again. The particle concentrations in $\mu\text{g m}^{-3}$ were calculated at standard conditions (25 °C and 1 atm).

2.2. Solvent extracted organic matter (SEOM)

The organic matter in the particles of each stage was extracted in an ultrasonic bath (Branson 3210) with methylene chloride (HPLC grade, Chromanorm) for 30 min at room temperature. This procedure was repeated twice with fresh solvent each time. The excess solvent was eliminated in a rotatory evaporator (Buchi). The SEOM mass in each stage was determined by evaporating the solvent under a low nitrogen flux down to a final volume of 1 mL. A 200 μL aliquot was poured into a vial that was pre-weighed on a calibrated balance (Sartorius). The solvent was evaporated and the vial weighed again. The SEOM air concentration in $\mu\text{g m}^{-3}$ was calculated taking into account the SEOM final mass (μg) and the total air volume filtered in cubic meters at standard conditions (25 °C and 1 atm).

2.3. Chemical analysis

The following PAH were analyzed (with abbreviations and selected ion masses in parentheses): phenanthrene (Phen)

(178,179,89 u), anthracene (Ant) (178,179,89 u), retene (Ret) (219, 234 u), fluoranthene (Flt) (202,203,101 u), pyrene (Pyr) (202,203,101 u), benzo[*a*]anthracene (BaA) (228,229,114 u), chrysene + triphenylene (Chrys + Triph) (228,229,114 u), benzo[*b*]fluoranthene (BbF) (252,253,126 u), benzo[*j* + *k*]fluoranthenes (Bj + *k*F) (252,253,126 u), benzo[*e*]pyrene (BeP) (252,253,126 u), benzo[*a*]pyrene (BaP) (252,253,126 u), perylene (Per) (252,253,126 u), indeno[1,2,3-*cd*]pyrene (I123cdP) (276,277,138 u), dibenzo[*a,h*]anthracene (DBaH) (278,279,139 u), benzo[*ghi*]perylene (BghiP) (276,277,138 u) and coronene (Cor) (300,301,150 u) (Chemservices, West Chester, PA, USA). Each extract was analyzed in a gas chromatograph/mass spectrometer (6890/5973N) (Agilent Technologies, USA) with a quadrupole mass filter and an autosampler (model 7683). One microliter was injected in splitless mode at 300 °C. A 30 m HP5-MS capillary column (0.25 mm i.d., 0.25 μm film thickness) was used. The oven temperature program was operated at 80 °C for 2 min and increased 5 °C min^{-1} to 300 °C for 10 min. High purity helium was used as the carrier gas at a flow rate of 1 mL min^{-1} . The mass spectrometer was operated in electron impact mode (70 eV) and selected ion monitoring. Three deuterated PAH were used as internal standards (PAH-*d*; selected ion masses): [²H₁₀]phenanthrene-*d*₁₀ (Phen-*d*₁₀; 188,189,94 u), [²H₁₂]chrysene-*d*₁₂ (Chrys-*d*₁₂; 240,241,120 u) and [²H₁₂]perylene-*d*₁₂ (Per-*d*₁₂; 264,265,132 u) (Chiron, Trondheim, Norway). The relative retention times of PAH target and secondary ions with respect to internal standards were used in the analysis identification, while the relative response factor of the target ion was used in the analytical quantification. Eight-point multi-point calibration curves for all PAH, ranging from 8 to 4500 $\text{pg } \mu\text{L}^{-1}$, were obtained ($r > 0.99$, $p < 0.001$). The method quantification limits for PAH were found between 7 pg m^{-3} (benzo[*a*]pyrene) and 130 pg m^{-3} (perylene).

2.4. Meteorological data and atmospheric pollutants

Wind velocity (m s^{-1}) values were acquired from the Observatorio de Radiación Solar, Instituto de Geofísica of the Universidad Nacional Autónoma de México, located 12 m above ground at the same site as the particle sampling. The values of temperature (°C), relative humidity (%), O₃, NO₂, SO₂ and CO were obtained from “Pedregal” which is the nearest monitoring station to our sampling site.

2.5. Quality control

The sampler was calibrated in accordance with the rules established in the Federal Register (40 CFR Part 50, 1987), when motor brushes were changed. The recovery efficiency of SEOM and of PAH was calculated by applying the urban dust standard reference material (SRM 1649a) from the National Institute of Standards and Technology (NIST). A SEOM recovery of $90 \pm 12.2\%$ was obtained, while efficiency for PAH was found to be between $47.3 \pm 1.4\%$ (anthracene) and $89.2 \pm 4.9\%$ (benzo[*ghi*]perylene), when 100 mg of urban dust were extracted. The PAH values in the actual samples were corrected by subtracting the low PAH amount in the filter field blanks and adjusting those values with their respective recoveries as a function of urban dust extracted between 5 and 150 mg.

2.6. Statistical analysis

“Statistica” Software v. 6.1 was used for statistical analysis. Medians for both seasons were compared with the Mann–Whitney *U* test. Associations among particles, SEOM, PAH, atmospheric pollutants and meteorological parameters were calculated through the Spearman rank order correlation.

3. Results and discussion

3.1. Size-segregated distribution and seasonal behavior of the mass of particle, SEOM and PAH

The medians (10th–90th percentiles) in the dry and rainy seasons for relative humidity (%) were 38.6 (29.3–47.7) and 52.5 (38.0–62.8), respectively; for temperature (°C) they were 14.2 (10.8–16.4) and 16.3 (14.9–18.8), respectively; and for wind velocity (m s^{-1}) they were 0.6 (0.3–1.0) and 1.0 (0.3–2.0), respectively. The medians of each variable were different between seasons ($p < 0.05$). The medians of seasonal mass concentration of particles (Fig. 1a) and SEOM (Fig. 1b) were higher in the dry than in the rainy season, for all stages ($p < 0.05$). The dry season exhibited a bimodal distribution of particle mass ($\Delta C/\Delta \log D_p$) with maximum values

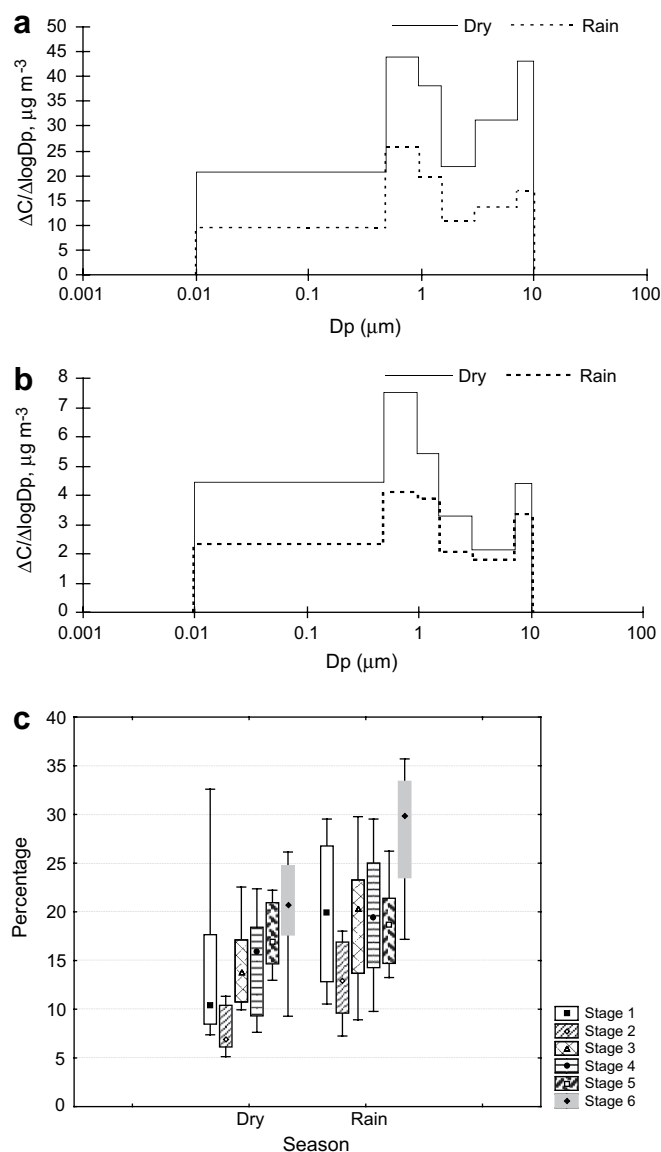


Fig. 1. Median seasonal mass concentration of a. particles ($\Delta C/\Delta \log D_p$), b. solvent extracted organic matter (SEOM) ($\Delta C/\Delta \log D_p$) and c. SEOM/particles ratios in each stage during dry (October 1998–February 1999, $N = 18$) and rainy (June–October 1999, $N = 24$) seasons. D_p – aerodynamic particle diameter. By box-whisker plot, median – middle square, box – 25–75% and whisker – 10th–90th percentiles. Stage 1 – $10 \geq d \geq 7.2 \mu\text{m}$, Stage 2 – $7.2 > d \geq 3.0 \mu\text{m}$, Stage 3 – $3.0 > d \geq 1.5 \mu\text{m}$, Stage 4 – $1.5 > d \geq 0.95 \mu\text{m}$, Stage 5 – $0.95 > d \geq 0.49 \mu\text{m}$, Stage 6 – $d < 0.49 \mu\text{m}$.

occurring in stages $0.95 > d \geq 0.49 \mu\text{m}$ ($43.9 \mu\text{g m}^{-3}$) and $10 \geq d \geq 7.2 \mu\text{m}$ ($43.2 \mu\text{g m}^{-3}$). The rainy season was uni-modal, with a maximum value in stage $0.95 > d \geq 0.49 \mu\text{m}$ ($25.6 \mu\text{g m}^{-3}$). For SEOM mass concentration, the highest value ($\Delta C/\Delta \log D_p$) in $0.95 > d \geq 0.49 \mu\text{m}$ of $7.5 \mu\text{g m}^{-3}$ was observed in the dry period, and $4.1 \mu\text{g m}^{-3}$ in the rainy season for the same diameter range. Higher mass concentrations of particles and SEOM in the dry period are favored by lower temperature and wind speeds as shown in Table 1. In addition, lower surface and boundary mixing layers (Eiguren-Fernandez et al., 2007; Guzmán-Torres et al., 2009) and a greater number of thermal inversions compared to the rainy season contributed to increased pollutant concentrations. Significant positive correlations ($p < 0.05$) were observed between particles and SEOM mass in the same stage: 0.368 (stage 1), 0.670 (stage 2), 0.493 (stage 3), 0.666 (stage 4), 0.905 (stage 5) and 0.810 (stage 6). Similar emission sources or atmospheric formation processes can be suggested from these associations, although the highest correlations in stages 5 and 6 probably indicate the same sources/processes. Fine particles $< 3 \mu\text{m}$ constituted 62.6% and 68.3% of particulate mass for the dry and rainy seasons, respectively. In the case of SEOM, 75.9% and 70.6% of their mass was concentrated in particles $< 3.0 \mu\text{m}$ in the dry and rainy seasons, respectively. Clearly, the highest mass of SEOM and non-SEOM (particles mass minus SEOM mass) were found in fine particles. SEOM mass/particle mass ratios indicate the contribution of the organic fraction to the total particle mass in each stage. Maximum SEOM contributions were observed in particles $d < 0.49 \mu\text{m}$, with 21% in the dry season and 30% in the rainy season; meanwhile, the lowest contributions for dry (7%) and rainy (13%) seasons were in the particle range $7.2 \mu\text{m} > d \geq 3.0 \mu\text{m}$ (Fig. 1c). A significant increase in SEOM mass/particle mass ratios ($p \leq 0.05$) in the rainy season with respect to the dry season is shown for five stages (except for $0.95 > d \geq 0.49 \mu\text{m}$ range, $p > 0.05$), which suggests a faster mass wet deposition of the non-SEOM from the atmosphere compared with the SEOM, which has less water-affinity. The exception is

Table 1

Spearman rank order correlations between: daily mass concentrations of particles ($\mu\text{g m}^{-3}$), SEOM ($\mu\text{g m}^{-3}$) and heavy PAH (ng m^{-3}) vs. average daily values of meteorological parameters, $N = 42$.

| Stage ^a | Variable | T | HR | WS |
|--------------------|-----------|---------------|---------------|---------------|
| 1 | Particles | -0.398 | -0.760 | -0.383 |
| | SEOM | -0.100 | -0.408 | 0.068 |
| | PAH | -0.133 | 0.041 | -0.236 |
| 2 | Particles | -0.351 | -0.736 | -0.440 |
| | SEOM | -0.152 | -0.467 | -0.417 |
| | PAH | -0.326 | -0.102 | -0.720 |
| 3 | Particles | -0.354 | -0.634 | -0.443 |
| | SEOM | -0.232 | -0.519 | -0.239 |
| | PAH | -0.592 | -0.245 | -0.445 |
| 4 | Particles | -0.328 | -0.400 | -0.528 |
| | SEOM | -0.222 | -0.293 | -0.331 |
| | PAH | -0.443 | -0.341 | -0.416 |
| 5 | Particles | -0.301 | -0.312 | -0.556 |
| | SEOM | -0.391 | -0.312 | -0.547 |
| | PAH | -0.560 | -0.388 | -0.457 |
| 6 | Particles | -0.400 | -0.742 | -0.481 |
| | SEOM | -0.360 | -0.537 | -0.602 |
| | PAH | -0.496 | -0.423 | -0.347 |

Bold and italics – 95% level of significance, SEOM – solvent extracted organic matter, PAH – polycyclic aromatic hydrocarbons, T – temperature (°C), RH – relative humidity (%), WS – wind speed (m s^{-1}). stage 1 – $10 \geq d \geq 7.2 \mu\text{m}$, stage 2 – $7.2 > d \geq 3.0 \mu\text{m}$, stage 3 – $3.0 > d \geq 1.5 \mu\text{m}$, stage 4 – $1.5 > d \geq 0.95 \mu\text{m}$, stage 5 – $0.95 > d \geq 0.49 \mu\text{m}$, stage 6 – $d < 0.49 \mu\text{m}$, d – aerodynamic particle diameter.

^a Correlation values were calculated between variables in the corresponding stage.

Table 2

Mean percentages of mass deposition from dry to rainy season for particles, solvent extracted organic matter (SEOM) and polycyclic aromatic hydrocarbons (PAH) per stage of cascade impactor.

| Stage | Size particle range | Particles | SEOM | Light PAH | Heavy PAH |
|----------------|----------------------|-----------|------|-----------|-----------|
| 1 | $10 \geq d \geq 7.2$ | 61.3 | 24.3 | 54.0 | 17.3 |
| 2 | $7.2 > d \geq 3.0$ | 56.2 | 17.0 | 61.4 | 30.7 |
| 3 | $3.0 > d \geq 1.5$ | 50.8 | 38.0 | 65.0 | 43.8 |
| 4 | $1.5 > d \geq 0.95$ | 48.7 | 28.9 | 79.0 | 56.7 |
| 5 | $0.95 > d \geq 0.49$ | 41.6 | 45.5 | 75.5 | 60.2 |
| 6 | $d < 0.49$ | 54.1 | 48.0 | 70.8 | 55.1 |
| Mean | | 52.1 | 33.6 | 67.6 | 43.9 |
| SD | | 6.7 | 12.3 | 9.3 | 16.9 |
| Variability, % | | 12.9 | 36.5 | 13.7 | 38.5 |

d – aerodynamic particle diameter. SD – standard deviation.

SEOM in stage 5 (Fig. 1c), which is probably more hydrophilic. Although lower concentrations were found in both the mass of particles and SEOM in all stages in the rainy season, the proportion

of SEOM/particles mass increased for all stages, which means that higher amounts of organic compounds per mass unit of inhaled particles were observed in the rainy than in the dry season.

A mean of $52.1 \pm 6.7\%$ of particle mass was removed from the atmosphere (difference in masses between the dry and the rainy seasons, divided by the mass in the dry season) in all stages when higher relative humidity was in the atmosphere, while only $33.6 \pm 12.3\%$ of SEOM mass was deposited (Table 2), indicating again more water-affinity by the non-SEOM fraction. There was less variation in the percentages of particle mass removed among stages (12.9%) compared with SEOM variation (36.5%). Cousin et al. (1999) established that particle scavenging is not dependent on the concentrations of compounds within particles, even though these compounds apparently have water-affinity. However, the major variability for SEOM is probably due to complex organic composition formed by non-, middle- and polar-organic compounds with a wider range of water-affinity.

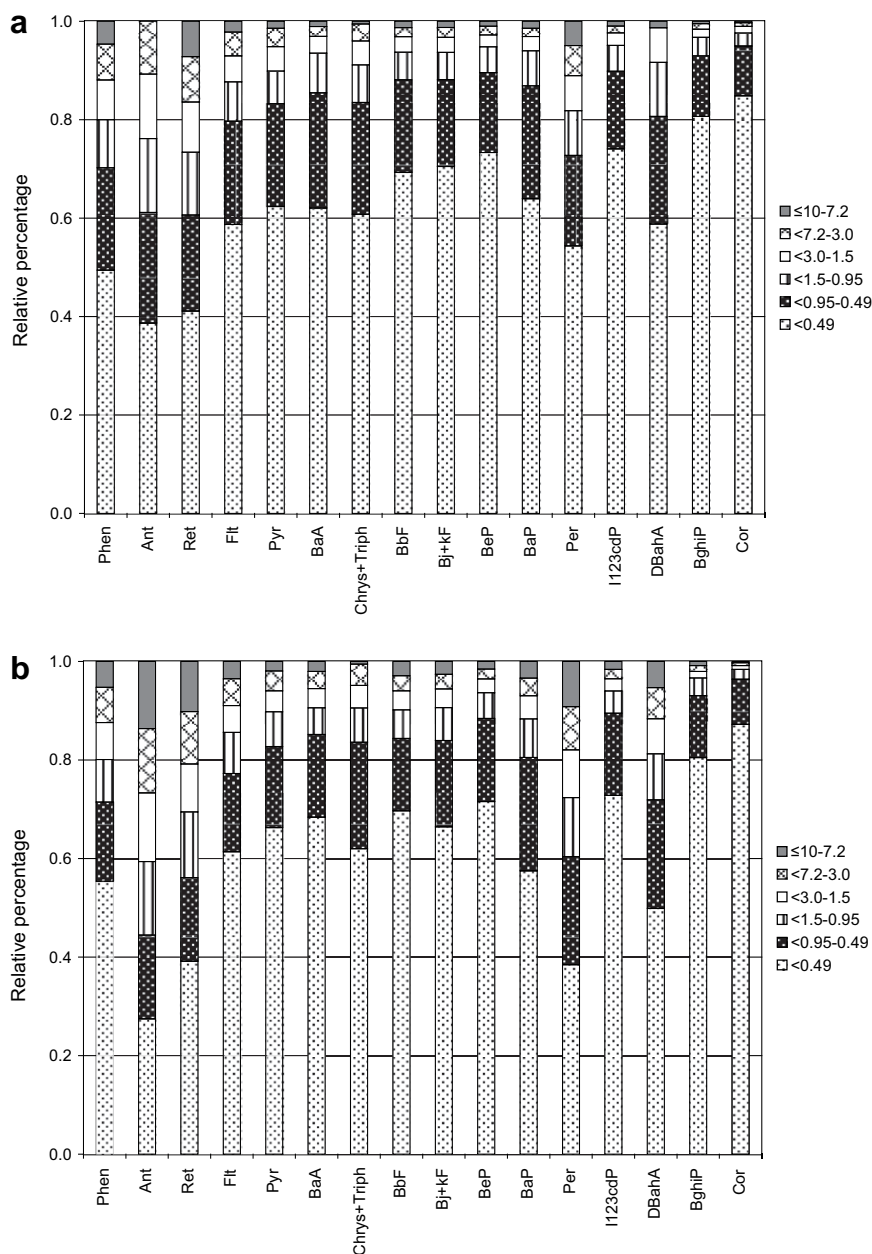


Fig. 2. Distribution of PAH median mass concentrations among stages in: a. dry season and b. rainy season. For PAH abbreviations see the text.

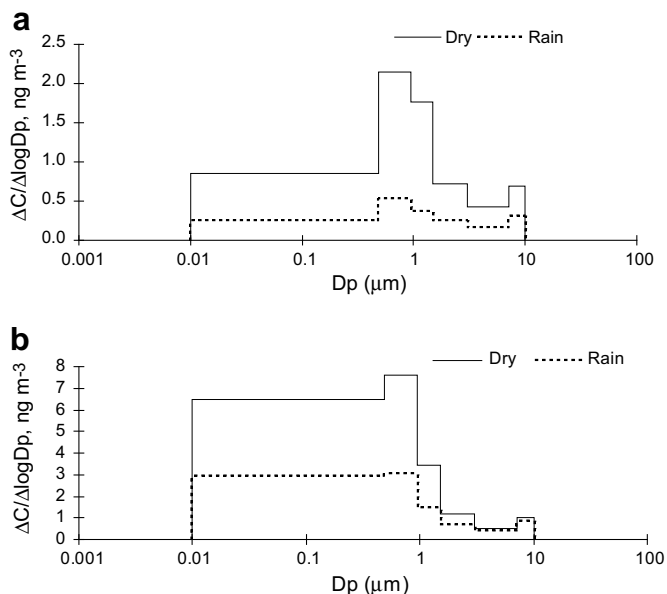


Fig. 3. Median seasonal PAH mass concentrations ($\Delta C/\Delta \log D_p$) in six diameter ranges of a. Light PAH sum of Phen, Ant, Ret, Flt and Pyr and b. Heavy PAH sum of BaA, Chrys + Triph, BbF, Bj + kF, BeP, BaP, Per, I123cdP, DBaH, BghiP and Cor, during dry (October 1998–February 1999, $N = 18$) and rainy (June–October 1999, $N = 24$) seasons, D_p – aerodynamic particle diameter. For PAH abbreviations see the text.

PAH with a molecular weight (MW) $< 228 \text{ g mol}^{-1}$ (including retene with 234 g mol^{-1}) (Phen, Ant, Ret, Flt, Pyr) are referred to in this study as light PAH; those PAH $\geq 228 \text{ g mol}^{-1}$ (BaA, Chrys + Triph, BbF, Bj + kF, BeP, BaP, Per, I123cdP, DBaH, BghiP, Cor), excluding retene, are referred to as heavy PAH. Light PAH masses were distributed mainly in larger particles, while heavy PAH mass were associated with smaller ones, as observed elsewhere (Allen et al., 1996; Alves et al., 2000). This was found in both seasons, dry (Fig. 2a) and rainy (Fig. 2b). A lower mean wet deposition for heavy PAH mass ($43.9 \pm 16.9\%$) with respect to light PAH mass ($67.6 \pm 9.3\%$) was observed ($p < 0.02$) from the atmosphere in all stages in the rainy season (Table 2); however, the temperature in the rainy season was higher than in the dry season, and the volatilization effect of light PAH must be considered in the deposition percentage. Volatilization rates of organic compounds with intermediate molecular weight depend on temperature mainly through its effect on vapor pressure which can increase three to four times for every 10°C increase in temperature (Jury et al., 1987). Similar deposition values were found by Masclat et al. (1988) with a 60% decrease in PAH concentration due to precipitation, and by Kaupp and McLachlan (1999) who observed around 50% of PAH, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, removed by wet deposition. Higher wet deposition values were observed for light PAH and particles, with respect to heavy PAH and SEOM. There was probably a different type of physical contact between light PAH and particles and heavy PAH and particles. It has been observed that the sorption of semivolatile organic compounds by aerosols can be due to adsorption onto a solid surface, absorption onto a liquid particle or onto a liquid organic film encapsulating a particle, or a combination of both (Pankow, 1994). Seasonal median mass concentrations ($\Delta C/\Delta \log D_p$) for both light PAH (Fig. 3a) and heavy PAH (Fig. 3b), were higher in the dry than in the rainy season ($p < 0.01$) for all stages, except for heavy PAH mass in the diameter $10 \geq d \geq 7.2 \mu\text{m}$ ($p = 0.66$). The maximum values for light and heavy PAH in the dry (2.15 and 7.62 ng m^{-3} , respectively) and rainy (0.53 and 3.03 ng m^{-3} , respectively) seasons were observed in $0.95 > d \geq 0.49 \mu\text{m}$, similar to that of SEOM mass, increasing their

concentrations in smaller particles in both seasons, as reported elsewhere (Venkataraman et al., 1994; Alves et al., 2000). Heavy PAH mass showed higher concentrations than light PAH mass ($p \leq 0.05$). Heavy PAH have four or more aromatic rings, lower vapor pressures ($\leq 5.0 \times 10^{-7} \text{ mm Hg}$, 20°C) and lower solubility constants ($< 0.011 \text{ mg L}^{-1}$) (ATSDR, 1995) than PAH with lower MW ($< 228 \text{ g mol}^{-1}$). Therefore, light PAH are in higher concentrations in the vapor phase than in the particle phase (van Vaeck et al., 1967; Cincinelli et al., 2007). Taking into account the PAH distribution in the six stages, the mass of heavy PAH found in particles $< 3.0 \mu\text{m}$ in the dry season was 92.5%, while in the rainy season was 87.2%. If we consider only the light PAH mass distributed in all stages, 83.2% of this mass was accumulated in particles $< 3.0 \mu\text{m}$ in the dry season while 74.5% was in the rainy season.

3.2. PAH risk assessment approach

DeMarini et al. (1994) showed that $\geq 50 \mu\text{g}$ of methylene chloride-extractable particle organics were mutagenic in *Salmonella typhimurium* and that much of the mutagenic activity of the whole composite urban air sample was due to PAH. Taking into account the SEOM mass sum of all stages ($\leq 10 \mu\text{m}$) in 20 m^3 of daily inhaled air (USEPA, 1997), the SEOM medians of $260 \mu\text{g}$ in the dry season and $160 \mu\text{g}$ in the rainy season were calculated; this was approximately five times and three times, respectively, the SEOM mass found by DeMarini et al. (1994) to be mutagenic. The adsorbed PAH were early suspects of producing lung cancer (Kotin et al., 1955). The U.S. Environmental Protection Agency has identified 16 unsubstituted PAH as priority pollutants (USEPA, 1985), from which seven are considered probable human carcinogens (NTP, 2005) (BaA, Chrys, BaP, BbF, BkF, DBaH, I123cdP). The intake of PAH by inhalation of polluted ambient air depends on their concentration and deposition rates. If we consider the carcinogenic PAH seasonal medians mass (10th–90th percentiles) (taking into account Chrys co-eluted with Triph and BkF with BjF), in 20 m^3 and the sum of all stages, we estimated the median to be 137 ng day^{-1} (74–246) in the dry season and 57 ng day^{-1} (21–101) in the rainy season. Both medians were lower than median (min–max) value of 160 ng day^{-1} (20–3000 ng day^{-1}) estimated by Menzie et al. (1992) as a daily potential dose of carcinogenic PAH (BaA, Chrys, BbF, BkF, BaP, I123cdP, DBaH, BghiP). Yajuan et al. (2008) proposed an integrated mixed uncertainty analysis method to estimate the confidence interval of risk based on the variability of human activities, PAH concentrations and inhalation rate. Therefore our results will contribute to estimating the risk analysis for decision making related to exposure of humans to PAH.

BaP has been considered a good index for whole PAH carcinogenicity (WHO, 1987; De Martinis et al., 2002). The average value of BaP in our study considering the sum of all stages was $0.98 \pm 0.56 \text{ ng m}^{-3}$ for the dry season and $0.40 \pm 0.20 \text{ ng m}^{-3}$ for the rainy season. The European directive (2004/107/CE) has proposed a maximum permissible risk level of 1 ng m^{-3} BaP in ambient air, based on the carcinogenic potential of inhaled particulate PAH (average calculated for one calendar year of the total contents of the PM_{10} fraction); however, the United Kingdom Government has adopted an annual average concentration value of 0.25 ng m^{-3} as a recommendation to be achieved by 2010 as a provisional objective, based on BaP as a marker for the total mixture of PAH (Vincent et al., 2007). The annual average for our study (considering the dry and the rainy seasons) was $0.69 \pm 0.41 \text{ ng m}^{-3}$ which was lower than the European directive proposal but higher than the UK recommendation for PM_{10} samples. Furthermore, PAH are not the only contributors to the carcinogenic risk presented by a given mixture; other chemicals and particulate matter (Heinrich, 1995) may also contribute. One approach for assessing dose–response relationships

Table 3a
Median concentrations (10th–90th percentiles) for particles ($\mu\text{g m}^{-3}$), SEOM ($\mu\text{g m}^{-3}$) and PAH (pg m^{-3}), in Southwest México City air samples by stage and by season.

| Dry season, N = 18 | Stage 1 | Stage 2 | Stage 3 | Stage 4 | Stage 5 | Stage 6 | Sum all stages (PM ₁₀) ^a |
|----------------------------|-----------------------|-----------------------|-----------------------|----------------|------------------|---------------------|--|
| Particles | 6 (4–7) | 12 (8–16) | 7 (5–8) | 8 (5–12) | 13 (9–18) | 35 (26–40) | 80 (58–102) |
| SEOM | 0.6 (0.5–1.3) | 0.8 (0.7–1.4) | 1.0 (0.6–1.4) | 1.1 (0.9–1.5) | 2.2 (1.6–2.8) | 7.5 (4.0–10.1) | 13.2 (8.2–18.4) |
| Phen | 16 (6–48) | 25 (14–46) | 27 (18–95) | 33 (20–139) | 70 (42–91) | 167 (124–248) | 337 (224–666) |
| Ant | 0 ^c (0–23) | 9 (0–23) | 11 (0–18) | 13 (0–18) | 20 (14–23) | 34 (19–41) | 87 (33–146) |
| Ret | 37 (7–277) | 47 (7–100) | 52 (19–136) | 65 (20–287) | 100 (26–170) | 210 (67–323) | 512 (146–1294) |
| Flt | 14 (6–32) | 32 (16–49) | 35 (14–56) | 53 (13–111) | 138 (67–280) | 387 (180–646) | 659 (295–1174) |
| Pyr | 12 (2–31) | 32 (17–59) | 42 (14–93) | 56 (10–141) | 177 (82–450) | 529 (240–848) | 848 (364–1622) |
| BaA | 6 ^c (3–13) | 11 (6–26) | 18 (10–52) | 42 (15–90) | 123 (62–232) | 326 (149–616) | 525 (247–1029) |
| Chrys + Triph ^a | 4 ^c (1–21) | 25 (17–49) | 35 (16–70) | 56 (33–117) | 165 (91–293) | 442 (245–832) | 728 (403–1382) |
| BbF | 20 (0–31) | 29 (19–47) | 51 (34–78) | 90 (46–240) | 302 (145–627) | 1111 (675–2165) | 1603 (917–3188) |
| Bj + kF ^b | 13 (5–19) | 20 (9–48) | 31 (21–70) | 56 (40–129) | 180 (107–325) | 720 (444–1512) | 1021 (626–2103) |
| BeP | 13 (8–21) | 23 (13–84) | 32 (22–60) | 68 (43–155) | 212 (126–430) | 956 (561–1715) | 1304 (772–2465) |
| BaP | 11 (0–16) | 13 (3–22) | 23 (16–42) | 56 (27–130) | 180 (86–403) | 503 (171–1319) | 786 (303–1933) |
| Per | 11 (0–17) | 14 (0–21) | 16 (10–27) | 20 (16–29) | 41 (25–87) | 122 (49–269) | 225 (100–449) |
| I123cdP | 17 (0–25.5) | 25 (4–46) | 46 (24–88) | 95 (36–242) | 288 (114–637) | 1349 (650–2530) | 1821 (828–3568) |
| DBahA | 2 ^c (0–15) | 0 ^c (0–13) | 13 (0–26) | 20 (12–37) | 41 (20–95) | 109 (53–311) | 186 (86–496) |
| BghiP | 15 (10–32) | 34 (11–73) | 50 (29–99) | 115 (50–282) | 377 (182–858) | 2473 (1215–4292) | 3065 (1498–5637) |
| Cor | 10 (0–26) | 23 (0–71) | 43 (4–89) | 84 (14–271) | 320 (47–770) | 2688 (965–4494) | 3167 (1030–5722) |
| Σ light PAH ^b | 98 (67–297) | 163 (109–208) | 219 (130–639) | 350 (160–561) | 618 (324–961) | 1436 (733–1977) | 2883 (1523–4644) |
| Σ heavy PAH ^b | 141 (72–198) | 202 (142–388) | 359 (246–668) | 678 (381–1738) | 2190 (1228–4578) | 10 919 (5390–19199) | 14 488 (7460–26768) |
| Rainy season, N = 24 | Stage 1 | Stage 2 | Stage 3 | Stage 4 | Stage 5 | Stage 6 | Sum all stages (PM ₁₀) ^a |
| Particles | 2 (2–4) | 5 (3–9) | 3 (2–6) | 4 (3–6) | 7 (4–10) | 16 (10–28) | 38 (24–64) |
| SEOM | 0.5 (0.3–0.7) | 0.7 (0.4–1.0) | 0.6 (0.4–0.9) | 0.8 (0.5–1.1) | 1.2 (0.7–1.9) | 3.9 (2.9–7.2) | 7.6 (5.2–12.8) |
| Phen | 8 (5–381) | 11 (7–22) | 11 (7–25) | 13 (8–45) | 25 (10–53) | 85 (49–125) | 153 (86–653) |
| Ant | 12 (0–340) | 11 (0–16) | 12 (0–15) | 13 (0–25) | 14 (11–26) | 23 (13–37) | 85 (24–459) |
| Ret | 18 (8–1126) | 19 (8–49) | 18 (8–33) | 24 (9–263) | 31 (8–81) | 71 (13–163) | 181 (54–1714) |
| Flt | 7 (3–25) | 11 (5–22) | 11 (5–43) | 17 (7–46) | 32 (13–117) | 125 (45–307) | 203 (77–561) |
| Pyr | 5 ^c (0–36) | 10 (2–31) | 10 (3–46) | 17 (5–52) | 40 (13–137) | 160 (59–472) | 242 (81–774) |
| BaA | 3 ^c (1–15) | 5 ^c (2–16) | 5 ^c (2–23) | 7 (3–37) | 23 (6–120) | 95 (41–299) | 138 (56–510) |
| Chrys + Triph ^a | 1 ^c (0–86) | 9 (1–46) | 10 (1–76) | 15 (5–63) | 46 (10–148) | 133 (48–367) | 214 (64–787) |
| BbF | 20 (14–42) | 22 (16–28) | 27 (17–56) | 41 (21–73) | 103 (39–222) | 490 (152–1063) | 703 (259–1484) |
| Bj + kF ^b | 11 (8–32) | 12 (9–17) | 16 (9–24) | 28 (15–55) | 74 (31–154) | 282 (117–526) | 425 (188–809) |
| BeP | 9 (6–34) | 11 (7–15) | 16 (9–28) | 29 (14–65) | 94 (45–187) | 398 (146–889) | 556 (227–1219) |
| BaP | 11 (8–36) | 11 (2–15) | 15 (9–25) | 25 (9–51) | 74 (29–152) | 185 (50–441) | 322 (108–721) |
| Per | 12 (7–30) | 11 (8–14) | 12 (7–18) | 15 (9–26) | 28 (11–38) | 49 (15–117) | 126 (57–244) |
| I123cdP | 14 (0–35) | 17 (0–27) | 22 (0–51) | 40 (0–110) | 148 (34–321) | 646 (191–1498) | 887 (225–2042) |
| DBahA | 6 ^c (0–45) | 7 (0–18) | 8 (0–14) | 11 (0–22) | 25 (0–43) | 57 (18–181) | 115 (18–323) |
| BghiP | 13 (5–37) | 18 (6–31) | 20 (7–68) | 54 (15–134) | 192 (51–461) | 1224 (359–2637) | 1520 (444–3369) |
| Cor | 4 ^c (0–20) | 9 (0–27) | 12 (0–44) | 31 (0–105) | 141 (12–429) | 1347 (244–2795) | 1544 (257–3421) |
| Σ light PAH ^b | 45 (33–1001) | 63 (33–130) | 76 (37–393) | 74 (41–272) | 152 (55–388) | 420 (263–1212) | 829 (462–3395) |
| Σ heavy PAH ^b | 117 (68–391) | 140 (60–213) | 202 (69–347) | 293 (116–699) | 872 (292–1989) | 4906 (1581–8596) | 6530 (2186–12235) |

^a Medians and percentiles resulted from the sum of all stages by sampling day and by season.

^b The values were calculated taking into account the corresponding PAH sum in each sampling day by season, stage 1 – $10 \geq d \geq 7.2 \mu\text{m}$, stage 2 – $7.2 > d \geq 3.0 \mu\text{m}$, stage 3 – $3.0 > d \geq 1.5 \mu\text{m}$, stage 4 – $1.5 > d \geq 0.95 \mu\text{m}$, stage 5 – $0.95 > d \geq 0.49 \mu\text{m}$, stage 6 – $d < 0.49 \mu\text{m}$, d – particle diameter, light PAH (Phen-Pyr), heavy PAH (BaA-Cor).

^c Values lower than method quantification limits. For PAH abbreviations see the text.

for PAH is the use of the toxic equivalent factors (TEFs) to characterize more precisely the carcinogenic properties of PAH mixtures, whereby BaP equivalent concentrations were calculated by multiplying the individual PAH concentrations by its corresponding TEF values (Nisbet and LaGoy, 1992). Table 3a shows the particle, SEOM and PAH mass concentrations for all stages in both seasons. Guzmán-Torres et al. (2009), determined PAH in PM₁₀ at two sites in Mexico City: Center and Southwest (same site as in this study) during a short campaign in March 2003. At Southwest, similar PAH concentrations were found for light PAH in dry season as in this study, while higher concentrations for heavy PAH were observed (~1.5–2 times). Table 3b indicates the TEFs for seven carcinogenic PAH, BaP equivalent concentrations and the contribution of the carcinogenic potency of BaP to México City air samples. This ranged from 44.9% to 59.6% for the dry season and between 46.8 and 55.0% for the rainy season. Similar values were found by Cincinelli et al. (2007) with 51.6% for Prato, Italy air samples and slightly lower than those found by Norramit et al. (2005) with 57.9–65.7% in Bangkok, Thailand. These results corroborate the importance of BaP as a marker for carcinogenicity; however, dibenzo[*a,h*]anthracene,

indeno[1,2,3-*cd*]pyrene and benzo[*a*]fluoranthene also play an important role in the total carcinogenicity of PAH in México City air. At this time there is no regulatory norm establishing the maximum limit of PAH concentrations in the atmosphere of México City. The Mexican norm (NOM-025-SSA1-1993) regulates only particle mass concentrations in 24 h of exposure (total suspended particles, $210 \mu\text{g m}^{-3}$; particles $\leq 10 \mu\text{m}$, $120 \mu\text{g m}^{-3}$; particles $\leq 2.5 \mu\text{m}$, $65 \mu\text{g m}^{-3}$); therefore, these results represent an important contribution to be considered in epidemiological and toxicological studies to determine the toxicity of specific classes of airborne particles (Schlesinger et al., 2006), which can provide for and improve the basis for regulation of particulate matter in México City.

3.3. Association among particles, SEOM and PAH with criteria atmospheric pollutants

Spearman rank order correlations showed significant, positive and linear correlations between particles vs. CO, NO₂, O₃ and SO₂ for all stages (95% level of significance), except with CO in stage 3 (Table 4). However, correlations with SEOM mass were positive

Table 3b

Toxic equivalent factors (TEFs) (Nisbet and LaGoy, 1992) and BaP equivalent median concentrations (pg m^{-3}) for seven carcinogenic PAH (NTP, 2005) in México City air samples by stage and by season.

| Dry season | TEFs | Stage 1 | Stage 2 | Stage 3 | Stage 4 | Stage 5 | Stage 6 | Sum all stages (PM ₁₀) |
|--|--------------------|------------------|------------------|------------------|---------|---------|---------|------------------------------------|
| BaA | 0.100 | 0.6 ^d | 1.1 | 1.8 | 4.2 | 12.3 | 32.6 | 52.6 |
| Chrys + Triph ^a | 0.010 | 0.0 ^d | 0.3 | 0.4 | 0.6 | 1.7 | 4.4 | 7.4 |
| BbF | 0.100 | 2.0 | 2.9 | 5.1 | 9.0 | 30.2 | 111.1 | 160.3 |
| Bj + kF ^b | 0.100 | 1.3 | 2.0 | 3.1 | 5.6 | 18.0 | 72.0 | 102.0 |
| BaP | 1.000 | 11.2 | 13.0 | 22.8 | 56.1 | 180.1 | 502.8 | 786.0 |
| I123cdP | 0.100 | 1.7 | 2.5 | 4.6 | 9.5 | 28.8 | 134.9 | 182.0 |
| DBahA | 1.000 ^c | 2.5 ^d | 0.0 | 13.0 | 20.5 | 40.6 | 109.3 | 185.9 |
| Sum carcinogenicity activity, pg m^{-3} | | 19.3 | 21.8 | 50.8 | 105.5 | 311.7 | 967.1 | 1476.2 |
| Carcinogenicity activity contribution of BaP, % | | 58.0 | 59.6 | 44.9 | 53.2 | 57.8 | 52.0 | 53.2 |
| Rainy season | TEFs | Stage 1 | Stage 2 | Stage 3 | Stage 4 | Stage 5 | Stage 6 | Sum all stages (PM ₁₀) |
| BaA | 0.100 | 0.3 ^d | 0.5 ^d | 0.5 ^d | 0.7 | 2.3 | 9.5 | 13.8 |
| Chrys + Triph ^a | 0.010 | 0.0 ^d | 0.1 | 0.1 | 0.1 | 0.5 | 1.3 | 2.1 |
| BbF | 0.100 | 2.0 | 2.2 | 2.7 | 4.1 | 10.3 | 49.0 | 70.3 |
| Bj + kF ^b | 0.100 | 1.1 | 1.2 | 1.6 | 2.8 | 7.4 | 28.2 | 42.3 |
| BaP | 1.000 | 10.9 | 11.5 | 15.1 | 25.2 | 74.0 | 185.1 | 321.8 |
| I123cdP | 0.100 | 1.4 | 1.7 | 2.2 | 4.0 | 14.8 | 64.6 | 88.7 |
| DBahA | 1.000 ^c | 6.1 ^d | 7.3 | 8.2 | 10.8 | 25.3 | 57.4 | 115.1 |
| Sum carcinogenicity activity, pg m^{-3} | | 21.8 | 24.5 | 30.4 | 47.7 | 134.6 | 395.1 | 654.1 |
| Carcinogenicity activity contribution of BaP, % | | 50.0 | 46.9 | 49.7 | 52.8 | 55.0 | 46.8 | 49.2 |

^a BaP equivalent based on TEF for chrysene.

^b BaP equivalent based on TEF for benzo[k]fluoranthene.

^c TEF from Malcolm and Dobson (1994); stage 1 – $10 \geq d \geq 7.2 \mu\text{m}$, stage 2 – $7.2 > d \geq 3.0 \mu\text{m}$, stage 3 – $3.0 > d \geq 1.5 \mu\text{m}$, stage 4 – $1.5 > d \geq 0.95 \mu\text{m}$, stage 5 – $0.95 > d \geq 0.49 \mu\text{m}$, stage 6 – $d < 0.49 \mu\text{m}$, d – aerodynamic particle diameter.

^d Values lower than method quantification limits. For PAH abbreviations see the text.

and significant only in some cases (95% level of significance) (Table 4). The relationship between SEOM mass and CO in diameters $< 1.5 \mu\text{m}$ probably suggests a vehicular origin; given that CO is a good indicator of vehicle emissions (Fernández-Bremauntz and Ashmore, 1995), while the correlation between SEOM and NO₂ can be indicative of vehicle emissions, power plants, fossil-fuel burning industries (Rijnders et al., 2001) and gas stoves in indoor environments (CEOHAATS, 1996). However, CO and NO₂ are emitted from burning vegetation as well (Barthelmie and Pryor, 1997) and this is confirmed by the presence of retene detected in this study (Fig. 2, Table 3a). Retene is considered a marker of wood combustion, mainly of coniferous trees (Ramdahl, 1983). The lack of correlation between SO₂ and SEOM mass showed that there are not industrial emissions near to the sampling site. The correlation between SEOM mass and ozone in diameters $< 0.95 \mu\text{m}$ is probably linked to the hydrophilic organic composition of SEOM. This is important if we consider that our sampling site is in the zone with the highest ozone concentrations in the Metropolitan Area (Informe del Estado de la Calidad del Aire y Tendencias, 2004). In fact, SEOM in diameters $< 0.95 \mu\text{m}$ showed the highest wet deposition percentages from the atmosphere (Table 2), suggesting major hydrophilic behavior compared to SEOM in greater sizes. The correlation between SEOM mass and ozone for the particle range $7.2 > d \geq 3.0 \mu\text{m}$ is not clear. However, triterpenic compounds originated from vascular plant waxes or as secondary oxidation products from precursors emitted by vegetation (Simoneit et al., 1991) were found in diameters $1.5 > d \geq 0.95 \mu\text{m}$ and $7.2 > d \geq 3.0 \mu\text{m}$ (Alves et al., 2000).

High molecular weight PAH such as benzo[ghi]perylene have been described as tracers of gasoline-powered vehicles, while light PAH have been found predominantly in diesel vehicle emissions (Miguel et al., 1998; Zielinska et al., 2004). In general, the most abundant PAH detected in our study were coronene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene followed by benzo[b]fluoranthene, benzo[e]pyrene, benzo[j+k]fluoranthenes, and benzo[a]pyrene for both

seasons (Table 3a). Similar behavior was observed by Villalobos-Pietrini et al. (2006) in the same region, related to the presence of strong vegetation burning around the sampling site during the most of that study. However, fires were not considered as the main source of PAH, except for retene, benzo[a]anthracene and fluoranthene, but they were for PM₁₀ and for SEOM mass. While denoting vehicles as the main PAH source, Villalobos-Pietrini et al. (2006) did not find correlation between PAH mass ($\geq 252 \text{ g mol}^{-1}$) and PM₁₀ mass, nor with SEOM mass. The same individual PAH abundance and the significant PAH correlation with particles, SEOM, CO and NO₂ therefore (Table 5) suggest that vehicles are an emission source for PAH. No

Table 4

Spearman rank order correlations between: daily mass concentrations of particles ($\mu\text{g m}^{-3}$), SEOM ($\mu\text{g m}^{-3}$) and maximum daily values of atmospheric pollutants (ppm), $N = 42$.

| Stage ^g | CO | NO ₂ | O ₃ | SO ₂ |
|--------------------|--------------|-----------------|----------------|-----------------|
| Part ^a | 0.384 | 0.379 | 0.551 | 0.440 |
| SEOM ^a | 0.022 | 0.057 | 0.130 | 0.028 |
| Part ^b | 0.380 | 0.441 | 0.569 | 0.393 |
| SEOM ^b | 0.118 | 0.347 | 0.440 | 0.205 |
| Part ^c | 0.302 | 0.372 | 0.530 | 0.379 |
| SEOM ^c | 0.208 | 0.407 | 0.305 | 0.143 |
| Part ^d | 0.351 | 0.454 | 0.581 | 0.403 |
| SEOM ^d | 0.305 | 0.353 | 0.274 | 0.296 |
| Part ^e | 0.377 | 0.464 | 0.637 | 0.378 |
| SEOM ^e | 0.434 | 0.486 | 0.533 | 0.291 |
| Part ^f | 0.493 | 0.486 | 0.528 | 0.481 |
| SEOM ^f | 0.514 | 0.709 | 0.667 | 0.304 |

Bold and italics form – 95% level of significance, part – particle, SEOM – solvent extracted organic matter.

^a $10 \geq d \geq 7.2 \mu\text{m}$.

^b $7.2 > d \geq 3.0 \mu\text{m}$.

^c $3.0 > d \geq 1.5 \mu\text{m}$.

^d $1.5 > d \geq 0.95 \mu\text{m}$.

^e $0.95 > d \geq 0.49 \mu\text{m}$.

^f $d < 0.49 \mu\text{m}$, d – aerodynamic particle diameter.

^g Correlation values were calculated between variables in the corresponding stage.

Table 5

Spearman rank order correlations between: PAH ≥ 228 g mol⁻¹ (excluding retene) (pg m⁻³), particles ($\mu\text{g m}^{-3}$), SEOM ($\mu\text{g m}^{-3}$) and maximum daily values of atmospheric pollutants (ppm), $N = 42$.

| Stage ^g | Part | SEOM | CO | NO ₂ | O ₃ | SO ₂ |
|--------------------|--------------|--------------|--------------|-----------------|----------------|-----------------|
| PAH ^a | 0.048 | 0.264 | -0.217 | 0.112 | 0.166 | -0.010 |
| PAH ^b | 0.492 | 0.513 | 0.311 | 0.417 | 0.514 | -0.001 |
| PAH ^c | 0.515 | 0.485 | 0.242 | 0.378 | 0.287 | 0.186 |
| PAH ^d | 0.514 | 0.646 | 0.524 | 0.549 | 0.271 | 0.241 |
| PAH ^e | 0.598 | 0.753 | 0.503 | 0.515 | 0.301 | 0.184 |
| PAH ^f | 0.624 | 0.633 | 0.369 | 0.392 | 0.177 | 0.146 |

Bold and italics – 95% level of significance, part – particle, SEOM – solvent extracted organic matter, PAH – heavy polycyclic aromatic hydrocarbons.

^a $10 > d \geq 7.2$ μm .

^b $7.2 > d \geq 3.0$ μm .

^c $3.0 > d \geq 1.5$ μm .

^d $1.5 > d \geq 0.95$ μm .

^e $0.95 > d \geq 0.49$ μm .

^f $d < 0.49$ μm , d – aerodynamic particle diameter.

^g Correlation values were calculated between variables in the corresponding stage.

association was observed between PAH mass and SO₂, nor between PAH and O₃ (except with PAH mass in stage $7.2 > d \geq 3.0$ μm).

4. Conclusions

The particle mass distributed ($\Delta C/\Delta \log D_p$) in the cascade impactor was bimodal with maximum values in $10 \geq d \geq 7.2$ μm and $0.95 > d \geq 0.49$ μm , while the SEOM and PAH mass distribution ($\Delta C/\Delta \log D_p$) showed a maximum value in $0.95 > d \geq 0.49$ μm . SEOM mass/particle mass ratios were higher in the rainy season compared to the dry season for five stages (except for $0.95 > d \geq 0.49$ μm range), suggesting higher amounts of organic compounds per mass unit of inhaled particles in the rainy season than in the dry season. SEOM in particles < 0.95 μm indicated an organic composition with a higher water-affinity than in greater particle sizes. Median average masses in dry and rainy season respectively, of 62.6% and 68.3% for particles, 75.9% and 70.6% for SEOM and 92.5% and 87.2% for heavy PAH (>202 g mol⁻¹, excluding retene) were found in diameters < 3.0 μm . Estimated potential doses of carcinogenic PAH by inhalation in 20 m³ in all stages were higher in the dry (137 ng day⁻¹) than in the rainy season (57 ng day⁻¹). The annual average of BaP exceeded the UK recommendation which is to be achieved by 2010. The contribution of the carcinogenic potency of BaP, with respect to the activity of all PAH, ranged from 44.9% to 59.6% for the dry season and between 46.9 and 55.0% for the rainy season. Vehicles were suggested as an emission source for SEOM and PAH, but burning vegetation around the sampling site was considered as well, as confirmed by the presence of retene. Coronene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene, which are considered tracers of gasoline-powered vehicles, were the most abundant. Our results will provide and improve the basis for regulation of particulate matter in México City together with epidemiological and toxicological studies to determine the toxicity of specific classes of airborne particles.

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