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Organic Compounds in Airborne Particles and their Genotoxic Effects in Mexico City

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1. Introduction

Air pollution is a local, regional and global problem concerning natural and human activities. The atmospheric pollution in urban areas is of great importance since those centers are densely populated and the degree of exposure to toxics in the air has a major impact on the inhabitants, compared to the exposure of people not living in them. Many urban areas experience uncontrolled growth which is especially acute in developing countries and leads to increasing demands for energy, transportation, and commercial and industrial activities (Lawrence et al., 2007). Although people in some microenvironments can be exposed to concentrations of specific pollutants higher than those for individuals exposed outside, our interest is in environmental atmospheric pollutants and specifically in atmospheric organic aerosols. This chapter will give a brief overview of the organic compounds in airborne particles and their impact on climate and air quality, chemical composition and source apportionment, as well as on instrumental determination and atmospheric transformation, besides their toxic effects and to risk human health. We will present those studies related with the organic chemical speciation of the compounds, particularly emphasizing polycyclic aromatic hydrocarbons, which are known to be ubiquitous environmental mutagens and carcinogens, and we will discuss the genotoxic effects of those compounds in Mexico City (MC); finally, we will describe the recent work and future studies of our research group.

2. Airborne particles

Aerosol is constituted by a mixture of gases and suspended particles (liquid and solid). However, the particulate phase is commonly referred to as aerosol. Aerosols have been considered to play a significant role in atmospheric chemistry physical processes, meteorology and climate change, justifying in all cases the impact on humans. Their study will add to the knowledge regarding their transport and atmospheric processes, their spatial and temporal behavior and their impact on materials, visibility, climate and human health. In this sense, the particle phase of an aerosol, called airborne particles, is of relevance to

public health due to their proven morbidity and mortality effects on humans (Pope & Dockery, 2006). The magnitude of these effects generally depends upon their seasonal behavior, sources, chemical composition, number, mass, surface area and size, which increases the human health risk when the particles are inhaled because particle size is inversely proportional to the deep deposition area in the respiratory system (Sugita et al., 2004). An essential step is to measure these variables which may all be important physical-chemical properties that influence particle toxicology (Sen et al., 2007). The risk to human health is related with a long period of exposure to environmental pollutants, which increases in children and elderly persons. Human exposure to particles for both a short- and a long-term has been associated with measures of genetic damage (Lewtas, 2007). Airborne particles can be generated through grinding activities, soil resuspension due to wind or other natural processes as soil erosion, or they can be a product of the incomplete combustion of fossil and non-fossil materials as well as a result of chemical reactions and condensation onto preexistent particles (Solomon et al., 2001). Their chemical composition is a complex mixture that depends upon several factors as emission sources, geographic and climatic conditions, atmospheric reactivity, and the like.

The main process of aerosol production in nature and the most important mass-transfer via gas-phase and particle-phase is by condensation, through a supersaturated vapor initiated by the presence of small particles (heterogeneous or homogeneous nucleation) or ions that serve as sites for particle formation (Hinds, 1999). Micrometer-sized particles are strongly attached to any surface they contact through the London -van der Waals forces-, which is one of the most important adhesive forces to form aggregates (Hinds, 1999). Particle size, density and shape are some of the physical properties that influence pulmonary deposition, ground deposition rate, aging during atmospheric transport and residence time in the air. These properties help identify emission sources and /or the atmospheric formation process. Size, which ranges from 10 nm to 100 μm and is commonly analyzed by lognormal distributions, is one of the most important physical properties of the particles. It is measured in terms of the aerodynamic diameter defined as the equivalent spherical particle diameter that has a density of 1 g cm^{-3} with the same settling velocity as the target particle, and it is used for characterizing filtration, respiratory deposition and the performance of many types of air cleaners and air particle samplers.

3. Organic aerosol

3.1 Impact on climate and air quality

Aerosol particles influence the Earth's radiative and hydrological balance (Ramanathan et al., 2001). Knowledge of their contribution to radiative forcing is still uncertain (IPCC, 2007). Soot particles, which are aggregated carbonaceous spherules of tens of nanometers in size, and which have graphitic structures, are emitted from incomplete combustion of fossil fuel, biofuel, and biomass carbon together with organic matter. Soot particles contribute to the warming effect in the atmosphere through absorption of sunlight (Bong & Bergstrom, 2006). Black carbon is found throughout the atmosphere, and it is thought to be the most important component to aerosol absorption of solar radiation although attention has recently turned to "brown" organic carbon (Sun et al., 2007) as a source of significant absorption, particularly in the near-UV. The scattering and absorption of incoming solar radiation is also affected by the organic aerosol component (Jacobson et al., 2000). Organics can alter the hygroscopicity

of the particles (Thomas et al., 1999), and this changes the radiative forcing that involves cloud condensation and nuclei formation; such forcing may have opposite signs depending on the type of particulate carbon (NRC, 1996). Emissions of organic species have the potential to influence aerosol-cold cloud interactions and climate (Cziczo et al., 2004). The hygroscopicity of atmospheric aerosols has a considerable effect on particle size and therefore on visibility (Vasconcelos et al., 1994). Dissolved and surface-active organic compounds in droplets and aerosols affect the albedo of clouds and rain development (Facchini et al., 1999). Size distributions as well as the optical and hydrophilic properties of organic particles are also uncertain due to the lack of data (Lioussé et al., 2005), in part owing to the complexity of the organic content which may involve several hundreds of compounds of a different chemical class and which have different biological effects. Although biological particles such as spores, bacteria, algae, pollen, vegetation and insect debris, animal cell fragments, and the like (Winiwater et al., 2009) can be considered as part of the particle organic fraction, their discussion goes beyond this chapter.

3.2 Chemical composition and source apportionment

Organic aerosol (OA) represents the second most abundant component after sulfates and nitrates in particles $< 1 \mu\text{m}$ (Jacobson et al., 2000) and contributes to 10-80 % of their total mass (Hildemann et al., 1996; Rogge et al., 1993a). The specific organic chemical composition of aerosol includes n-alkanes, sugar derivatives, aldehydes, mono- and di-carboxylic acids, substituted phenols, polycyclic aromatic hydrocarbons (PAH) and their derivatives, ketones, quinones, diterpenoids acids and some nitrogen-compounds (Rogge et al., 1993a, 1993b, 1993c, 1993d), all of which are emitted from a variety of natural and anthropic sources. The range of their molecular weight, vapor pressure, polarity, reactivity and the like, have limited the chemical speciation ~ 10 % of the total mass (Rogge et al., 1993a), and recent efforts have focused on methods that classify the OA (Zhang et al., 2005). Polycyclic organic matter (POM) is considered by the Air Clean Act of the USA as one of the 189 air pollutants most risky for humans (Kelly et al., 1994). Among these, PAH and their nitro-derivatives (nitro-PAH) are very important, given their mutagenic and carcinogenic properties (IARC, 1983, 1989; Rosenkranz & Mermelstein, 1983). PAH are primary pollutants emitted from combustion sources, while the nitro-PAH are also primary pollutants, but they are generated by combustion mainly from diesel engines and they are also formed in the gas phase by the interaction between PAH and NO_x with OH radical during the day and with NO_3 radical during the night (Atkinson et al., 1990; Nielsen, 1984). Opposite to adverse effects of POM, fatty acids have showed antimutagenic properties (Hayatsu et al., 1988). In MC, the palmitic and stearic acids were the most abundant fatty acids (Villalobos-Pietrini et al., 2008). Fatty acids and n-alkanes are two of the most abundant organics which make up organic aerosol (Feng et al., 2007), and although no adverse effects on human health for n-alkanes have been reported, they are used as anthropic and biogenic emission markers (Amador-Muñoz et al., 2011; Kavouras et al., 1999).

Depending on the emitted amount, some organic compounds can be used as tracers of emitting sources or atmospheric transformations (Rogge et al., 1993a; Schauer et al., 1996). The development of effective control strategies for airborne organic pollution is necessary for good air quality. The knowledge of emission sources in each site is extremely important to satisfy this demand. Two methods have been widely employed to evaluate source contribution: source-oriented models and receptor-oriented-models (Schauer et al., 1996).

Source modeling uses emissions data and fluids mechanics to predict pollutant concentrations at a specific receptor site. Receptor modeling infers source contributions based on the best-fit linear combination of the chemical compositions of the effluents from specific emission sources needed to reconstruct the chemical composition of specific atmospheric samples (Watson, 1984). Schauer et al. (1996) constructed a chemical mass balance (CMB) receptor modeling based on the use of organic tracers that has been widely accepted. Dual diagnostic ratios to determine the origin of the atmospheric pollutants have also been employed (Ravindra et al., 2008); however, the huge uncertainty due to different methodologies and reactivity of the pollutants (Robinson et al., 2006a, 2006b) suggests that this method must be used with caution because it is difficult to discriminate between sources (Ravindra et al., 2006). The other limitation is that interpretation is ambiguous, because it depends on the ratio considered and on the source profile chosen (Goriaux et al., 2006). However, the diagnostic ratio with similar physicochemical properties for example among PAH can be used to minimize bias due to chemical reactivity, volatility, and solubility of PAH species. Diagnostic atomic ratios have been recently employed as a metric degree of oxidation of organic species in the atmosphere to describe organic mixtures in the organic aerosol (Kroll et al., 2011). Aiken et al. (2008) used oxygen-to-carbon (O/C) ratios to characterize the oxidation state of OA. The O/C from ambient urban OA for primary emissions was 0.2, and it increased to 0.8 because of photochemical processing and secondary OA formation. They also analyzed the high resolution OA spectra generated from High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) by Positive Matrix Factorization (PMF) analysis, and they were able to identify emissions from chemically-reduced urban primary, oxygenated OA, and biomass burning OA that correlated with levoglucosan and acetonitrile. PMF has several advantages over common versions of factor analytical approaches based on the correlation matrix (Lanz et al., 2007). Principal components analysis (PCA) is the most widely multivariate statistical technique used in atmospheric science to simplify the interpretation of complex systems; it is also used to reduce the dimensionality of the variables into a smaller set of linear combinations that explain the greatest variance of the original set, called factors, which can be interpreted as an emission source or a chemical interaction. In general, each factor from PCA is associated with a source characterized by its chemical marker. Amador-Muñoz et al. (2011) applied PCA to show that in the Northeast (NE) of the Mexico City Metropolitan Area (MCMA) the main sources were diesel combustion, in Central (C) Mexico City they were gasoline combustion and in the Southwest (SW) they were of biogenic origin. Furthermore, the authors were able to describe the origin of the particles less than 2.5 μm ($\text{PM}_{2.5}$) in the Northwest (NW) and Southeast (SE) associated to primary sources, while in the NE, in Central MC and the SW the $\text{PM}_{2.5}$ had a secondary origin.

3.3 Instrumental determination

The OA consists of hundreds of compounds with a wide range in polarity and aqueous solubility. Knowledge of these compounds implies a better understanding of aerosol organics in atmospheric processing (Pang et al., 2006). Bulk aerosol characteristics have been measured using infrared spectroscopy, nuclear magnetic resonance, ion chromatography and aerosol mass spectrometry (Allan et al., 2003; Schmeling et al., 2000; Suzuki et al., 2001). In real-time particle mass spectrometric analysis, techniques have been developed for atmospheric measurements (Canagaratna et al., 2007). The application of the HR-ToF-AMS

is an example of on real-time measurement elemental analysis and organic aerosol (Aiken et al., 2007); however, incomplete speciation of chemical composition remains a challenge. A number of different ambient ionization techniques (Venter et al., 2008) are promising for identifying the organic component of SOA. For example, desorption electrospray ionization has been applied to particles collected on filters either with or without extraction (Laskin et al., 2010). One of these new ambient ionization techniques is the atmospheric solids analysis probe mass spectrometry, which was applied to identify organics in particles from laboratory systems as well as from ambient air, with a minimal sample preparation (Bruns et al., 2010).

Off-line organic composition of atmospheric aerosols has been characterized by a number of studies by their collection on filters or impactors, followed by solvent extraction, evaporation, derivatization and analysis using several analytical techniques (Laskin et al., 2009; Zheng et al., 2006). One approach is detailed chemical characterization through identification and quantification of individual constituents by gas or liquid chromatography coupled with mass spectrometry (GC-MS and LC-MS, respectively). Currently, off-line measurements are the procedures most employed to elucidate the organic aerosol composition, although the identified components depend on the details of the analytical techniques used, and both positive and negative artifacts can occur during sampling (Turpin et al., 2000). Determination of the carbon content associated to the atmospheric aerosol is carried out by various extraction techniques. The two most commonly used methods are thermal extraction and solvent extraction. Thermal extraction is used to differentiate between organic carbon and elemental carbon (Johnson et al., 1981) or to characterize the organic chemical composition (Vogt et al., 2007). Solvent extraction (Alves et al., 2000; Tran et al., 2007) is a method by which the organic matter extracted with organic solvents is used to determine the organic mass concentration (Alves et al., 2000; Villalobos-Pietrini et al., 2006), to speciate organic compounds (Amador-Muñoz et al., 2010, 2011; Valle-Hernández et al., 2010) and to perform genotoxic studies (Villalobos-Pietrini et al., 2006, 2007). Gas chromatography-mass spectrometry is the analytical technique most used to characterize their composition. Recently, two-dimensional comprehensive gas chromatography (GCxGC) coupled to time of fly mass spectrometry (TOF/MS) has focused attention on some studies because of the increased resolution and sensitivity of organic compounds in aerosol samples (Welthagen et al., 2003). Thermal desorption aerosol (TAG) was developed for in-situ identification of organic aerosols (William et al., 2006), and a newer version of this system coupled to GCxGC (2D-TAG) was applied for the time-resolved measurement of organic compounds in ambient aerosols (Goldstein et al., 2008), showing extraordinary improved separation capabilities for the OA. Although GCxGC offers a great deal of information at the molecular level, quantitative analysis has been less developed (Amador-Muñoz & Marriott, 2008). In a recent paper, we proposed a simple method based on isotope-dilution mass spectrometry to quantify PAH on aerosol samples employing a reference material of urban dust (NIST SRM1649a). Results agreed well with certified PAH (Amador-Muñoz et al., 2008), without a pre-treatment of the samples after their organic extraction.

3.4 Atmospheric transformation

Primary Organic Aerosol (POA) is emitted directly as particles by anthropic or natural sources, whereas Secondary Organic Aerosol (SOA) is formed in the atmosphere through

chemical reactions that result from the more volatile species conversion into lower volatility oxidized condensation products and the subsequent partition to the particulate phase (Kanakidou et al., 2005; Pöschl, 2005). The formation of SOA is impacted by the amount and reactivity of gas-phase precursors, the presence of oxidants in the atmosphere, incoming solar radiation, the chemical composition of existing particles, and meteorological parameters as relative humidity and temperature (Pöschl, 2005). On a global scale, biogenic volatile organic compounds (VOCs) account for $\sim 90\%$ of VOC emissions and of SOA formation (Hallquist et al., 2009). SOA particles scatter radiation, act as cloud condensation or ice nuclei, and have influence on the Earth's radiation balance and climate (Hallquist et al., 2009; IPCC, 2007). However, emission sources, atmospheric transformation, and properties of OA remain poorly understood, and consequently offer uncertain information for chemical-transport models (Hallquist et al., 2009; Kanakidou et al., 2005). Current modeling assumptions and the oxidation of VOC gaseous precursors can not explain the SOA levels in polluted regions (Volkamer et al., 2006) as in the case of biogenic SOA levels formed in clean regions (Slowik et al., 2010). Evidence for new precursors and pathways of SOA formation has recently been described, in particular, the semi-volatile character of POA (Robinson et al., 2007), which has been modeled as a group of hydrophobic non-volatile compounds in particulate phase. POA coexist with semi-volatile organic compounds (SVOC) of low volatility that are in the particle-phase; besides, POA also coexist with intermediate-volatile organic compounds (IVOC) which are highly volatile and are in the gas-phase. Both groups are ignored in SOA modeling and commonly not included in VOC emission inventories (Robinson et al., 2007). They are composed of species such as long-chain alkanes, which can be oxidized to produce a large amount of lower volatility precursors that are likely to partition to the aerosol phase. Unfortunately many IVOCs and SVOCs are not separable by GC-MS and they are part of the "unresolved complex mixture", which lead to the need to parameterize their amounts and SOA formation (Robinson et al., 2007). The treatment of the POA emissions is a huge uncertainty (Murphy & Pandis, 2009). In addition to anthropic emissions, the POA emitted from biomass burning (BB) should also be considered semi-volatile (Huffman et al., 2009). These SVOC are oxidized quickly in the gas-phase (Yokelson et al., 2009). Gas-particle partitioning is another important parameter to be considered in the modeling of the dynamics of biogenic SOA formation. The gas/aerosol partitioning is assumed to be governed by equilibrium partitioning into an absorptive, well-mixed liquid or amorphous organic matter phase (Pankow, 1994), yet Virtanen et al. (2010) recently presented experimental evidence that biogenic SOA particles are amorphous solid state (glassy state) under ambient conditions. This result may influence the kinetics and thermodynamics of SOA formation and transformation, impacting several processes: the partitioning of semi-volatile compounds, the rate of heterogeneous chemical reactions, the particles' ability to accommodate water, cloud condensation or ice nuclei, and the atmospheric lifetime of the particles (Mikhailov et al., 2009). All of these important physical-chemical parameters will have implications for air quality and climate. The improved agreement between observed and predicted SOA when including SI-SOA in both studies also suggested that the POA emissions inventory in MC does not include SVOC that evaporate after POA emission.

Stone et al. (2010) calculated anthropic secondary organic carbon (SOC) as 20-25% of ambient OC at peripheral and urban sites of MC, while biogenic SOC was less abundant but relatively twice as important at the peripheral site. The OC that was not attributed to

secondary sources or to primary sources in a previous study (Stone et al., 2008) showed temporal consistency with BB events, as demonstrated by the correlation with levoglucosan. Based on a factor analysis, Amador-Muñoz et al. (2011) observed that organic matter in PM_{2.5} did not originate in primary emission sources (petrogenic combustion, pyrolysis or biogenic emissions) in the MCMA, and that the weak correlations between organic matter vs. PM_{2.5} (except in the SW), heavy PAH, n-alkanes and nitro-PAH (except in the SW), indicated that organic matter was formed by processes different from the other variables, where BB would play an important emission source. In this sense, organic matter was probably explained by the emissions and the aging of Mexico Basin outflow and not from inside the Mexico Basin. The oxidation level of the organic matter around MCMA was classified based on the ratios between organic matter vs. some n-alkanes sum and organic matter vs. some heavy PAH (Fig. 1). These compounds were selected due to their chemical stability and no evaporative losses in the atmosphere (Schauer et al., 1996).

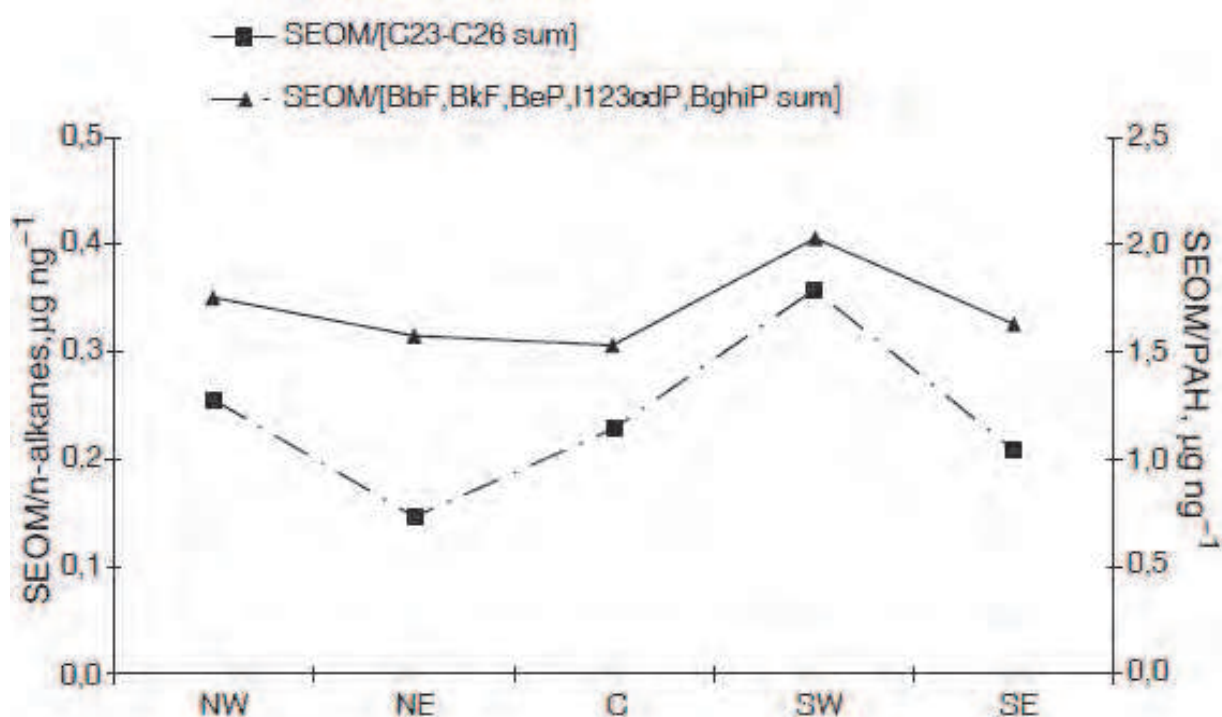


Fig. 1. Annual median ratios of SEOM/[C₂₃-C₂₆ sum] (dashed line) and SEOM/[BbF, BkF, BeP, I123cdP and BghiP sum] (continuous line) of five sites around the MCMA during 2006. Taken from Amador-Muñoz et al. (2011).

Results showed that organic chemical composition in the SW was dominated by secondary organic species with a higher oxidation level with respect to organic compounds in the NE. The non-significant difference of ratios among the Central area, the NW and the SE suggests an organic composition with mixed secondary and primary organic compounds. This matches up with a decrease in the ratios between PAH and humidity, probably due to a major coverage of oxidized organic compounds during the transport of pollutants from NE to SW, as it has been established elsewhere in MC (Baumgardner et al., 2007; Thornhill et al., 2008; Volkamer et al., 2006).

At present, the sources and composition of OA are uncertain, with current models under predicting SOA by large factors (Volkamer et al., 2006), and the models have difficulty in predicting the loadings, spatial and temporal variability, and degree of oxidation of ambient OA (Kroll et al., 2011). Some studies related with aerosol modeling have been performed at the Centro de Ciencias de la Atmósfera, UNAM. In a recent investigation, Díaz-Nigenda et al. (2010) studied the effect of particle less than 10 μm (PM_{10}) from aeolian erosion episodes in MC using the wind erosion and air quality model Multiscale Climate and Chemistry Model during specific episodes in 2006 and 2008. In all extreme PM_{10} episodes, wind erosion was a major cause of high PM_{10} concentrations in MC, mainly originated in agricultural lands and the Texcoco areas from the NE, East and SE. 3D analysis of the modeling results showed that transport of PM_{10} is accelerated horizontally when nearby confluences are formed generating low pressure systems and vertical transport of the particles is enhanced. Confluence lines are a main factor for vertical mechanical convection of dust particles. In the case of the November 2008 episode, the particles were transported to the mixing layer height and then transported out of the Basin of Mexico. Jazcilevich et al. (2003) used a prognostic air quality model to show vertical fumigation episodes due to the complex orography of the MCMA where reactive and non-reactive atmospheric pollutants can travel near the surface, be transported vertically and land in an area opposite to its initial route due to convective downward currents, changing the surface pollutant concentrations on the landing area. Another meteorological mechanism shown by Jazcilevich et al. (2005) gives rise to high atmospheric pollution episodes over the MCMA: a local confluence line created when two airflows meet over the city almost canceling their horizontal speed, accumulating pollutants and favoring photochemical reactions. It was concluded that the occurrences of the confluence lines over MCMA are relatively common during the autumn–winter period. The confluence phenomenon explains why the measured pollutant assumes its distribution. It also explains how biogenic and anthropic photochemical smog precursors can meet within the Basin of Mexico aiding to the formation of ozone.

4. Studies of organic aerosol in Mexico City Metropolitan Area

The MCMA is located in a basin on the central Mexican plateau with a population of around 20 million, in addition to 4 million vehicles and 35,000 industries. It has tropical latitude, an urban area of about 3,500 km^2 at 2,240 m altitude, and is surrounded by high mountains on three sides, degrading the air quality (Fast et al., 2007). One of the first campaigns to provided comprehensive information into meteorological measurements and particulate composition in the MCMA was the IMADA-AVER study (Investigación sobre Materia Particulada y Deterioro Atmosférico-Aerosol and Visibility Evaluation Research) carried out in February–March 1997 (Doran et al., 1998). A subsequent campaign developed during April 2003 (MCMA-2003) generated observations of oxidant precursors, photochemical products, radicals species, speciated VOCs, particulate matter, as well as meteorology and emissions information (Molina et al., 2007). The most recent and intensive campaign named MILAGRO (Megacity Initiative: Local and Global Research Objectives), characterized the pollutant emissions in MC and their transformation and impact on the atmosphere from local to global scales. The study involved multiple ground sites inside and downwind from MC, as well as multiple research aircraft (<http://mce2.org/>, Molina et al., 2010).

4.1 Chemical speciation

Carbon is one of the major contributors to fine particle mass. It can be found as elemental (EC) and organic carbon (OC). Chow et al. (2002) reported crustal material (~50%), carbon (~32%) and sulfate, ammonium and nitrate (~17%) as the main components of PM₁₀, while those PM_{2.5} were carbon (~50%), crustal material (~30%), and sulfate, ammonium and nitrate (~15%), around and in MC during February and March 1997. PM_{2.5} contributed to ~50% of PM₁₀ mass. Chemical composition mass was heterogeneous among sites. In November of the same year, the chemical analysis of aerosols measured in the SW indicated again that soot, organic compounds, and sulfate dominate their composition (Baumgardner et al., 2000), and that the relative fractions of sulfate that make up their composition are controlled by water vapor and cloud droplets. Baumgardner et al. (2002) suggested that black carbon in urban areas can be estimated by carbon monoxide measurements. Salcedo et al. (2006) determined that organic and elemental carbon constituted ~66% of fine particle concentration, while inorganic and crustal species accounted for the remaining ~33% during MCMA-2003. The concentrations and compositions were consistent at various locations within MC, suggesting widespread sources of precursors and secondary aerosol formation. The OA total mass can be estimated from the organic carbon content commonly multiplying by a conversion factor of 1.4 (Turpin & Lim, 2001), although it can vary from 1.0 to 2.5 depending on location (Pang et al., 2006).

Although total carbon (EC+OC) determination is an important parameter to explain several atmospheric conditions due to particles found there, the chemical speciation is a key to comprehensively understand, for example, source apportionment, concentration levels, chemical transformation, air quality models and human health risk. One of the most important groups in airborne particles in terms of health risk are polycyclic aromatic compounds (PAC), which include PAH, oxygenated-PAH, nitro-PAH, amino-PAH, and heterocyclic aromatic compounds (Finlayson-Pitts & Pitts, 1997). PAC is a fraction of several classes of organic compounds found in atmospheric aerosol. Among them, PAH have been the most studied PAC in gas and particle phases, in part owing to carcinogenic effects (Denissenko et al., 1996; IARC, 1983, 1989) and genotoxic properties (Villalobos-Pietrini et al., 2007), although their derivatives as nitro- and oxy-compounds can represent a higher risk than their parent PAH (Durant et al., 1996). PAH are present in a larger proportion in fine particles (Allen et al., 1996; Amador-Muñoz et al., 2010). The main intake route by humans is the respiratory system; the particles generally occur as complex mixtures emitted as a result of incomplete combustion processes and are generated from both natural and anthropic sources (ATSDR, 1995). Several studies have been developed to determine PAH in MC, including on-real and off-real time analysis.

4.1.1 On-real time PAH measurements

Velasco et al. (2004) measured personal exposure to PAH in different outdoor and indoor environments, as well as along roadways in MC developed in December 2001. PAH were analyzed based on the aerosol surface properties using a photoelectric aerosol sensor (PAS) which quantifies bulk particle-bound PAH (PPAH) (Burtscher & Siegmann, 1993). For outdoor environments (bus stations) PPAH concentrations varied from 17 to 582 ng m⁻³. For indoor environments the major contributors were hand smokers, poorly adjusted pilot stoves, inefficient ventilation and faulty air-conditioning systems. Marr et al. (2004) measured PPAH with a PAS during October 2002 at three points in MC with a high influence of diesel combustion. Median PPAH concentrations in roadways along MC ranged

from 60 to 910 ng m⁻³. Particles freshly emitted by vehicles, PPAH and elemental carbon concentrations were well correlated, suggesting that surface PPAH concentrations may diminish with particle aging. In a subsequent study, Marr et al. (2006) compared different methods for characterization of PAH concentrations in the SE of MC during April 2003 (MCMA-2003). The diurnal concentration patterns captured by aerosol photoionization and aerosol mass spectrometry were generally consistent. Ambient PPAH typically show a peak at ~ 110 ng m⁻³ during morning rush hour, with a quick decrease due to sources in activity pattern, air dilution and surface coated by secondary organic aerosol. Speciated measurements suggest that motor vehicles are the predominant daytime source of PPAH, while wood and garbage burnings are important nighttime sources. Jiang et al. (2005) estimated PAH from motor vehicles in MC during April 2003 (MCMA-2003). On the basis of ~ 30,000 exhaust measurement points that represent a variety of vehicle types and driving conditions, and supported by a method of automatically identifying exhaust plumes, an estimate was made of an emission inventory and a fleet-average emission factor of 57±6 tons PPAH per year, not including cold start emissions. However, this estimate may be low by ~10% due to the lower response type of the PAS. Dzepina et al. (2007) reported the technical aspect of particle-bound PAH analysis using real-time quadrupole aerosol mass spectrometer (Q-AMS) and the comparison with PAS and GC-MS analysis. A subtraction method to remove the contribution of non-PAH organics to the ion signals of the PAH in ambient data was developed. The mass concentration of ambient PAH from 202 to 328 g mol⁻¹, as well as their sum was reported with an uncertainty of +35% and -38%. Comparisons with PAH-PAS measurements were well correlated, while those of PAH concentrations in filter determined by GC-MS analysis were in agreement for some PAH and higher for others. The signals of ambient cyclopenta[*cd*]pyrene and dicyclopentapyrenes were higher by Q-AMS than by GC-MS analysis of filter samples, suggesting artifacts during filter sampling. Thornhill et al. (2008) measured PAH with PAS at several sites throughout MC during the MILAGRO campaign. PPAH concentrations in the north of Central exhibited a consistent diurnal pattern and frequently exceeded 200 ng m⁻³ during the morning rush hour. PPAH concentrations were poorly correlated in space, and therefore for risk assessment studies, a single monitoring site was not adequate to represent an individual's exposure. PPAH were strongly correlated with NO_x, reflecting the importance of diesel combustion engines. Results suggested that primary particles emitted from combustion are rapidly coated by secondary aerosol in MC, protecting PPAH against photodegradation or heterogeneous reactions, increasing the PPAH lifetime in the atmosphere. Since some other organic compounds can be ionized by the PAS and contribute to their signal (Matter et al., 1999), PPAH should be considered a relative, rather than absolute, indicator of the concentration of PPAH, elemental carbon and some trace amounts of other organics (Baumgardner et al., 2007). Given this uncertainty, a mass concentration of PPAH in the SW of MC during April 2005 was reported by Baumgardner et al. (2007). A reproducible diurnal pattern with the daily maxima (~120 ng m⁻³) occurring from 6 to 8 a.m. was observed, and the maximum occurred at the same time as the condensation nuclei (CN), indicating that the majority of the particles containing PAH are quite small, which are those that dominate the CN concentration. A rapid decrease of PPAH, similar to findings by Marr et al. (2004, 2006) and Thornhill et al. (2008), was observed, suggesting a removal process by photochemical reactions which suppresses the response of the PAS; however, caution is recommended in using this type of analyzer for studying urban PPAH.

4.1.2 Off-real time PAH measurements

Several Mexican research groups have contributed to determine specific PAH in aerosol based on off-real time measurements. Our Environmental Mutagenesis Group (EMG) is one of them. It is dedicated to evaluating not only PAH, but also several organic compounds in aerosols, their temporal and spatial behavior, sources and genotoxic effects. The follow studies were done using high volume samplers for PM₁₀ in the SW of MC on the campus of Universidad Nacional Autónoma de México, considered as a pollutants receptor site (Amador-Muñoz et al., 2011; Guzmán-Torres et al., 2009). In all campaigns, the analyses were done by GC-MS operated in electron impact mode. Calderón-Segura et al. (2004) measured PAH present in PM₁₀ in April, August and November 1997. The highest concentrations were obtained in dry-season (November), while the lower ones were obtained in rainy season (August). Furthermore, the effects of seasonal weather on genotoxicity, mitotic changes and cytotoxicity in human cells exposed to extracts of airborne particles were evaluated as will be shown in the section on toxic effect and human health risk. Bravo et al. (2006) proposed a multivariate linear model made up with data from August 1998 to September 2000 to estimate PM₁₀ as a function of meteorological parameters behavior. The model was evaluated to estimate non-seasonal PM₁₀ concentrations from November 2000 to June 2001 ($r=0.57$, $p<0.05$). PM₁₀ concentration values from February to May 1998 were higher than the rest of the data, due to the abundant emissions of smoke from the forest fires in the surroundings of the sampling site and confirmed by the presence of high amounts of retene (Fig. 2), which is a branched PAH considered a molecular marker of wood burning (Ramdahl, 1983).

In addition to retene, specific PAH were quantified by Villalobos-Pietrini et al. (2006). The presence of benzo[ghi]perylene, coronene and indeno[1,2,3-*cd*]pyrene as the most abundant PAHs (Fig. 3) indicate vehicles with gasoline combustion as the main source (Miguel et al., 1998), in spite of the wood burning presence. Statistical analysis suggested that fluoranthene and benz[*a*]anthracene could also mainly originate in wood combustion, which was the opposite for perylene and coronene, where the fires were not their principal origin.

In a subsequent study, Amador-Muñoz et al. (2010) evaluated the seasonal behavior of particle mass, solvent extracted organic matter (SEOM) and PAH in dry (October 1998-February 1999) and rainy (June-October 1999) season, using a cascade impactor with six stages (<0.49-10 μm). Higher mass concentrations were distributed in particles with diameters < 3.0 μm in both seasons (Fig. 4). The most abundant PAH detected in this study were coronene, benzo[ghi]perylene, and indeno[1,2,3-*cd*]pyrene, indicating vehicular gasoline combustion. Heavy PAH were distributed in fine particles, while light PAH were more abundant in coarse particles. SEOM in particles <0.95 μm indicated an organic composition with a higher water-affinity than in greater particle sizes. 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. Greater human risk in the dry season was determined when the potential doses of carcinogenic PAH by inhalation were evaluated. In a campaign carried out from February to April in 2004 at the same sampling zone (Saldarriaga et al., 2008), we found higher concentrations of coronene, benzo[ghi]perylene, benzo[*b+j+k*]fluoranthenes and indeno[1,2,3-*cd*]pyrene in PM₁₀, indicating again a strong contribution from incomplete combustion of gasoline.

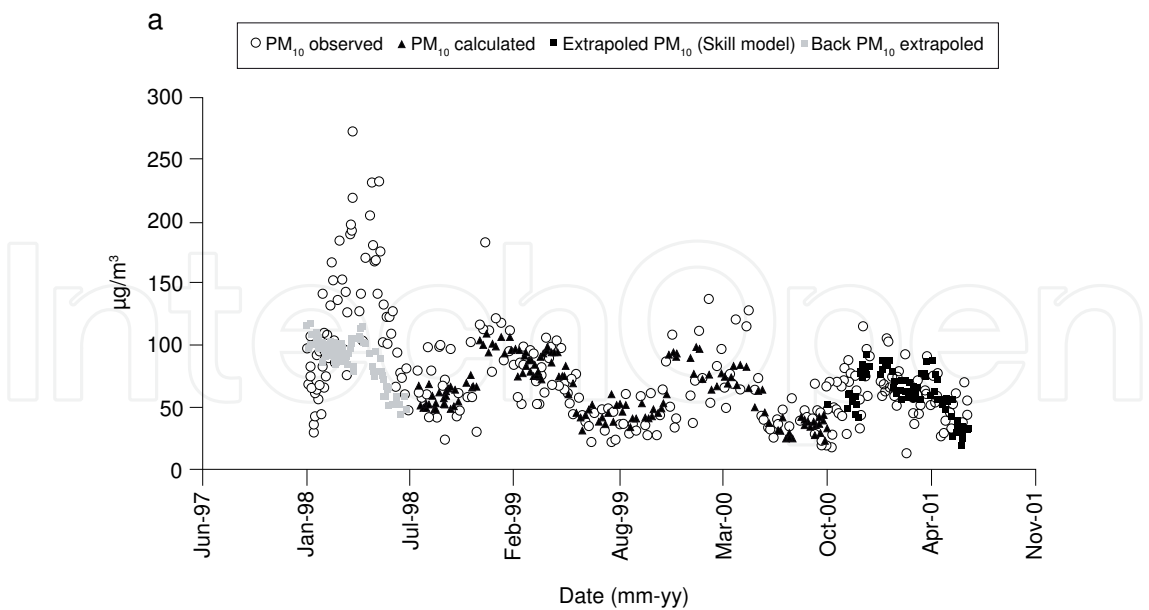


Fig. 2. Observed and estimated PM₁₀ vs. date from January (1998) to June (2001). SWof MC. Higher values ($> 200 \mu\text{g m}^{-3}$) due to forest fires. Taken from Bravo et al. (2006).

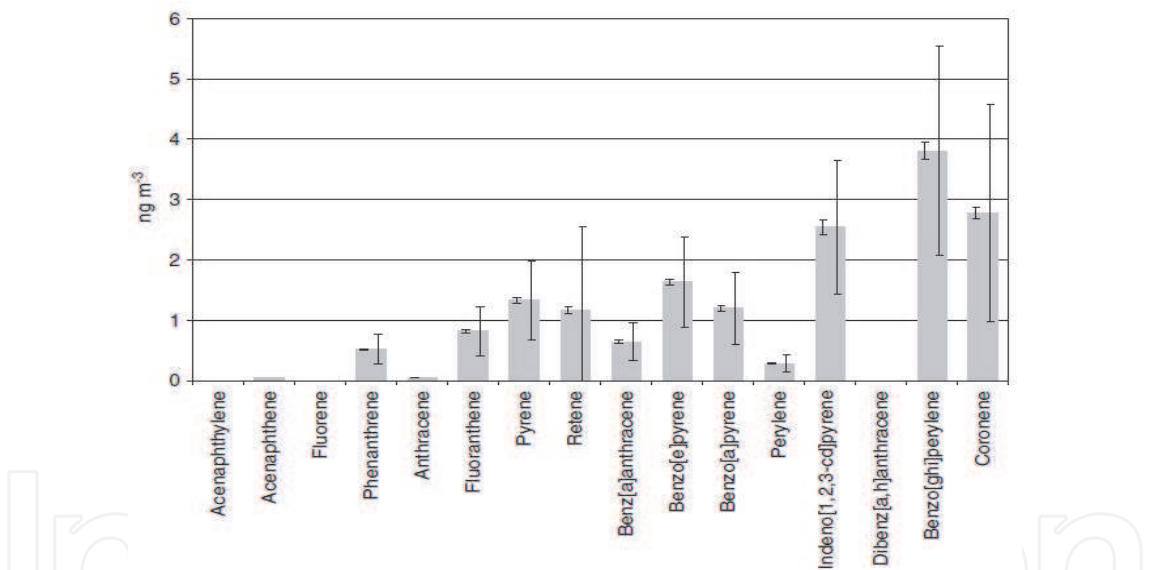


Fig. 3. PAH annual mean concentrations in SW of MC during 1998; the smaller deviation lines indicate the uncertainty associated to measurements, and the largest lines represent the standard deviations. Taken from Villalobos-Pietrini et al. (2006).

Other Mexican research groups have also contributed to studies on PAH concentrations in airborne particles in the MCMA. In a study carried out in 2003 (November and December) in the NW (UAM-A) of MC, Mugica et al. (2010a) reported PAH in PM₁₀, employing high-volume samplers and GC-MS analysis developed in different seasons and sites. Benzo[ghi]perylene was the most abundant PAH, associated to vehicle emissions. Guzmán-Torres et al. (2009) carried out a study during March 2003 at two sites in MC: Center (source site) and SW (receptor site). Higher PAH concentrations were found during the morning period, while the ratios between organic and elemental carbon also measured indicated that

the SW is impacted by secondary aerosols during the afternoon hours. Similar to the last mentioned studies, benzo[ghi]perylene was the most abundant PAH, suggesting exhaust emission by light-duty vehicles as an important contributor to the atmospheric PAH burden. In a subsequent campaign by Mugica et al. (2010a) from February 2005-2006, spatial and seasonal PM₁₀-PAH differences were found among four sites in MCMA. The highest amount of PAH was found in the NE (Xalostoc) (considered as the most important industrial area in the MCMA), while the lowest was found in the NW (UAM-A). Dry-cold season (October to February) showed PAH levels up to three times greater than rainy (June-September) and dry-warm (February-May) seasons. A high number of thermal inversions and calm wind events during dry-cold season, and photochemical reactivity and evaporation on PAH during dry-warm season, explained the temporal PAH variations. In a similar period (February 2005 to January 2006), Mugica et al. (2010b) characterized and evaluated the seasonal behavior of PAH in the gas phase and in PM₁₀ in the NW (UAM-A) of MC. Vapor-phase PAH comprised 86–97% of the total PAH mass. Major PAH concentrations in dry-cold season were found. Vehicular emissions and diesel and gas combustion were the most important PAH sources. Similar to other studies, benzo[ghi]perylene was the most abundant PAH. A more recent campaign developed by the same group from April 2006 to March 2007 in the North of MC (CINVESTAV), benzo[ghi]perylene was the PAH most abundant followed by indeno[1,2,3-*cd*]pyrene. Dry-cold season showed the highest PAH concentrations with respect to warm and rainy season. Table 1 shows a comparison of PAH concentrations in PM₁₀ developed in the MCMA.

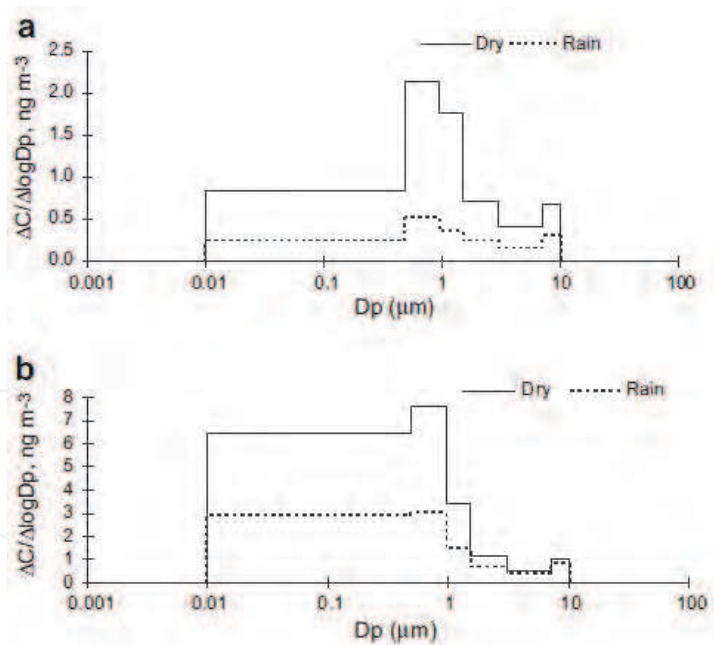


Fig. 4. Median seasonal PAH mass concentrations ($\Delta C / \Delta \log D_p$) in six diameter ranges of a. Light PAH sum (phenanthrene, anthracene, retene, fluoranthene and pyrene) and b. Heavy PAH sum (benzo[a]anthracene, chrysene, triphenylene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and coronene), during dry (October 1998–February 1999) and rainy (June–October 1999) seasons at SW of MC, D_p – aerodynamic particle diameter. Taken from Amador-Muñoz et al. (2010).

| PAH | SW ¹ (98) | SW ^{2a} (98-99) | SW ^{2b} (98-99) | Central ^{3a} (03) | SW ^{3b} (03) | SW ⁴ (04) | SW ^{5a} (05-06)* | SW ^{5b} (05-06)* | SW ^{5c} (05-06)* | Central ^{5a} (05-06)* | Central ^{5b} (05-06)* | Central ^{5c} (05-06)* |
|---------------------------------|-------------------------|-----------------------------|-----------------------------|-------------------------------|--------------------------|-------------------------|------------------------------|------------------------------|------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Acenaphthylene | n.f. | n.r. | n.r. | 201 | 85 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Acenaphthene | 46 | n.r. | n.r. | 35 | 29 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Fluorene | n.f. | n.r. | n.r. | 85 | 23 | n.r. | < 200 | < 200 | < 500 | 100-300 | 100-300 | < 500 |
| Phenanthrene | 516 | 337 | 153 | 561 | 249 | n.r. | 200-500 | 200-500 | 500-1 000 | 500-1 000 | 500-1000 | 1 000-1 500 |
| Anthracene | 49 | 87 | 85 | 133 | 76 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Fluoranthene | 815 | 659 | 203 | 1 438 | 681 | 200 | 500-800 | 400-600 | 500-1 000 | 1 000-1 500 | 1 000-1 500 | 2 000-3 000 |
| Pyrene | 1 330 | 848 | 242 | 1 702 | 791 | n.r. | 600-1 000 | 600-1 000 | 1 000-1 500 | 1 200-1 600 | 1 500-2 000 | 2 000-3 000 |
| Retene | 1 162 | 512 | 181 | n.r. | n.r. | 30 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Benzo[<i>a</i>]anthracene | 639 | 525 | 138 | 2 174 | 887 | 180 | 1 000-1 200 | 1 100-1 400 | 1 000-1 500 | 1 500-2 000 | 1 500-2 000 | 2 000-3 000 |
| Chrysene | 1 204 ^I | 728 ^I | 214 ^I | 3 132 | 1 441 | 240 ^I | 1 200-1 500 | 1 000-1 300 | 1 000-1 500 | 3 000-3 500 | 1 500-1 800 | 5 000-7 000 |
| Benzo[<i>b</i>]fluoranthene | 3 388 ^{III} | 1603 | 703 | 3 412 | 1 560 | 740 ^{IV} | 1 500-1 800 | 1 500-1 800 | 1 500-2 500 | 2 000-2 500 | 3 000-3 200 | 5 000-7 000 |
| Benzo[<i>k</i>]fluoranthene | n.r. | 1 021 ^{III} | 425 ^{III} | 2 858 | 1 474 | n.r. ^{IV} | 1 200-1 500 | 1 000-1 300 | 1 000-1 500 | 2 000 | 1 000-1 300 | 3 500-5 000 |
| Benzo[<i>e</i>]pyrene | 1 630 | 1 304 | 556 | n.r. | n.r. | 370 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Benzo[<i>a</i>]pyrene | 1 195 | 786 | 322 | 4 004 | 1 522 | 320 | 1 200-1 500 | 1 000 | 1 000-1 500 | 3 500-4 000 | 4 000 | 5 000-6 000 |
| Perylene | 282 | 225 | 126 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Indeno[1,2,3- <i>cd</i>]pyrene | 2 541 | 1 821 | 887 | 5 660 | 2 516 | 670 | 1 400-1 600 | 1 500-1 800 | 1 000-1 500 | 4 000-4 500 | 5 000-5 500 | 12 000-14 000 |
| Dibenzo[<i>a,h</i>]anthracene | n.f. | 186 | 115 | 887 | 734 | 70 | 1 000 | 1 000 | 1 000-1 500 | 500-1 000 | 500-1 000 | 1 000-1 500 |
| Benzo[<i>ghi</i>]perylene | 3 802 | 3 065 | 1 520 | 7 174 | 2 777 | 870 | 1 600-2 000 | 2 000 | 2 500-3 000 | 5 000 | 6 000-7 000 | 16 000-18 000 |
| Coronene | 2 776 | 3 167 | 1 544 | n.r. | n.r. | 1 250 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Σ PAH | 21 634 | 17 371 | 7 359 | 34 300 | 15 600 | 4 900 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |

Table 1. Comparison of PAH concentration (pg m⁻³) in PM10 among different sites and seasons carried out in the MCMA. The year of the campaign is indicated in parenthesis.

| PAH | NW ^{6a} (05-06) | NW ^{6b} (05-06) | NW ^{6c} (05-06) | N ^{5d} (06-07)* | N ^{5e} (06-07)* | N ^{5f} (06-07)* |
|---------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Acenaphthylene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Acenaphthene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Fluorene | 100 | 100 | 300 | 500-800 | 100-300 | 400-600 |
| Phenanthrene | 80 | 50 | 260 | 500-800 | 500-800 | 700-900 |
| Anthracene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Fluoranthene | 120 | 110 | 250 | 700-900 | 600-800 | 1 200-1 400 |
| Pyrene | 350 | 250 | 580 | 1 000-1 100 | 700-900 | 1 400-1 600 |
| Retene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Benzo[a]anthracene | 220 | 440 | 1 580 | 1 000-1 300 | 1 000 | 1 400-1 600 |
| Chrysene | 240 | 270 | 1 360 | 1 100-1 400 | 800-1 000 | 1 000 |
| Benzo[b]fluoranthene | 150 | 280 | 1 740 | 1 000-1 300 | 1 400-1 600 | 2 800-3 000 |
| Benzo[k]fluoranthene | 120 | 210 | 1 150 | 1 100-1 400 | 1 000-1 200 | 1 800-2 000 |
| Benzo[e]pyrene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Benzo[a]pyrene | 250 | 290 | 810 | 1 400-1 600 | 1 300-1 500 | 2 300-2 500 |
| Perylene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Indeno[1,2,3- <i>cd</i>]pyrene | 70 | 90 | 390 | 1 800-2 000 | 1 700-1 900 | 3 200-3 400 |
| Dibenzo[<i>a,h</i>]anthracene | 110 | 270 | 900 | 1 100-1 400 | 1 100-1 300 | 1 300-1 500 |
| Benzo[<i>ghi</i>]perylene | 340 | 380 | 1 360 | 1 800-2 000 | 1 700-1 900 | 3 400-3 600 |
| Coronene | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| Σ PAH | 1 990 | 2 760 | 10 480 | n.r. | n.r. | n.r. |

Continuation of Table 1.

SW (Pedregal), NW (UAM-A), N (CINVESTAV), * Range of approximated values since they were obtained directly from figures described by Mugica et al. (2010a), n.f. – not found, n.a. – not analyzed, n.r. – not reported, ^I Chrysene+Triphenylene, ^{II} Benzo[*b+k*]fluoranthenes, ^{III} Benzo[*j+k*]fluoranthenes, ^{IV} Benzo[*b+j+k*]fluoranthenes

¹ Villalobos-Pietrini et al. (2006). PAH annual mean concentrations (adjusted to standard conditions in 25°C and 1 atm) from January to December 1998. Forest fires were present from February to May 1998 (Bravo et al., 2006). SW is a residential and commercial zone, with green areas. 24 h collection, high volume samplers (1.13 m³ min⁻¹).

² Amador-Muñoz et al. (2010). PAH seasonal median concentrations (adjusted to standard conditions in 25°C and 1 atm):

^a Dry-cold season (October 1998-February 1999) and ^b Rainy season (June-October 1999). SW is a residential and commercial zone, with green areas. 24 h collection, in a cascade impactor on high volume samplers (1.13 m³ min⁻¹), PAH in PM₁₀ was calculated as the sum of all stages.

³ Guzmán-Torres et al. (2009). PAH monthly mean concentration in March 2003 (Dry-warm season). ^a The zone is highly impacted by vehicular emissions, and it was considered as a source site, ^b The zone is a low density residential area with low vehicular flow, and it was considered as a receptor site during the prevalent diurnal wind directions. 8 h collection, high volume samplers (1.13 m³ min⁻¹).

⁴ Saldarriaga et al. (2008). PAH seasonal mean concentration (adjusted to standard conditions in 25°C and 1 atm) from February to April 2004 (Dry-warm season). SW is a residential and commercial zone, with green areas, 24 h collection, high volume samplers (1.13 m³ min⁻¹).

⁵ Mugica et al. (2010a). PAH seasonal mean concentration: ^a February-May 2005 (Dry-warm season), ^b June-September 2005 (Rainy season), ^c October 2005-February 2006 (Dry-cold season), ^d Dry-warm season, ^e Rainy season, ^f Dry-cold season. Months were not specified for ^{d,e,f}. Center zone is close to downtown MC with heavy and light traffic on many avenues, and N (CINVESTAV) site has intense industrial activities, surrounded by main roads with large transit volumes, connecting northern and central regions of the MCMA, 24 h collection, high volume samplers (1.13 m³ min⁻¹).

⁶ Mugica et al. (2010b). PAH seasonal mean concentration: ^a February-May 2005 (Dry-warm season), ^b June-September 2005 (Rainy season), ^c November 2005-January 2006 (Dry-cold season). NW (UAM-A) is an urbanized zone with mixed land occupation of housing and industrial areas, 24 h collection, high volume samplers (1.13 m³ min⁻¹).

PAH sum concentrations in the SW during 2003 found by Guzmán-Torres et al. (2009) were similar to those found by Amador-Muñoz et al. (2010) compared with the dry season during 1998-1999, but higher compared with the rainy season in 1999. PAH sum in the Center and the SW reported by Guzmán-Torres et al. (2009) were similar to those described by Mugica et al. (2010a) during 2005-2006, but three times higher than those reported by Saldarriaga et al. (2008) for the SW during 2004. The NW of the city showed lower PAH concentrations during 2005-2006 (Mugica et al. 2010b) compared to PAH in the North during 2006-2007. PAH differences in space were also observed by Thornhill et al. (2008), where different primary emission sources resulted in different PAH emitted concentrations in PM₁₀. This spatial heterogeneity implies the importance of the primary emission combustion sources in each site and implies that PAH concentrations in PM₁₀ in a specific site can not be extrapolated to other sites. This is important since the development of effective control strategies for fine particulate air pollution abatement requires knowing the importance of the diverse sources that contribute to the particulate matter concentrations at ambient air monitoring sites (Atkinson & Lewis, 1974).

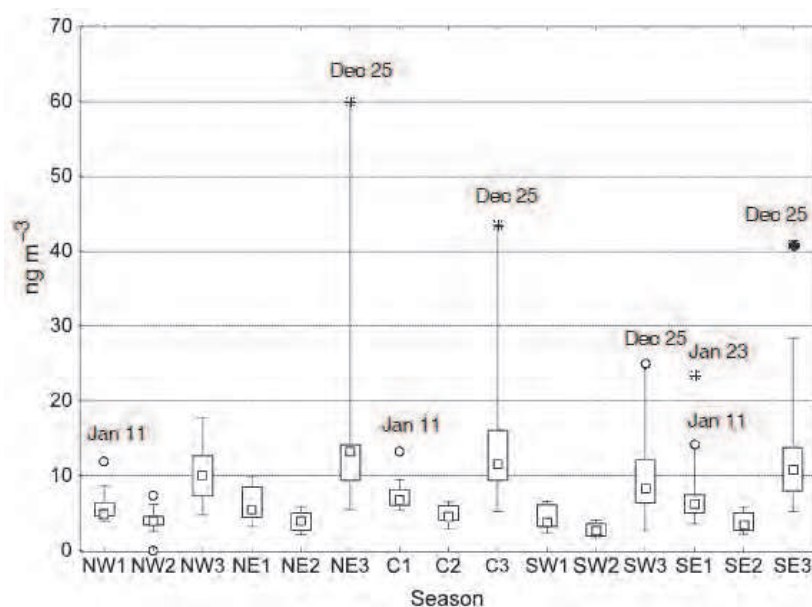


Fig. 5. Median (middle squares) seasonal heavy PAH sum (benzo[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, dibenzo[*a,c*]anthracene and benzo[*ghi*]perylene) mass concentrations of five sites around MCMA during 2006. Boxes – 25–75% and whiskers – 10th–90th percentiles, circles – outliers, asterisks – extremes values. 1 – Dry season 1 (January–April), 2 – Rainy season (May–October), 3 – Dry season 2 (November–December). Taken from Amador-Muñoz et al. (2011).

Stone et al. (2008) determined PAH, alkanes, hopanes, steranes, carboxylic acids and levoglucosane in PM_{2.5} in the North of MC during the MILAGRO campaign. Motor vehicles accounted for 49% of OC in the urban area and 32% on the periphery. The OC generated by biomass burning ranged from 5–26% at the urban site and 7–39% at the peripheral site. The remaining OC not related to primary sources showed a strong correlation with real-time water soluble organic carbon which was considered to be secondary in nature. Amador-Muñoz et al. (2011) determined PAH, nitro-PAH, n-alkanes and solvent extracted organic matter (SEOM) in

PM_{2.5} in five simultaneously sites in MC. Instead, a uniform distribution of PM_{2.5}, SEOM, biogenic n-alkanes (C₂₄-C₃₃) and nitro-PAH was observed in the MCMA regarding gravimetric mass concentration, while petrogenic n-alkanes (<C₂₃), fossil fuel combustion n-alkanes (23≤C_{max}≤26) and PAH (Fig. 5) showed mass heterogeneity in the MCMA. Spatial PAH heterogeneity across MCMA was observed as in the case of PAH in PM₁₀, suggesting again a significant impact of combustion primary sources in each site. These last authors also described that the highest mass concentrations of PAH occurred in the dry season with respect to the rainy season (Fig. 5). Bonfires and fireworks were probably responsible for extreme values of PAH. Benzo[ghi]perylene was again the most abundant PAH.

Table 2 shows a comparison of PAH concentrations in PM_{2.5} developed in MCMA. The most abundant light PAH were found in the NE zone, because it is known (Miguel et al., 1998) that this type of PAH are mainly emitted by diesel combustion, which suggests this source is a main generator in the area (Amador-Muñoz et al., 2011). The majority of the heavy PAH were more abundant in the Central zone, suggesting gasoline combustion as main source (Miguel et al., 1998). Regarding seasonal variation, there was greater concentration of PAH in PM_{2.5} in the dry-cold season. Concentrations quite similar to those PAH found by Stone et al. (2008) in the Northern zone (urban site) were observed with those in the NW and the NE reported by Amador-Muñoz et al. (2011).

| PAH | N ^{1a, *} | NE ^{1b, *} | NW ² | NE ² | C ² | SW ² | SE ² |
|-------------------------|--------------------|---------------------|-----------------|-----------------|----------------|-----------------|-----------------|
| Naphthalene | n.a. | n.a. | 107 | 588 | 151 | 96 | 89 |
| Acenaphthylene | n.a. | n.a. | 50 | 76 | 49 | 25 | 39 |
| Acenaphthene | n.a. | n.a. | 0 | 0 | 0 | 0 | 0 |
| Fluorene | n.a. | n.a. | 16 | 60 | 0 | 0 | 0 |
| Phenanthrene | n.a. | n.a. | 173 | 386 | 199 | 115 | 134 |
| Anthracene | n.a. | n.a. | 40 | 66 | 40 | 23 | 26 |
| Fluoranthene | n.a. | n.a. | 223 | 554 | 222 | 139 | 187 |
| Pyrene | n.a. | n.a. | 285 | 711 | 292 | 178 | 241 |
| Benzo[a]anthracene | n.a. | n.a. | 219 | 313 | 254 | 140 | 207 |
| Chrysene+Triphenylene | n.a. | n.a. | 598 | 883 | 662 | 391 | 477 |
| Benzo[b]fluoranthene | 572 | 475 | 576 | 548 | 764 | 402 | 601 |
| Benzo[k]fluoranthene | 487 | 317 | n.r. | n.r. | n.r. | n.r. | n.r. |
| Benzo[j+k]fluoranthenes | n.a. | n.a. | 486 | 506 | 534 | 347 | 517 |
| Benzo[e]pyrene | 597 | 438 | 313 | 383 | 474 | 275 | 408 |
| Benzo[a]pyrene | n.a. | n.a. | 380 | 404 | 455 | 265 | 452 |
| Perylene | n.a. | n.a. | 105 | 110 | 118 | 69 | 94 |
| Indeno[1,2,3-cd]pyrene | 475 | 353 | 500 | 477 | 690 | 408 | 608 |
| Dibenzo[a,c]anthracene | n.a. | n.a. | 38 | 53 | 38 | 23 | 50 |
| Dibenzo[a,h]anthracene | 110 | 97 | 63 | 60 | 73 | 46 | 94 |
| Benzo[ghi]perylene | 1108 | 548 | 1333 | 1229 | 1840 | 1119 | 1619 |

Table 2. Comparison of PAH mass concentrations (pg m⁻³) in PM_{2.5} at different sites in the MCMA.

n.a. – not analyzed, n.r. – not reported. * Values were updated to standard conditions (298 K, 1 atm), which represent ~ 21.5 % more than real values.

¹ Stone et al. (2008). ^a Urban zone, ^b Suburban zone. Average of the sampling days (17-30, March 2006). PM_{2.5} was collected with medium volume samplers on quartz fiber filters, during 12 h.

² Amador-Muñoz et al. (2011). Annual medians (January to December 2006). PM_{2.5} were collected with high volume samplers on glass fiber filters covered with Teflon during 24 h.

4.1.3 Nitro-PAH in PM₁₀ and in PM_{2.5}

In addition to PAH determination, another important class in terms of human health risk is their nitro derivatives by their mutagenic and carcinogenic properties mentioned earlier. In a PM₁₀ sampling carried out from February to April in 2004 in the SW of MC, Saldarriaga et al. (2008) found 9-nitroanthracene, indicating direct emission from diesel combustion, and heterogeneous nitrating reactions on sorbed particles, while 2-nitrofluoranthene, indicated atmospheric transformation. The total average concentration of PAH was 14 times greater than that of nitro-PAH, whereas the n-alkanes concentration was 17 times greater than that of PAH.

In an effort with researchers of Universidad Autónoma Metropolitana Unidad Azcapotzalco, we carried out a campaign to determine nitro-PAH in PM_{2.5} and in PM₁₀ sampled simultaneously (Valle-Hernández et al., 2010). The study was developed in three seasons from April 2006 to February 2007 in the North of MC. The analytical extraction and purification method for nitro-PAH was evaluated employing a standard reference with and without matrix, the former giving the best results. Eight PAH in PM₁₀ were quantified by GC-MS operating in the negative chemical ionization mode. Nitro-PAH sum ranged from 111 to 819 pg m⁻³, depending on the season. The greatest concentration was for 9-nitroanthracene, detected during the dry-cold season. This nitro-PAH showed greater concentrations than those found in the SW by Saldarriaga et al. (2008), while the 2-nitrofluoranthene was lower. This suggests more sources of diesel combustion in the North, whereas more secondary organic aerosol is present in the SW.

Table 3 shows the medians of nitro-PAH mass concentrations in PM_{2.5} during 2006 and early 2007 in different zones in MC. 2-Nitrofluoranthene (2-NFlt) and 9-Nitroanthracene (9-NAnt) appear to be among the most abundant nitro-PAH in PM_{2.5}. The North showed a higher mass of 9-NAnt with respect to the other sites, probably emitted from diesel combustion of heavy trucks (Feilberg et al., 2001) circulating in a major proportion in this area. 2-NFlt was the nitro-PAH with the highest concentration found in the Central zone, where the presence of this compound is exclusively attributed to atmospheric formation (Nielsen, 1984). At present, nitro-PAH have only been determined by our research group in the MCMA. Valle-Hernández et al. (2010) and Amador-Muñoz et al. (2011) have described their seasonal

| nitro-PAH | N ¹ | NW ² | NE ² | C ² | SW ² | SE ² |
|---------------------------|----------------|-----------------|-----------------|----------------|-----------------|-----------------|
| 9-Nitroanthracene | 45.7 | 36.8 | 36.0 | 35.7 | 27.7 | 35.8 |
| 9-Nitrophenanthrene | 13.7 | n.f. | n.f. | n.f. | n.f. | n.f. |
| 3-Nitrophenanthrene | 14.7 | n.f. | n.f. | n.f. | n.f. | n.f. |
| 2-Nitrofluoranthene | 41.7 | 52.8 | 59.4 | 67.4 | 47.8 | 52.9 |
| 3-Nitrofluoranthene | 3.1 | n.f. | n.f. | n.f. | n.f. | n.f. |
| 1-Nitropyrene | 10.9 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 7-Nitrobenzo[a]anthracene | 16.3 | 9.3 | 11.3 | 15.7 | 8.7 | 14.4 |
| 6-Nitrochrysene | 1.7 | n.f. | n.f. | n.f. | n.f. | n.f. |

Table 3. Comparison of nitro-PAH mass concentrations (pg m⁻³) in PM_{2.5} at different sites (urban zones) in MC. The values are adjusted to standard conditions (298 K, 1 atm), n.f. – not found, n.a. – not analyzed.

¹ Valle-Hernández et al. (2010). Medians of the sampling days (April 2006 to February 2007, twice per month). PM_{2.5} was collected with high volume samplers on quartz fiber filters during 24 h.
² Amador-Muñoz et al. (2011). Annual medians (January to December 2006). PM_{2.5} were collected with high volume samplers on glass fiber filters covered with Teflon during 24 h.

behavior classified in three periods: dry-warm, rainy and dry-cold. The highest concentrations of nitro-PAH in $PM_{2.5}$ were found during the dry-cold season and the lowest values corresponded to the rainy season in both studies. In general, quite similar concentrations in both studies of those similar nitro-PAH were found.

Annual median of nitro-PAH in PM_{10} and in $PM_{2.5}$ in the N of MC is depicted in Fig. 6 (Valle-Hernández et al., 2010). All nitro-PAH exhibited similar behaviors and concentrations between PM_{10} with respect to $PM_{2.5}$, suggesting that these compounds are mainly located in $PM_{2.5}$. One exception was for 9-NAnt with greater concentration and variability in PM_{10} , probably given by a mixing of primary and secondary origins (Bamford & Baker, 2003; Pitts et al., 1978).

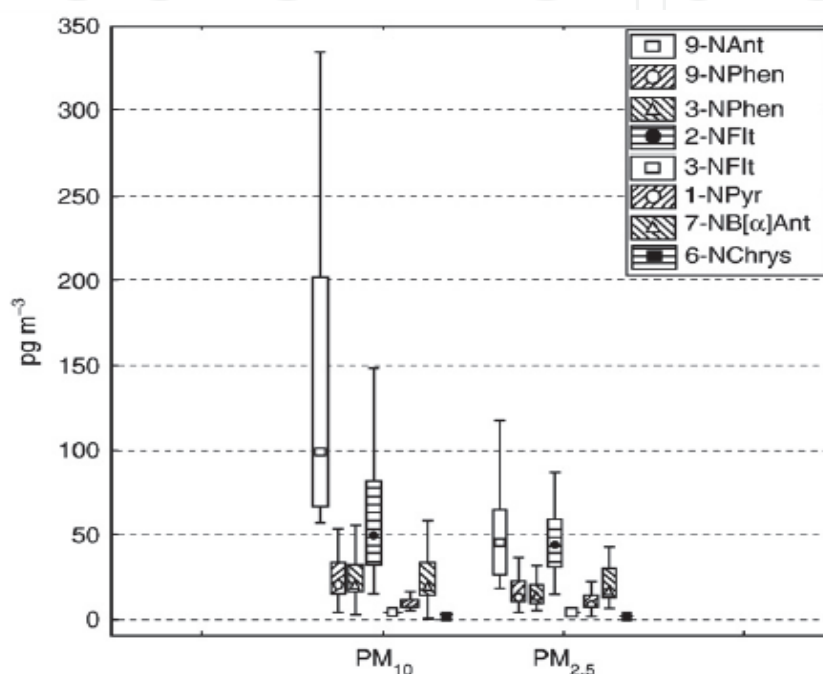


Fig. 6. Annual median concentrations (middle square), boxes 25–75% and whiskers 10th–90th percentiles of the nitro-PAH in PM_{10} and $PM_{2.5}$ during 2006–2007 at North of MC. Taken from Valle-Hernández et al. (2010).

Analytical methodology optimization is another important activity developed by the EMG focused to reduce the uncertainty and increase the efficiency in the measurements. A recent purification procedure based on solid phase extraction was proposed for determining oxy-PAH from PAH and n-alkanes in $PM_{2.5}$ (Murillo-Tovar et al., 2010). Multivariate parameters were adjusted on a standard mixture, and on a different amount of solvent extracted organic matter (SEOM) spiked with pure standard mixture solutions. Cyanopropylsilyl-bonded phase material was the selected stationary phase. Oxy-PAH was totally separated from n-alkanes and PAH by applying different SEOM pooled masses. Fig. 7 shows an example of the separation obtained. Mean recoveries \pm confidence intervals (95%) for n-alkanes ranged from $53 \pm 17\%$ (n-tetracontane) to $101 \pm 11\%$ (n-hexacosane); for PAH from $58 \pm 5\%$ (phenanthrene) to $85 \pm 9\%$ (benzo[k]fluoranthene); and for oxy-PAH from $68 \pm 12\%$ (9,10-dihydrobenzo[a]pyren-7(8H)one) to $108 \pm 9\%$ (1,2-benzopyrone). This method is an efficient fractionation procedure to apply to oxy-PAH, PAH and n-alkanes in complex organic mixtures extracted from $PM_{2.5}$.

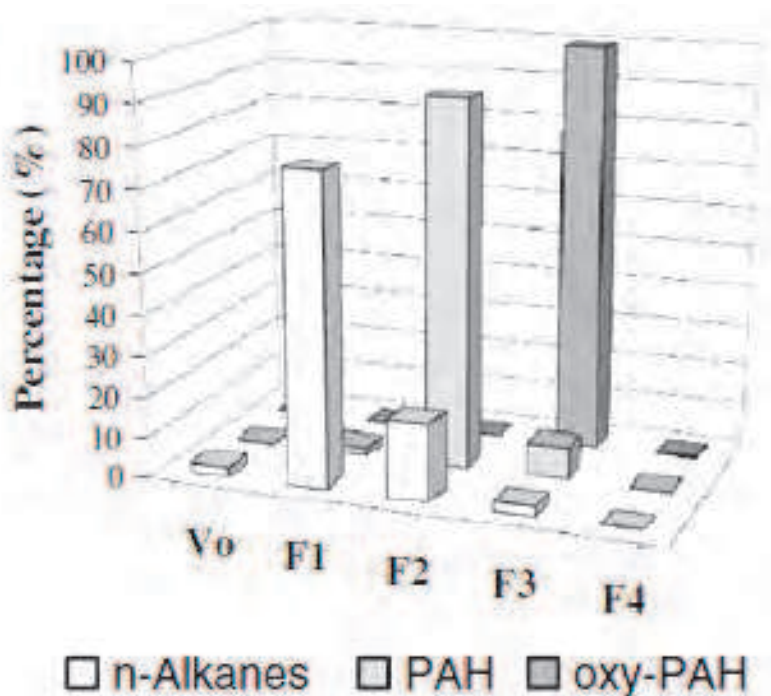


Fig. 7. Percentage distributions (mass per fraction) of organic classes in a real sample by applying 8.5 mg of SEOM pooled mass. Vo – Death volume, F1 to F4 – Organic fractions. Taken from Murillo-Tovar et al. (2010).

4.2 Toxic effects and human health risk

New methods have been developed to identify mutagens related to potential carcinogens more efficiently (Lewtas, 1988) in airborne complex mixtures combining bioassay directed fractionation and chemical characterization (Schuetzle & Lewtas, 1986). Several Environmental Agencies around the world have tried to regulate the air particle concentrations in a defined period of time; however, there are no threshold values under which humans are protected. The permissible limits are restricted to mass concentrations and should be important to relate those compounds with mutagenic and carcinogenic effects.

Airborne particles are formed by complex mixtures of hundreds of compounds, some of which are extracted organic matter (EOM) potentially mutagenic, cytotoxic and carcinogenic (Lewtas, 1993; Villalobos-Pietrini et al., 2006, 2007). For this reason special attention has been applied in assays to evaluate the genotoxicity produced by these pollutants. The *Salmonella* assay (Ames test) has been a convenient and usable test to compare genotoxic activity. Pitts et al. (1975) were the first authors who treated *Salmonella typhimurium* with EOM adsorbed airborne particles, now recognized as a bioassay of the reference Ames test to detect a wide range of chemicals that can produce genetic damage leading to gene mutation (Mortelmans & Zieger, 2000) in the histidine operon of the mentioned bacteria that revert to wild type condition (Ames et al., 1973). When an agent induces a reversion in the mentioned operon, then the bacteria can synthesize the amino acid and can reproduce itself, when it is more mutagenic, the revertant cells increase. As the bacteria cannot metabolize some chemicals, it is useful to include in the test the metabolic activation of mammals known as enzymatic fraction S9 (Ames et al., 1975).

The use of some strains allows recognizing whether the effect is in a direct acting mutation (without S9) or if it includes the mammal metabolism (with S9) by indirect acting mutagens. Therefore, it is important to choose the strains based on the purpose of the study. When rural and urban monitoring sites are studied during different seasons in the year, the plate incorporation assay with TA98 and TA100 furnishes more reproducible and comparative results (Claxton et al., 2004); when the effect of series of strains are compared, the strains YG are more sensitive to mutagenic nitroaromatic than the TA (Claxton et al., 2001). When the sample amount is very small, another important change in the technique is the microsuspension assay that is more sensitive than the plate incorporation assay, this last one differing in the increment of the number of bacteria and in the time of contact to them (Kado et al., 1983, 1986).

Biological effects of organic matter *in vivo* and *in vitro* have been scarcely developed in Mexico. Recent studies have shown different responses as a function of their own biological mechanisms. In a study carried out in SW of MC, Villalobos-Pietrini et al. (2006) observed that the mutagenicity of strain TA98+S9 did not correlate with the monthly concentration of PM₁₀ and of EOM, while strains TA98-S9 and YG1021 correlated well, which suggests that there exist different emission sources of direct and indirect pollutants. The same organic compounds selectively separated in less complex groups (Fig. 8a, b), means fractionating the PM₁₀ in fractions of increasing polarity: 1) hexane; 2) hexane-methylene chloride (6:4); 3) methylene chloride; and 4) methanol. In 77 % of the cases, mutagenic activity was higher in the sum of fractions than in their EOM (Villalobos-Pietrini et al., 2007). The same study revealed that the moderately polar and the polar fractions induced higher mutagenicity in relation to less polar fractions, and perhaps this effect depends upon mass concentration of organic matter; these polar fractions are correlated with thermal inversions in the dry-cold season (Villalobos-Pietrini et al., 2007).

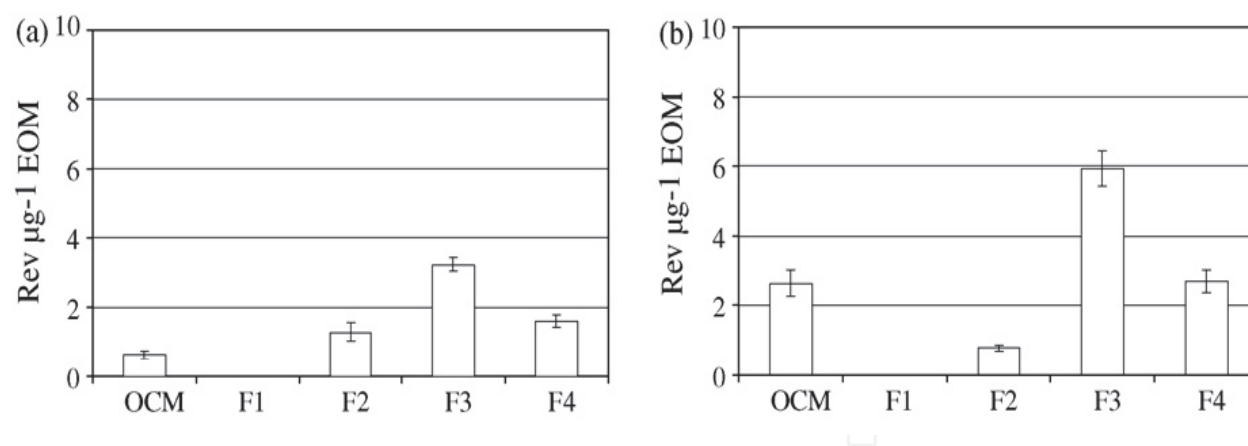


Fig. 8. Mutagenic potency of extracted organic matter (EOM) of January 1998 in the organic complex mixture (OCM) and in its fractions; (a) with TA98 + S9 and (b) with YG1021. Taken from Villalobos-Pietrini et al. (2007).

Several studies have been made using the sister chromatid exchange (SCE) which is a sensitive biomarker to detect genotoxicity. It represents symmetric change between homologous loci of replication products. SCE occur without loss of DNA and do not change the morphology of chromosome. This assay is based on the incorporation of the 5-bromodeoxyuridine (BrdU), an analog of the DNA base thymidine inside the DNA cell that replicates twice (Latt et al., 1981). In addition to SCE analysis, the BrdU differential staining

method can be used to assess the effect of the compounds in cell replication proliferation kinetics and in the replication index in human blood culture as a useful tool in genotoxicity testing. In this way, Calderón-Segura et al. (2004) assayed the EOM from PM₁₀ collected in three seasons in MC to evaluate SCE (genotoxicity), mitotic index (cytotoxicity) and replication index (cytokinetic) in human lymphocyte cultures. The SCE obtained was dose-dependent with the greatest effect in response to indirect acting mutagens. The direct acting mutagens produced significant effects as well, but in lower frequency. The results show that the EOM effect also depended on the weather because in April (dry-warm), August (rainy-warm) and November (dry-cold) different responses were obtained. The lowest was observed in August and the highest in November, both of the direct (without S9) and indirect-acting mutagens (with S9) due to the fact that the content of PAH was different, possibly because the heavy rains in August reduce the amount of EOM and in November frequent thermal inversions tend to prevent the dispersion of contaminants, because of the atmospheric stability favoring photochemical reactions, among other reasons. Cytokinetics showed a decrease as the concentration of EOM increased independently of bioactivation and weather. Cytotoxicity occurred when higher concentrations of EOM were used.

Another useful assay to evaluate the effect of the compounds on the DNA is alkaline single cell gel electrophoresis, also called comet assay. This is a rapid and sensitive technique to analyze the damage to the DNA in individual cells on alkaline conditions (pH > 13) that detects the effects of different compounds on DNA at the individual cell level. It is based on the migration of DNA in an electric field, and its displacement from the nucleus could be used as an indicator of DNA damage (Östling & Johanson, 1984); the alkaline version is capable of detecting DNA single-strand breaks and alkali-labile sites. The name refers to the fact that the head has no DNA damage while the tail is the fragmented DNA. Rojas et al. (2000) used the comet assay in exfoliated tear duct epithelial cells of young adults, residents of the Northern and the Southern areas of MCMA; individuals in the last area showed the highest frequencies of DNA damage by the environmental pollution exposure. Gutiérrez-Castillo et al. (2006) made two fractions with the particle matter (PM), one a water soluble and the other an organic soluble. They treated the human cell line lung epithelial with both extracts and applied to them the alkaline single cell gel electrophoresis, concluding that more DNA damage was induced by the extracts obtained of the water soluble fraction, and that PM composition was more important than PM mass for producing genotoxicity.

Another genotoxic damage biomarker is the micronucleus assay that is based on chromosomal effects produced by the EOM that impact the chromosomes and produce fragments (clastogenic effect) or alter complete chromosomes (aneugenic effect) that are not included in the main nuclei of the daughter cells during mitosis; they remain in the cytoplasm and are present in the interphase cell as small nuclei. Roubisek et al. (2007) exposed human alveolar epithelial cells and found significant correlation between the induction of micronuclei and the presence of PAH, obtaining higher frequencies of micronuclei in the water-soluble industrial extracts than in residential extracts.

An increase in morbidity and mortality was associated with the exposure to urban PM₁₀ obtained in three zones of the MCMA (North, Center and South), which were cytotoxic, genotoxic and proinflammatory (Alfaro-Moreno et al., 2002, 2007; García-Cuellar et al., 2002; Osornio-Vargas et al., 2003;). Montiel-Dávalos et al. (2010) showed that oxidative stress and apoptosis (programmed cellular death) are induced in human endothelial cells exposed to MC particulate matter. PM₁₀ induced impairment of the antioxidant defense systems, without changes in cell viability (Chirino et al., 2010).

Furthermore, this has been described in children chronically exposed to complex mixtures of air pollutants in the SW of urban areas of MC, producing respiratory damage, as well as systemic and endothelial inflammation (Calderón-Garcidueñas et al., 2006), also residents of MC who are exposed to strong pollution present neuroinflammation and neurodegeneration, suggesting that the brain is affected by pollutants (Calderón-Garcidueñas et al., 2010). Barraza-Villarreal et al. (2008) show that the exposure to PM_{2.5} provokes airway inflammation and decrement of lung function, and Holguin et al. (2003) observed that the concentrations of PM_{2.5} are related with cardiac dysfunction especially in elderly persons in MCMA.

Another research related to organic matter of airborne particles refers to the content of PAH, which recognizes how the carcinogenic and mutagenic potential compounds are emitted by incomplete combustion and vegetation burning. In the MCMA, the most abundant PAH in the fine particulate matter are usually benzo[ghi]perylene, coronene and indeno[1,2,3-cd]pyrene with indirect acting mutagenic activity, and the most abundant nitro PAH are 2-nitrofluoranthene and 9-nitroanthracene (Amador-Muñoz et al., 2011), with direct acting mutagenic effects (Villalobos-Pietrini et al., 2007). Due to their lipophilic characteristics, the PAH may penetrate the cell membrane and change its properties inducing their effects through activation of aryl hydrocarbon receptors (AhR) and of cytochromes CYP that metabolize PAH, which leads to ROS formation and reactive metabolites that can covalently bind to nucleophilic sites on macromolecules and alter signaling pathways that are involved in cell survival proliferation, inflammatory response and cell death (Schwarze et al., 2010). This seems to cause changes in ion transport, in intracellular pH as well as lysosomal breakage. Along with PAH, other compounds (as transition metals and some quinones) have the potential to interact with airway epithelial cells and macrophages to generate ROS which have been linked to respiratory inflammation and other adverse effects (Cho et al., 2005; Xia et al., 2004).

In order to reduce the human health risk caused by airborne pollutants, researchers must continue studies on their chemical characterization, distribution, formation and sources emission, as well as on their effects such as complex mixture and their fraction, so as to detect compounds that cause damage and discover their mechanism of action.

5. Conclusions

Organic aerosol in the atmosphere is composed by hundreds of organics from primary or secondary origin. The knowledge of their composition is of relevant importance due to their impact on climate, chemical and physical processes, modeling and human health. New analytical techniques have been recently developed to identify and quantify the organics in the complex mixtures, where mass spectrometry has been the most employed. Multivariate statistical techniques are the most useful methods to classify pollutant sources. Given their mutagenic and carcinogenic effects, PAH have been the organic compounds most studied in the MCMA. They have been determined mostly in particle phase showing spatial heterogeneity around MCMA in both on-real and off-real time measurements. Benzo[ghi]perylene has been the most abundant PAH determined in all studies and it must be considered for health studies due to the indirect correlation with in vitro ROS formation. The cold dry-season (November-February) contained the highest organic pollutant concentrations, while the rainy season (May-October) showed the lowest. Indirect mutagenic activities in the Ames test have showed significant correlation with PAH when

they are not mixed with other compounds, suggesting a greater risk for those people exposed to direct emissions rich in these compounds. Results of the Environmental Mutagenesis Group (EMG) suggest heterogeneity in PAH concentrations around MCMA, indicating higher human health risk for those living in Downtown of MC, based on the higher mass per cubic meter of inhaled air containing carcinogenic PAH. Different oxidation degrees of the organic matter were observed in the MCMA, indicating aging of the aerosol from the NE to the SW.

6. Future research

Organic aerosol on climate, atmospheric chemistry and the impact on human health are uncertain and scarcely known. Therefore, more comprehensive data on spatial and seasonal distribution is needed to investigate further the regional nature of airborne particles and their organic composition, so as to support the development of strategies for reducing ambient concentrations. Although off-line measurements techniques are the most employed to elucidate the specific organic aerosol composition, the components are dependent on the details of the analytical techniques used, and both positive and negative artifacts can occur during sampling (Turpin et al., 2000), thus indicating that and more research is needed in this field.

Studies on PAH determination in MCMA should be included in regulations in order to properly establish air quality standards according to their atmospheric conditions. This is why part of our future research will be focused on obtaining emissions due to the introduction of new car technologies (Jazcilevich et al., 2011), and the use of mixtures of ethanol and bio-diesel in vehicles, an international trend that Mexico might follow. At present, secondary organic aerosols are underestimated by the current models due to the extreme chemical complexity which has prevented the precise measurement and prediction of the oxidation process associated with the formation and evolution of atmospheric organic aerosol. Further studies are needed to improve estimations and to understand the relative importance of anthropic versus natural aerosol precursors. Analytical methodology optimization to determine organic aerosols is a continuous challenge to evaluate new analytical methodologies increasing precision and efficiency, and decreasing uncertainty in the measurements of the target compounds in the complex mixture of the organic aerosol. These methods are developed under the criteria of “green chemistry” to reduce the consumption of materials and time and therefore, to reduce waste and energy. New approaches are being developed to bio-direct the effect of specific organic pollutants on specific cultures of epithelial cells, human lymphocytes and bacterial assays, all of them for explaining different action mechanisms to know the risk of people exposed living mainly in urban centers.

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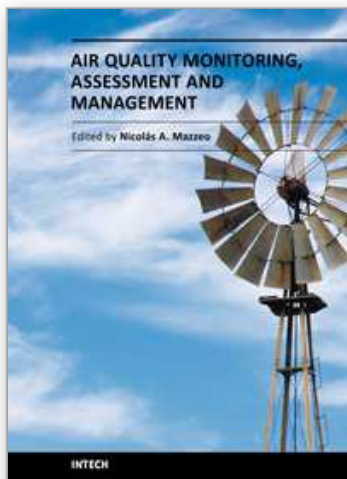
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Human beings need to breathe oxygen diluted in certain quantity of inert gas for living. In the atmosphere, there is a gas mixture of, mainly, oxygen and nitrogen, in appropriate proportions. However, the air also contains other gases, vapours and aerosols that humans incorporate when breathing and whose composition and concentration vary spatially. Some of these are physiologically inert. Air pollution has become a problem of major concern in the last few decades as it has caused negative effects on human health, nature and properties. This book presents the results of research studies carried out by international researchers in seventeen chapters which can be grouped into two main sections: a) air quality monitoring and b) air quality assessment and management, and serves as a source of material for all those involved in the field, whether as a student, scientific researcher, industrialist, consultant, or government agency with responsibility in this area.

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