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Air Pollution in an Urban Area of Mexico: Sources of Emission (Vehicular, Natural, Industrial, and Brick Production)

Valeria Ojeda-Castillo, Sergio Alonso-Romero,
Leonel Hernández-Mena,
Paz Elizabeth Álvarez-Chávez and
Jorge del Real-Olvera

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Abstract

In recent years, the interest in aerosol particles has increased due to concerns about the effects on human health. The study of the chemical characterization (organic matter, sulfates, nitrates, and black carbon) has improved the knowledge about the negative contribution of chemicals to the environment. The identification of secondary processes (from pollutants such as SO₂, NO_x, and PAHs) and their role when combined with environmental factors such as humidity, solar radiation, and temperature are also of interest. With this background, this chapter seeks to highlight the most recent findings on the chemical composition of aerosol particles in the ambient air of one of the main cities of Mexico: the Metropolitan Area of Guadalajara. This megalopolis has almost 60% of the population of the Jalisco state, approximately 2.2 million vehicles and an extensive artisan brick production. Furthermore, due to its geographical position, it experiences frequent episodes of thermal inversion and exposition to high levels of solar radiation, mainly during the first half of the year.

Keywords: emissions, particle composition, sources, secondary formation, human health

1. Introduction

This chapter briefly describes the results about specific studies of the concentration of particulate pollutants in ambient air and on the presence of several associated chemical species

in the Guadalajara Metropolitan Area (GMA), the second most important city of Mexico due to its territorial extension and the size of its population. The particulate material implies the coexistence of hundreds and even thousands of chemical compounds with different physical, chemical, and biological properties; responsible in part for the numerous adverse effects on the environment and the health of the human population. These effects are the main reasons that motivate the study of particles in this and other cities of the world. Specifically, those particles less than or equal to 2.5 microns ($PM_{2.5}$) are considered as a criterion contaminant since they determine the quality of the ambient air. Therefore, the information presented here focuses mainly on data of $PM_{2.5}$ concentrations and chemical components, such as trace metals and toxic elements, anions and cations, black carbon, and polycyclic aromatic hydrocarbons (PAHs), oxy-PAHs, and quinones. However, only a few studies show results about particles of other sizes, such as those smaller than or equal to 10 μm (PM_{10}), particles less than or equal to 1 micron (PM_1) (which are not regulated in Mexico), and the chemical composition of organic compounds such as PAHs and derived quinones. Moreover, the study and analysis of chemical species could insinuate the potential sources of emission (direct or indirect, natural or anthropogenic) and also indicate the existence of processes of secondary formation of particles in the ambient air (as in the case of nitrates, sulfates, and quinones). Studies on the chemical characterization of particles in the GMA have been carried out mainly in two sites inside of the city, Centro and Miravalle. In this context, this chapter addresses the most significant findings regarding the knowledge of GMA particles in the ambient air, as well as some aspects of its chemical composition and how the latter may suggest its origin.

2. Aerosols

2.1. Definition and properties

Aerosols are a collection of solid or liquid particles suspended in a gas (also called particulate material and defined by the acronym PM). The term aerosol refers to “aerosol particles” without considering the suspension gas [1]. The aerosols formed by particles of different sizes (among them TSP, PM_{10} , $PM_{2.5}$, and PM_1 , as well as ultrafine particles), together with other gases in the ambient air, in some cases are considered criteria pollutants and define the quality of the air in a city or town [2].

The aerosols come from numerous natural and anthropogenic sources, such as the burning of biomass, incomplete combustion of fossil fuels, volcanic eruptions, soil and mineral dust, sea salt and biological materials (plant fragments, microorganisms, pollen, etc.). In addition, aerosols can be formed in the atmosphere (secondary aerosol) by the conversion from a gas to particles (e.g., through mechanisms such as nucleation and condensation) and by heterogeneous and multiphase chemical reactions [3].

Among the properties of aerosols that negatively influence the health of the human population are the aerodynamic diameter and the chemical composition of the particles [4]. The size of the PM ranges from micrometer to nanometer, and those with a diameter smaller than 10 μm (PM_{10}) could enter the respiratory tract reaching the lungs.

The chemical composition of the particles is extremely complex and has a wide range of chemical species (inorganic acids and salts, metals, water, and a mixture of organic compounds of low volatility) in variable concentrations. Given that coarse, fine, and ultrafine particles are generated through different processes, it is expected that each of these groups of PM has a unique composition of chemical species, which allows establishing inferences about the sources and training processes. Because the chemical composition of PMs has adverse environmental and human health effects, research is still underway intensively to clarify the molecular composition of PM chemical species [5].

As an illustrative example, typical elements found in the Earth's crust may contribute to the chemical composition of coarse particles [6]. Sulfates (derived from SO_2 gas) and organic compounds are prominent compounds present in ultrafine particles due to their formation by homogeneous nucleation. In addition to inorganic species such as nitrates (derived from NO_x) and ammonium, the chemical composition of fine particles also includes sulfates and organic polar species, obtained from the coagulation of ultrafine particles. The formation of fine particles through the combustion and condensation processes of low volatility vapors also results in particular combustion products such as organic carbon (between 20 and 90% of the mass of particles in the troposphere [7]), elemental carbon, and traces of metals. In this way, these two properties together cause particles to serve as carriers of toxic substances into the body, a situation that associates them with different health problems in human populations around the world.

It should be mentioned that the physical and chemical diversity of PM particles manifests itself in different ways. The particle sizes vary in different orders of magnitude, which strongly influences the life of the particles in the atmosphere and therefore, in the spatial extent of their influence. The shape and morphology of the particles are also highly variable and may comprise spheres, crystalline, or irregular fragments, needles, agglomerates, and dendritic entities. The individual particles may be chemically uniform or contain chemically different surrounding and nuclear materials, while a set of particles may comprise similar particles or a diversity of geometries [8].

2.2. Human health and environmental effects

The PM has a significant adverse impact on human health. The World Health Organization (WHO) estimates that in 2016, 95% of the world's population lived in places where pollution levels are higher than the standards of health protection over air quality, that the ambient air pollution in cities and rural areas caused 4.1 million deaths worldwide, and the loss of 106 million years of human disability that same year [9]. Since PMs are a critical component of the air whose presence defines its quality, the International Agency for Research on Cancer (IARC) has classified PMs in its Group 1 (carcinogenic to humans), together with agents such as arsenic and asbestos [10].

Recent investigations have reported that exposure to $\text{PM}_{2.5}$ may also contribute to the incidence and development of diabetes mellitus, premature birth, low birth weight, and post-neonatal infant mortality [11]; moreover, low neurodevelopment [12, 13] and the diagnosis of autism [14].

About the environmental impacts, the low visibility (an optical indicator of air quality) is attributed mainly to the dispersion and absorption of visible light by particles in the atmosphere [15] with diameters mostly between 0.1 and 1.0 μm . The fine particles scatter visible light much more effectively per unit mass since their size is comparable to the wavelength of visible light [16]. Additionally, damage to ecosystems can also be mentioned that can result in the reduction of biodiversity and loss of environmental goods and services [17].

3. Studies of aerosol in the GMA

3.1. Concentration of PM

The average concentrations of $\text{PM}_{2.5}$ in Centro and Miravalle exceeded the annual limits during the periods of January–December 2007, January–June 2008, and April 2009–January 2010 (as a whole the three periods represent 27 months of sampling, justifying its comparison with the annual limit of the standard of $15 \mu\text{g m}^{-3}$). In Miravalle, concentrations of $\text{PM}_{2.5}$ were higher during 2007, probably due to higher industrial activity and the natural barriers in that area that prevent the evacuation of pollutants; in Centro and Miravalle were between 2.9 and 3.5 times higher than the annual limit of the standard, respectively. At the Miravalle site, the higher levels of PM were evident in the dry seasons (warm and cold) when compared to the ones measured in the rainy season. In general, during the cold period, particle levels are increased by low temperatures, unfavorable conditions for the dispersion of pollutants, by the increase in the consumption of fossil fuels, and because the conversion of gases to particles is favored [18]. The lowest temperatures were recorded in February 2008; they occurred particularly in Miravalle, and it is likely that the processes already mentioned were related to the high concentrations of $\text{PM}_{2.5}$.

Other studies considered $\text{PM}_{2.5}$ measurements at shorter sampling periods and the values contrasted against the standard limit for a period of 24 h ($65 \mu\text{g m}^{-3}$, [19]). Only sites like Miravalle in May–June 2009, and Centro and Tlaquepaque in March–May 2014, showed concentrations close to this limit, but not exceeding it. It should be mentioned that the levels of this same particle size in the studies carried out at the end of 2014 were compared with the 24 h standard of $45 \mu\text{g m}^{-3}$ [19] without exceeding the limit in any case (**Figure 1**).

PM_{10} levels in the area of the Environmental Fragility Polygon (POFA, by the acronym in Spanish) exceeded 1.6 times the standard for 24 h ($120 \mu\text{g m}^{-3}$), which suggests a risk for the health of the local population. Likewise, concentrations of PM_{10} were 4–10 times higher than those of $\text{PM}_{2.5}$ (in their daily levels), indicating the domain of emission sources of coarse particles. The low correlation between fine and coarse particles suggests different emission sources (**Table 1**).

Another environmental factor, the rain, contributes to the temporal variation of the particles, which are grounded by direct drag or because air humidity induces their growth in size and precipitation. Some hygroscopic compounds favor this phenomenon in the particles, such as

Figure 1. Map of monitoring stations (gray circles) into GMA, the red circles indicate the sampling sites.

sulfates and nitrates [33]. For the 2009–2010 period, Centro and Miravalle sites did not show differences in their particle concentrations; only in Miravalle were observed higher levels during the cold dry season against the rainy season.

Other studies considered PM_{2.5} measurements at shorter sampling periods and the values contrasted against the standard limit for a period of 24 h (65 µg m⁻³, [34]). Only sites like Miravalle in May–June 2009, and Centro and Tlaquepaque in March–May 2014, showed concentrations close to this limit, but not exceeding it. It should be mentioned that the levels of this same particle size in the studies carried out at the end of 2014 were compared with the 24 h standard of 45 µg m⁻³ [19] without exceeding the limit in any case.

PM₁₀ levels in the area of the Environmental Fragility Polygon (POFA, by the acronym in Spanish) exceeded 1.6 times the standard for 24 h (120 µg m⁻³), which suggests a risk for the health of the local population. Likewise, concentrations of PM₁₀ were 4–10 times higher than those of PM_{2.5} (in their daily levels), indicating the domain of emission sources of coarse particles. The low correlation between fine and coarse particles suggests different emission sources.

Regarding PM₁ levels, there is no Mexican regulation. It is impossible to conclude about the impacts as done before. However, Centro and Tlaquepaque sites seem to have equal PM₁ concentrations, despite the characteristics of each of them concerning the types of emission sources, so that further studies on this particle size will be needed in other parts of the city to establish relationships. It is important to note that the concentrations of PM₁ are recent and the first for this type of pollutants in the GMA.

Sampling period	Sites	Size	Average ($\mu\text{g m}^{-3}$)	Chemical compounds	NOM-025-SSA1 1993 and 2014
Jan–Dec, 2007	Centro	PM _{2.5}	44.10	Heavy metals and toxic elements[20]; anions & cations [21]; black carbon** [22]	
	Miravalle		52.80		
Jan–Dec, 2008	Centro	PM _{2.5}	59.09	Anions & cations [23]; heavy metals and toxic elements [22], black carbon*** [24]	
	Miravalle		81.36		
May 25th–June 6th, 2009	Centro	PM _{2.5}	39.30	Heavy metals and toxic elements; anions & cations [25].	NOM-025-SSA1-1993
	Miravalle		58.00		
	Centro	PM _{2.5}	21.00	Heavy metals and toxic elements; anions & cations; black carbon [26]	PM ₁₀
	Miravalle		37.00		120 $\mu\text{g m}^{-3}$ (24 h)
	AUG		21.00		50 $\mu\text{g m}^{-3}$ (annual)
	Centro	PM ₁₀	46.00		PM _{2.5}
	Miravalle		79.00		65 $\mu\text{g m}^{-3}$ (24 h)
	AUG		43.00		15 $\mu\text{g m}^{-3}$ (annual)
	Centro	PM _{2.5}	33.00 ^{1,2}	Oxy-PAHs [27]	NOM-025-SSA1-2014
	Miravalle		45.00 ^{1,2}		
Apr 2009–Jan 2010	Centro	PM _{2.5}	33.00 ^{1,2}	Oxy-PAHs [27]	PM ₁₀
	Miravalle		45.00 ^{1,2}		75 $\mu\text{g m}^{-3}$ (24 h)
Apr 6th–18th, 2013	POFA*	PM ₁₀	187.83	Anions & cations**** [28]	
		PM _{2.5}	29.33		
Mar–May, 2014	Centro	PM _{2.5}	57.07 ^{1,2}	PAHs & quinones [29, 30]	
July–Sep, 2014	Tlaquepaque		61.68 ^{1,2}		
	Centro		28.97 ^{1,2}		
	Las Águilas		28.23 ^{1,2}		
Aug 24th–30th, 2014	Oblatos	PM _{2.5}	22.67	Black carbon & VOCs [31]	
	Loma Dorada		15.67		
	Las Pintas		30.00		
	Las Águilas		17.33		
	Centro		17.00		
Apr–June, 2015	Centro	PM ₁	30.92 ²	PAHs & quinones [32]	
	Tlaquepaque		21.80 ²		

¹Corresponds to the medians of the sampling periods.²in ng m⁻³.

*Acronym in Spanish.

**For this study, the sampling sites were Centro and CIATEJ.

***Corresponds to the period of January–August, 2008.

****The chemical species mentioned were only determined in PM₁₀.**Table 1.** GMA aerosols research.

3.2. Heavy metals and toxic elements

The objective of these studies was also to generate reliable information about the possible sources of emission into the atmosphere, essential to establish actions that could reduce current levels of pollution in the ambient air and to even be able to estimate the degree of exposure of the human population. From the study of $PM_{2.5}$ (2007) and its elemental composition in Centro and Miravalle, emission sources were established through the estimation of the enrichment factors (EF).

The EF must be understood as a relation of the elements of interest with an abundant element of the soil (usually Fe and K), but also present in the particles. An $EF > 5$ suggests an anthropogenic source (different to the geological or natural origin). In Centro and Miravalle, Pb, Cd, Cr, Cu, Mo, Sb, Se, Tl, and Zn, as well as Ni and V in Centro had high FE, suggesting that they came from anthropogenic sources. On the other hand, Co, Fe, Mg, Ca, Mn, Sr, and Ti, clearly showed evidence from resuspension of dust either by the winds or by vehicular traffic (natural origin).

For the study of January–June 2008, the most abundant elements in both sites were Fe, Ti, Zn, Mg, and Pb. Fe, Ti, and Mg showed FE values that indicate a geological origin, while Zn and Pb probably are incorporated into the atmosphere by vehicle emissions and the use of these elements in non-ferrous alloys [35, 36]. The elemental composition profile of this study was related to the $PM_{2.5}$ elementary profiles of the international USEPA SPECIATE database (version 4.2). This database gathers scientific data from the profiles of specific particle sources. The profiles of Miravalle and Centro coincided with the profiles of Paved Road Dust (PRD), Diesel Exhaust (DE) and industrial soil (IS) ($r^2 = 94\%$, $r^2 = 72\%$, $r^2 = 68\%$, and $r^2 = 89\%$, $r^2 = 75\%$, $r^2 = 66\%$, respectively). Miravalle, in addition to the high industrial activity, has an intense flow of heavy vehicles which can be the origin of the resuspension of particles, phenomenon increased by large land areas without vegetation during the dry-season months. In Centro, the coincidence with the profiles of PRD and IS could be understood by the phenomenon of particle resuspension, or by the transport of emissions from nearby places with some industrial activity. In both sites, the DE profile was influenced by public transportation that works with diesel.

During 2009, some trends were consistent with those observed in 2008 regarding the abundance of those elements related to $PM_{2.5}$. It is highlighted that the Fe contributed 60 and 72% to the total elemental mass in Centro and Miravalle, respectively. In this way, it can be seen how different emission sources, whether natural or anthropogenic, could affect the composition of the $PM_{2.5}$ particles, and at the same time give indications of the specific emission sources.

3.3. Anions and cations

From the study in 2009, sulfate, nitrate, and ammonium were the more abundant compounds in Centro and Miravalle; sulfate and calcium showed high concentrations in Miravalle. In the case of sulfate, this is a derivate from SO_2 which comes from direct industrial emissions and the burning of fossil fuels with sulfur content. While nitrates and ammonium are formed from NO_x and NH_3 (ammonia), the latter gas is emitted mainly by the vehicle fleet that uses fuels such as gasoline and diesel in the GMA [37, 38]. These results suggest that the relatively constant concentrations of sulfate and nitrate in both sites during the year are because the levels emitted from parent gases are similar. For sulfates during winter, for example, the precursor gas is at high concentrations, while during the summer, the high temperature and high solar

radiation favor the oxidation of the precursor and increase the formation of sulfate [39]. This study was complemented by an ion balance, which established the existence of neutralization processes between the chemical species of the particles. For Centro, the presence of slightly acidic particles was determined, while in Miravalle, the particles showed an alkaline nature. The acid form of sulfates can influence the bioavailability of some metals, increase the toxicity of the particles [40], augment the adsorption of compounds into the particles, or create hygroscopic environments in them, all of which favor the solubility of some gases, promoting that they can reach deep areas of the respiratory tract [41], increasing the deposition of toxic compounds in the lungs. In the case of alkalinity, the potential effects on human health from exposure to particles with this property are now not very clear [42].

On the other hand, during 2008, sulfate, nitrate, and ammonium compounds showed the highest levels, without differences between sites, suggesting sources and formation processes in common, particularly in the southwest of the GMA. In Centro, the ion mass represented 46% of the mass of the $PM_{2.5}$, while in Miravalle, they did not exceed 28%. Studies like [43] indicate that the mass of these three ion species contributed with 40% and up to 65% to the mass of $PM_{2.5}$. The results on the contribution of the major inorganic ions to $PM_{2.5}$ can serve as a basis for establishing the connection between fine particles and possible adverse impacts on human health.

The short study on ion species also in 2009 in the two sites mentioned above, coincide in sulfate, nitrate, and ammonium as those of higher abundance in the previous works, but also highlight the presence of calcium and potassium. An impressive result was to find higher levels of nitrates concerning sulfates and ammonium. In Miravalle, nitrate represented 68% of the mass of total ions, while in Centro it was 57%. The abundance of these ions shows the critical role that secondary sources have in the formation of fine particles.

The last study about species of ions and particles (PM_{10}) was carried out on three different sites within the POFA area (on specific days of April 2013) [28]. In this area pollution problems are recurrent in the soil, water, and air because it has changed land use, environmental deterioration, loss of its original fauna and flora. The low air quality due to particles, ozone, and the presence of unpleasant odors is the most severe environmental problem in the POFA. Species such as sulfate, nitrate, chloride, calcium, sodium, and ammonium were the most abundant, without differences in their concentrations between sites (except chloride), which suggest the probable homogeneity of their levels in the area of study (**Figure 2**).

The total ions contributed with 15% of the PM_{10} mass (other components such as organic matter, elemental carbon, and mineral silica could integrate the particles). Calcium and sulfate showed significant correlations with PM_{10} ($r = 0.70$ and $r = 0.64$, respectively), evidence of emission sources of coarse particles in the POFA. Also, chloride could derive from local industry, burning biomass, and burning of agricultural waste. Finally, the PM_{10} collected in this study had an acidic nature; this is based on the ratio of total sulfate and total ammonium.

3.4. Black carbon

Black carbon (BC), or elemental carbon, comes from incomplete combustion of diesel vehicles, electric power plants and various industrial processes, wood burning and forest fires. BC plays an important role due to its porous nature and absorption, as well as in global climate

Figure 2. Average monthly concentration of different species of anions and cations associated with $PM_{2.5}$ of Miravalle during 2007. Sulfate, nitrate, and ammonium are the species that contribute most to the concentrations of fine particles throughout the year.

change by affecting the intensity of solar radiation [44]. Due to the porosity of the BC particles and their enormous surface area, they can adsorb significant amounts of mutagenic and carcinogenic organic compounds [45]. Therefore, BC is a risk to human health due to its ability to carry carcinogens to lungs [46].

During 2007, BC associated with $PM_{2.5}$ was monitored in Centro and CIATEJ [22]. Overall, low temperatures and unfavorable conditions for the dispersion of pollutants resulted in high concentrations at both sites (November and December). During July and August, a significant reduction of this pollutant was observed (factor 1:0.5 or 1:0.3). The presence of humidity and the intensity of the winds that generate vertical movements of air masses may also favor the BC dispersion, altogether with the frequency and severity of rainfall.

Furthermore, BC concentrations during 24 h periods were studied. In the morning, between 8 and 9, the highest level of concentration was observed during all months of the year (the magnitude of this peak is high or low, depending on the months of the dry or rainy season). This phenomenon occurred in both places, but with higher levels in Centro. During evenings, both sites showed a second-high level of BC concentrations, and this can be seen between 20 and 21 h. With some exceptions, the concentrations of this last event do not exceed the levels observed during the morning. **Figure 3** shows the trends and variations of BC concentrations throughout the day.

The abovementioned results are due to the increased population activities during the mornings, mainly because of the displacement from home to job, which implies a higher use of the public transport and private vehicles. Around midday not only the intensity of this activity of the population is reduced, but also better environmental conditions for the dispersion of

Figure 3. Hourly variation of BC concentrations per season in the Centro site during 2008. DS1—corresponds from January to May; RS—corresponds from June to October; DS2—corresponds from November to December.

pollutants are favored, thus generating lower concentrations of BC. The increase in BC at night is due to vehicles circulation related to people returning home after workday.

The BC data from the Centro could be correlated with the environmental concentrations of criteria pollutants measured at the same site. It is highlighted that with CO, NO₂, and SO₂ the correlations were high, but not in the case of ozone (a contaminant of secondary origin). These results support the primary origin of BC (mainly diesel vehicles). The second study on BC was conducted between January and August 2008, in addition to being carried out along with a manual sampling of PM_{2.5}; both pollutants were monitored and sampled at Centro and Miravalle sites. The results confirm some of the trends described for the previous year of monitoring (variations throughout the day and time when the concentration increase due to peaks in population activities).

An interesting contribution of this last study was the estimation of the contribution that BC makes to the PM_{2.5}, less than 10%. This value is similar to that estimated in other cities such as City of Mexico, Santiago de Chile, Helsinki, among others [47–49]. In Centro and Miravalle, a moderate relation was found between the concentrations of BC and CO (carbon monoxide) and confirms a common source of emission (burning of biomass and petroleum fuels).

Regarding BC emissions, those sources that use organic matter (burning biomass) as fuel during simple combustion processes and that lack of technological equipment to control their

emissions (gases and particles), could be responsible for a large part of the pollution problems in urban areas of our country; this is the case of artisan brick producers. In Mexico, Jalisco is the second state with the largest number of artisan brick producers, 2500 for 2012, 46% of which are in the GMA. The artisan brick industry contributes significantly to the emission of particulate ($PM_{2.5}$ and PM_{10}) and gaseous pollutants such as CO , CO_2 , NH_3 , among others. It should be noted that a significant fraction of these particles, especially $PM_{2.5}$, corresponds to BC [50], another relevant reason for their study. The scarce technology and standardization in the artisan brick production is a constant not only locally, but also in the country. Although there are numerous variants of kiln types designed for this productive activity (such as the MK2 one), the most common are the field campaign kiln and the fixed-walls kiln [51]. Few of these kilns (including the MK2 one) have additional emission control systems to reduce the gases and emitted particles. In this sense, it is possible to minimize particles dragging by water curtains, being one of the most straightforward and most efficient principles [52], although it does not act in the same way as the emission gases (the absorption of gases is sensitive to the increase in the temperature of the washing water). Our research group has observed the behavior of particles removal during the process of brick cooking when using recirculated washing water in an MK2 kiln, finding increasing water turbidity with time. The change in turbidity and its level (583 ± 16.7 , FTU) is related to the number of total solids (827 ± 62.38 , $mg\ L^{-1}$) therein which are removed by the washing water, thus contributing to the efficiency of reducing emissions to the atmosphere [53]. As part of these observations, a significant increase in the temperature of the washing water was also measured (up to $52^\circ C$), as well as a decrease in pH (3.45) due to the absorption of part of the CO_2 emissions (the most abundant gas). Both of the washing water properties change with time up to the final limit removal of CO_2 , CO , and NO not exceeding 26, 37, and 22%, respectively. The washing water of this process could experience a physical-chemical treatment due to the ratio $BOD/COD = 0.17$ because the BOD level is low compared to other types of wastewater.

3.5. Organic components as emission indicators (polycyclic aromatic hydrocarbons and oxy-PAHs)

As regards the organic matter associated with the particles, only a small percentage of groups of compounds have been characterized, such as polycyclic aromatic hydrocarbons (PAHs), oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs), among others [54]. The identification and quantification of PAHs, a diverse group of complex compounds with two or more fused benzene rings, has been intensively investigated [55]. In the atmosphere, PAHs can be present in particles (adsorb/absorb on their surface) or in the gas phase. It is expected that high molecular weight PAHs can be found mainly in the fine particles [56] because they have a more upper specific surface area and therefore greater adsorption than coarse particles [57].

The United States Environmental Protection Agency (USEPA) has defined 16 PAHs as a priority due to the known carcinogenic and mutagenic properties of them. It is important to note that only the European Union considers the regulation of PAHs in ambient air expressed in benzo[a]pyrene concentration (the carcinogen of reference by the IARC) at levels of $1\ ng\ m^{-3}$ per year [58].

An essential aspect of PAHs is that they can be decomposed by photodegradation, chemical reactions with others pollutants in the urban environment, or gas-particle partition.

Photodegradation is the central mechanism of chemical decomposition of 4–6 ring PAHs associated with particles. While the processes of degradation of PAHs in the gas phase involve reactions with hydroxyl radicals ($\cdot\text{OH}$), ozone (O_3), nitrate radicals (NO_3), and reactions of basic species with acids [59]. On the other hand, in the atmosphere, the oxidation of PAHs through homogeneous and heterogeneous reactions leads to the formation of oxy- and nitro-PAHs [60, 61]. These last species are also emitted with PAHs during incomplete combustion processes [62, 63]. Oxy- and nitro-PAHs are potentially more mutagenic than PAHs, and some of these substances are furthermore potentially carcinogenic [64, 65].

PAHs are typical components of gasoline and diesel. They are mainly emitted into the ambient air by exhaust gases from vehicles and other sources of incomplete combustion (approximately 90% of total PAHs from these sources) [59, 66]. PAH emissions can also arise from tobacco smoke and biomass burning [67, 68]. Knowledge of the sources, chemistry, and fate of each PAHs is crucial to propose successful prevention and mitigation, thus reducing the exposure of the population [69].

A study developed in the GMA evaluated the environmental levels of 14 PAHs and 14 oxy-PAHs, associated with $\text{PM}_{2.5}$ in Centro and Miravalle. Three seasons from April-2009 to January-2010 were investigated [27]. In general, the highest concentrations occurred during the cold dry season, due to the steady trend of organic pollutants to bind to particles; this behavior is directly influenced by metrological phenomena such as thermal inversions (presented 78% of the days of the year) and the stagnation of pollutants due to the orographic characteristics of the area. The most abundant compounds were benzo[a]pyrene, indene[123-cd]pyrene and benzo[ghi]perylene; the former contributing to 75% of the total carcinogenic potential and representing a public health risk in addition to the concentration of respirable $\text{PM}_{2.5}$. Regarding sources of PAHs, indene[123-cd] pyrene and benzo[ghi]perylene can be considered as markers for gasoline [70]. About oxy-PAHs, the most abundant were perinaphtenone, 2-methylanthracenedione, 7H-benzo[de]anthracene-7one, and 9,10-anthraquinone. The correlations between oxy-PAHs and criteria pollutants suggest that they come from combustion processes, specifically the burning of gasoline or diesel; also, there are indications of contribution by secondary transformation sources.

Barradas-Gimate et al. [29] carried out a study in 2014 at the Centro and Tlaquepaque during the warm dry season and at Centro and Las Aguilas during the rainy season, with the objective of determining the atmospheric levels and sources of quinones in $\text{PM}_{2.5}$. The highest concentration of $\Sigma_{16}\text{PAHs}$ occurred in Tlaquepaque ($7.62 \pm 2.03 \text{ ng m}^{-3}$) in the warm dry season and the lowest was recorded in Las Aguilas ($2.98 \pm 0.55 \text{ ng m}^{-3}$). During the rainy season, since Tlaquepaque has the characteristics of a site for the reception of pollutants concerning the Centro station, it can be inferred that there is an influence of the masses of air coming from the emission sites that promote higher concentrations of these pollutants. In this study compounds such as benzo[ghi] perylene, indene [123-cd] pyrene, benzo[a]pyrene and benzo[b] fluoranthene, 1,2-benzanthraquinone, followed by 9,10-anthraquinone and 5,12-naphtacenoquinone were the most abundant. It is suggested that some of the compounds may be associated with diesel particles and heavy vehicle activity. In general, the quinones indicate having a primary origin (vehicular). However, evidence of secondary formation was found for 9,10-phenanthrenequinone, a compound toxic for humans [71].

Similarly, Ojeda-Castillo et al. [32] carried out a simultaneous sampling of gas phase and PM_{10} for the 16 priority PAHs and 8 quinones during the warm dry season of 2015 in the Centro and Tlaquepaque, being the first time that this particle size is measured in conjunction with the organic gas phase in the GMA. The levels of $\Sigma_{16}PAHs$ (sum of gas phase and PM_{10}) were found in the range of 69.34–209.77 $ng\ m^{-3}$. The most abundant compounds in the gas phase were naphthalene and acenaphthylene, while in PM_{10} was benzo[b]fluoranthene and chrysene. The ratios of PAHs confirmed that these compounds come from the combustion of diesel. It is important to note that in previous studies, this trend is followed regardless of the particle size, which reaffirms the need to take actions to mitigate vehicle emissions in the city.

Additionally, the health risk of lung cancer is calculated by exposure of PAHs to the respirable aerosol at a level of 1.7×10^{-3} . It is considered that population exposure to PAHs lower than 10^{-6} is acceptable [72, 73]. Therefore, this result could indicate a potential risk to health. More research is needed on this topic to reduce uncertainties and to specify the evaluation by vulnerable groups and exposure times. Regarding to other chemicals, the environmental levels of Σ_8 Quinones were found in the range of 1.36–12.23 $ng\ m^{-3}$. The most abundant quinone in both phases was 1,4-phenanthrenequinone, which has been reported as a direct emission marker [74]. In the gas phase, quinones represent about 58% of the collected emissions. Inference results from sources with criteria pollutants and meteorological parameters indicate primary sources as the main contribution of quinones in PM_{10} , and secondary formation of high molecular weight quinones in the gas phase and PM_{10} .

4. Conclusions

For the GMA, the analysis of the chemical composition of particulate pollutants, especially $PM_{2.5}$, has allowed us to have reliable information on some of the most common sources of emissions that affect the ambient air and probably the health of its population. The geological origin of some of the components of the particles, or an anthropogenic origin such as diesel or gasoline emissions, is one of the main sources of emission of heavy metals and toxic elements of the particles. At the same time, the most abundant species such as sulfates, nitrates, and ammonium allow us to understand that there are chemical compounds that are formed in the atmosphere and end up being incorporated into the mass of the particles. The parent gases of these secondary pollutants are frequently emitted directly from the combustion processes, highlighting the importance of this source. In the case of BC in the particles, its porous absorption nature makes them a relevant component in the issue of human health, since it is not only its abundance greater in the smallest particles, but also particulate matter reaches deeper regions of the respiratory tract, bringing numerous chemical compounds into the body, a situation that could be the origin of multiple respiratory diseases. It is probable that in some areas of the GMA one of the most critical sources of BC is the artisanal bricks industry. Thus, particular attention and monitoring must be given to the measurement of their emissions, as well as to public policies for modernization of its production processes. As for PAHs, oxy-PAHs, and quinones, the results suggest that the predominance comes from

gasoline or diesel burning emissions, that is, direct emissions. It is emphasized that for the PM_{10} the quinones come from primary sources, while a secondary origin is attributed to the high molecular weight of quinones in the gas phase and the PM_{10} .

Although there have been advances in the knowledge of the origin of some of the components of the particles of different sizes in the ambient air of the GMA, the studies have focused only on a few groups of chemical compounds, and in a few places; therefore, for most of the city pollution information is not really known. In this way, direct efforts of local authorities and research groups trying to understand the particulate pollutants processes in the GMA are still needed.

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Author details

Valeria Ojeda-Castillo^{1*}, Sergio Alonso-Romero², Leonel Hernández-Mena¹, Paz Elizabeth Álvarez-Chávez¹ and Jorge del Real-Olvera¹

*Address all correspondence to: ojeda.c.v@gmail.com

¹ Center for Research and Assistance in Technology and Design of the State of Jalisco (CIATEJ, A.C.), Guadalajara, Jalisco, México

² Center of Applied Innovation in Competitive Technologies (CIATEC, A.C.), León, Guanajuato, México

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