

Capítulo VIII Material Particulado Fino (PM₁) y fracción orgánica

Chapter VIII Fine Particulate Matter (PM₁) and organic fraction

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Resumen

Las PM₁ son las partículas ambientales más citotóxicas. Hasta la fecha, pocos estudios realizados alrededor del mundo se han centrado en PM₁ debido a la falta de disponibilidad de equipos de monitoreo de aire. Por lo tanto, la composición orgánica de una fracción respirable significativa de PM es desconocida. Los hidrocarburos aromáticos policíclicos (HAP) y las quinonas en partículas finas son preocupantes debido a sus propiedades potencialmente carcinógenas y mutagénicas. En el aerosol (mezcla de partículas y líquidos en una fase gaseosa), los HAP y quinonas absorbidos se producen a partir de una combustión incompleta o pirólisis de material orgánico, y pueden formarse por procesos atmosféricos.

Los procesos atmosféricos gaseosos y heterogéneos de los HAP puede producir quinonas adicionales a través de la actividad fotoquímica y las reacciones con oxidantes atmosféricos, incluidos los radicales libres $\cdot\text{OH}$, O_3 y NO_3 . Existe una falta general de información sobre los niveles, las fuentes y la exposición a estos contaminantes. Por lo tanto, las regulaciones y las estrategias de control aún no existen.

Material particulado fino, Quinonas, HAP, Contaminantes atmosféricos.

Abstract

PM₁ are the most cytotoxic ambient particles. To date, few studies conducted around the world have focused on ambient PM₁ due to the unavailability of air monitoring equipment. Therefore, the organic composition of a significant fraction of respirable PM is unknown. Polycyclic aromatic hydrocarbons (PAHs) and quinones in fine particulate matter raise concerns due to their potentially carcinogenic and mutagenic properties. In the aerosol (mix of particles and liquids in a gas phase), sorbed PAHs and quinones are produced from incomplete combustion or pyrolysis of organic material, and can be formed also by atmospheric processes.

Gaseous and heterogeneous atmospheric processing of PAHs can yield further quinones via photochemistry and reactions with atmospheric oxidants including $\cdot\text{OH}$ free radicals, O_3 and NO_3 . There is an overall lack of information about levels, sources, and exposure to these pollutants. Therefore, regulations and control strategies are still non-existent.

Fine particulate matter, Quinones, PAHs, Atmospheric pollutants

1. Introduction

The World Health Organization pronounce that, in 2012, an estimated 3.7 million premature deaths were due to air pollution. The level of air pollution increasing in urban areas is a major concern. Recently, an environmental projection to 2050 carried out by the Organization for Economic Co-operation and Development determined that, if new policies are not implemented, the quality of urban air (typically governed by levels of particulate matter and ground-level ozone) will continue to deteriorate worldwide, becoming in 2050 the leading cause of environmental deaths worldwide.

Even though the importance of aerosols in atmospheric chemistry, climate and air pollution has been recognized, our ability to assess the impact of aerosols on the physics and chemistry of the atmosphere remains limited due to insufficient understanding of many processes associated with the sources of particles (mechanisms of formation). Atmospheric aerosols can be seen as a complex conglomerate of thousands of chemical compounds in a giant, strongly oxidizing chemical reactor in the Earth's atmosphere.

The complexity of the chemical and physical processes involving aerosols has not yet been fully evaluated due to the distribution and lifetimes of air pollutants that are strongly dependent on many meteorological parameters. It is likely that the fate of the air pollutants will be altered under changed climate conditions although the anthropogenic emissions are stagnated to levels of today.

Atmospheric aerosols can be categorized into primary, which are directly emitted by their sources, and secondary, in the atmosphere from inorganic and gaseous organic precursors. Approximately, that 10^4 - 10^5 different organic compounds have been identified in the atmosphere, each of which can undergo distinct atmospheric degradation processes to produce a range of oxidized products, which can take part in to the formation and growth of secondary organic aerosols (SOA). Also, a range of organic compounds associated with particles are emitted in the atmosphere directly in the form of primary organic aerosol (POA).

The distinction between primary and secondary particles diffuses with time, since the particles are subjected to a battery of physical (gas-particle repartitioning, particle coagulation, water uptake by particles, etc.) and chemical (reactive uptake of gases by particles, cloud/fog processing of particulate compounds, photochemistry, etc.) processes. All of these processes are known as “aging” of aerosols, and photochemistry is at the core of many particle aging processes in the atmosphere.

In the process of formation of organic particles during combustion, Polycyclic aromatic hydrocarbons (PAHs) are components of organic carbon (OC) on PM (fine fraction) and are products of incomplete combustion. In contrast to PAHs which are emitted directly from combustion processes, the sources of oxygenated PAHs emission in the atmosphere can be both by direct introduction and by tropospheric conversion of PAHs or other precursor molecules.

2. Theoretical bases

2.1 Particulate Matter (Atmospheric aerosol)

2.1.1 Overview

Particulate matter (PM) is a mixture of solid and liquid particles that vary in size, shape and chemical composition suspended in the air (Wenger et al., 2009). It is an atmospheric pollutant originated from a wide variety of natural sources (vegetation, volcanoes) and anthropogenic (fossil fuel burning, industrial processes) or may be the result of gas phase chemical conversions, heterogeneous particulate reactions and multiphase processes (Spindler et al., 2013). The PM can be found in sizes ranging from 10^{-3} μm to 100 μm and according to health experts the PM fraction ≤ 100 μm (PM_{100}) is known as PM inhalable.

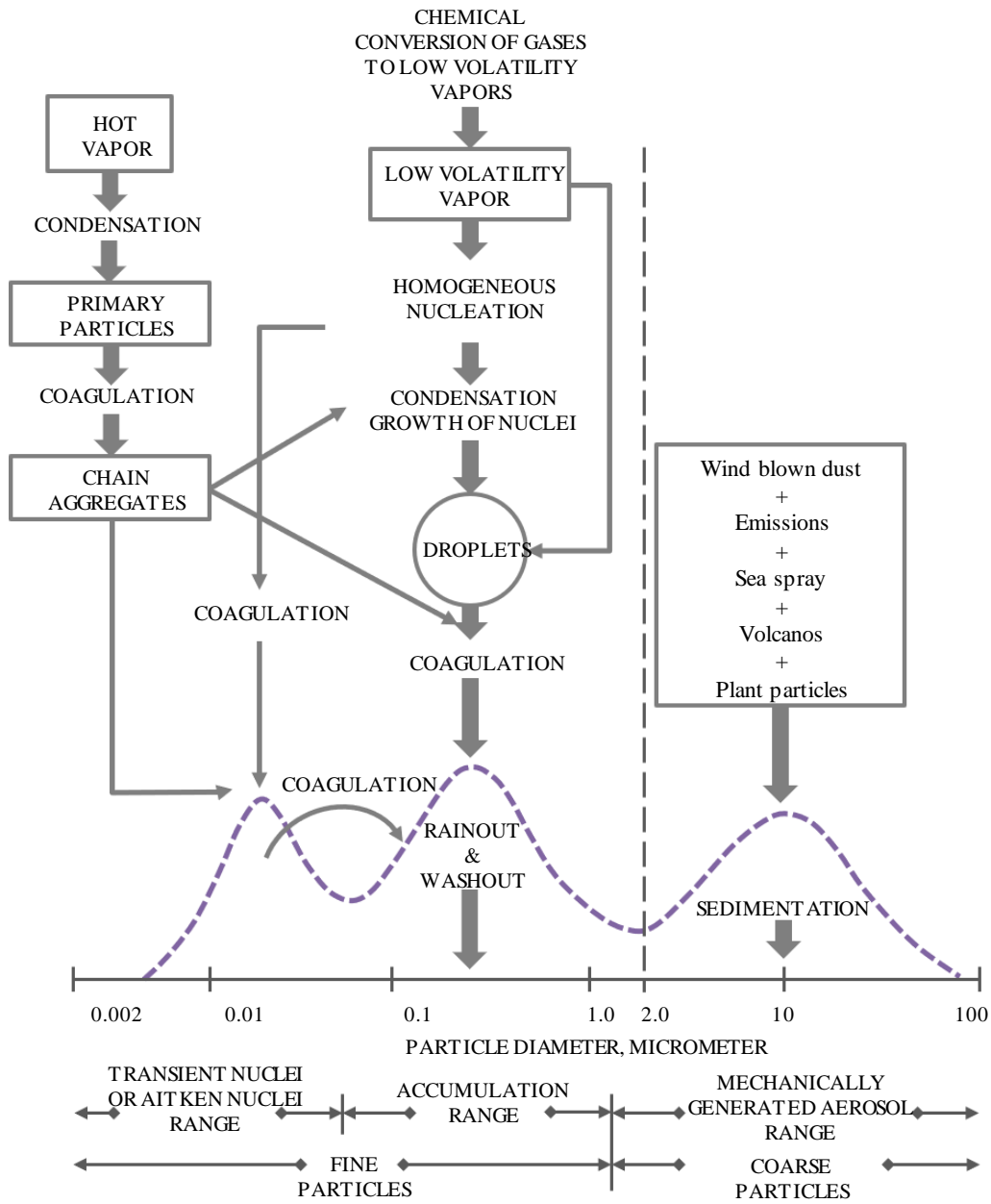
The fraction $\text{PM} \leq 10$ μm (PM_{10}) is known as the thoracic fraction because it is able to enter the thoracic pathways, and finally, there is a finer fraction ($\text{PM} \leq 4$ μm or PM_4) that can penetrate the tracheobronchial tree pathways that act as air exchange sites in the lungs, this fraction is known as respirable PM (Pérez et al., 2008). Similarly, PM_{10} and $\text{PM}_{2.5}$ ($\text{PM} \leq 2.5$ μm or alveolar fraction) are selected as monitoring parameters in global air quality standards.

Thus, in air quality, the coarse fraction is considered between 2.5 and 10 μm ($\text{PM}_{2.5-10}$), while $\text{PM}_{2.5}$ is considered the fine fraction. This particular classification over the years has lost accuracy with respect to the definition given by Whitby and is due to the fact that fine and coarse particles generally have different sources and formation mechanisms (Whitby, 1978).

So, it is essential to distinguish between fine and coarse particles for any discussion of physics, chemistry, measurements or air quality standards. Whitby (1978) includes fine particles in ≤ 1 μm (PM_1) because most of the particles in the coarse fraction (>1 μm) are primary and generated by mechanical processes aerosol (Figure 8.1). Also, secondary coarse particles can be found by the chemical interaction of gases with primary particles of marine origin or of the earth's crust (greater than 1 μm).

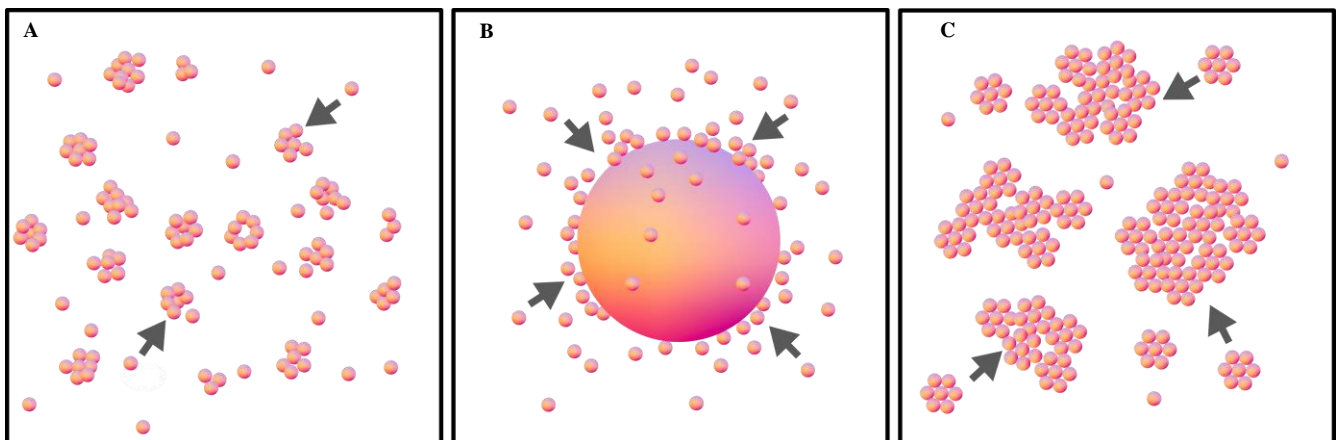
In the fine fraction (PM_1), primary particles (such as diesel soot), or secondary particles formed by precursor gases can be found via nucleation or condensation of existing particles (Figure 8.2).

Figure 8.1 Schematic of an atmospheric aerosol size distribution showing the three modes, main source of mass for each mode, the principal processes involved in inserting mass into each mode, and the principal removal mechanisms



Source: Whitby, 1978

Figure 8.2 Scheme of the mechanisms of formation of the secondary particles, A) Homogenous nucleation, B) Condensation and C) Coagulation



2.1.2 Formation process

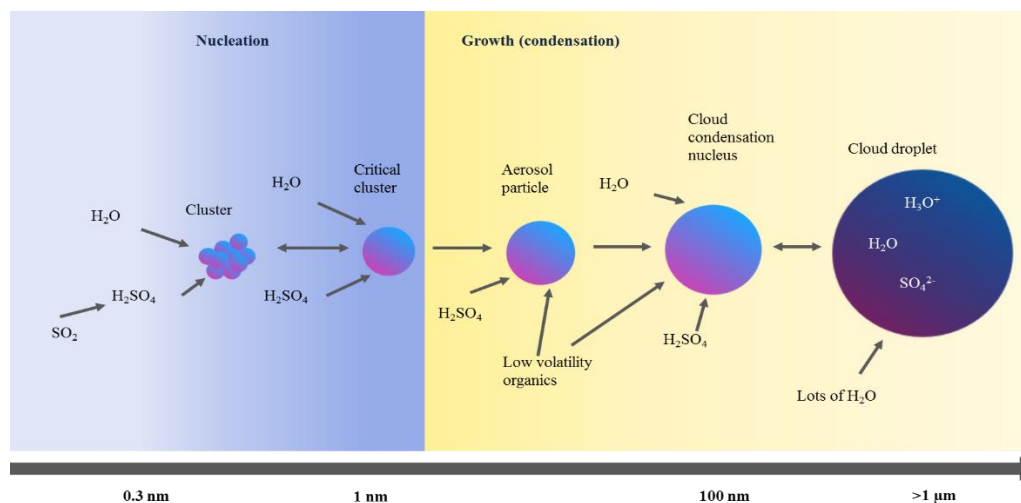
Nucleation

The new particles are formed by nucleation of low or zero volatility gas phase compounds emitted from biogenic or anthropogenic sources, followed by their growth into small particles. The generation of new particles has been observed in a variety of environments (Holmes, 2007) and varied atmospheric and climatological conditions. Many of the open questions are about the details of nucleation mechanisms and nucleation agents. So far, in general, it cannot be predicted when and where nucleation will take place. However, nucleation and subsequent growth processes influence the total number of particles, the particle size distribution, as well as the chemical and optical properties of the atmospheric aerosol. Both the climatic and the indirect effects of aerosols are potentially influenced by the number of growing nucleation particles in sizes at which they can become active nuclei of cloud condensation (Spracklen et al., 2006).

Pure sulfuric acid (H_2SO_4) has a low vapor pressure (0.3 mmHg at 20 °C) at atmospheric temperatures, and is lower in the presence of water, due to the large enthalpy that is released when two substances are mixed (Spindler et al., 2013; Viana et al., 2008). When H_2SO_4 is produced from sulfur dioxide (SO_2) in the gas phase, it is therefore easily super-saturated and the gaseous H_2SO_4 begins to condense. Water vapor is ubiquitous in the atmosphere and therefore a co-condensation of H_2SO_4 and H_2O is always occurring. If H_2SO_4 gaseous molecules do not find pre-existing surfaces (particles) to condense before colliding with other H_2SO_4 and H_2O molecules, they can be grouped with other molecules. If these aggregates continue to grow and exceed the nucleation barrier, then new thermodynamically stable aerosol particles will be formed from the gas phase (Curtius, 2006).

Two important steps have been recognized in the generation of new particles that can grow to a detectable size (Agudelo-Castañeda et al., 2014; Křůmal et al., 2013). The first for the formation of an initial nucleus and the second is the growth of particles to a larger size. The mechanisms proposed as candidates for the passage of the formation of an initial nucleus based on observations and theoretical considerations include: 1) homogeneous binary nucleation of sulfuric acid and water (Weber et al., 1999) (Figure 8.3); 2) homogeneous ternary nucleation of ammonia-water-sulfuric acid (Allen et al., 1997; Cho et al., 2004; Chung et al., 2006); 3) homogenous nucleation of organic compounds with low vapor pressure (O'Dowd et al., 2002); and 4) ion-induced nucleation (Kim et al., 2002). The second step in the formation of new detectable particles, growth, is also uncertain. These particles can grow by condensation of sulfuric acid or by self-coagulation. However, of the hundreds of different compounds trace in the atmosphere, only very few can nucleate as new particles. Sulfuric acid, in combination with water vapor and ammonia, iodine oxides and some organic substances such as certain sesquiterpene oxidation products are currently the only compounds that produce significant amounts of new particles in the ambient atmosphere (Curtius, 2006).

Figure 8.3 Schematic representation of nucleation and the subsequent growth process for homogeneous binary nucleation of H_2SO_4 and H_2O . Once stable groups are formed, other substances such as low volatility organic compounds may also participate in the growth process. Particles can grow to sizes large enough to act as cloud condensation nucleus and over time can be cloud droplets



Growth

Particle growth occurs through coagulation and condensation, both dependent on particle size. Coagulation involves the collision of particles with each other due to their kinetics. Although large particles provide a bigger surface area for absorption, the smaller particles have a higher diffusion rate. Condensation is a function of the vapor pressure saturation and the available surface area of the particle (both are related to the particle diameter). Within the different environments, the varying concentrations of sulfuric acid and low VOCs (volatile organic compounds) levels between clean and contaminated areas result in growth rates with a significant difference (Holmes, 2007).

Coagulation

Coagulation consists of aggregations between particles (mainly nucleation mode) and resulting in the fusion or aggregation of particles into a single. From the kinetic point of view, coagulation is a second-order process, whose constant rate, leaving aside an efficiency factor, depends on the radius and diffusion coefficients of the particles (Cozzi and Cadorin, 1972). The method of collision or aggregation is a major factor in determining the coagulation effect. Brownian motion or thermal coagulation is the dominant mechanism in the coagulation of submicron particles (in high concentrations) (Otto and Fissan, 1999). Where hydrodynamic, electrical and gravitational forces of the molecules that surround a particle result in collisions or aggregations asymmetric, causing movement and consequent impact with other particles (Seinfeld and Pandis, 2006). As a consequence, a decrease in the number of particles is obtained, but the mass is maintained (Holmes, 2007).

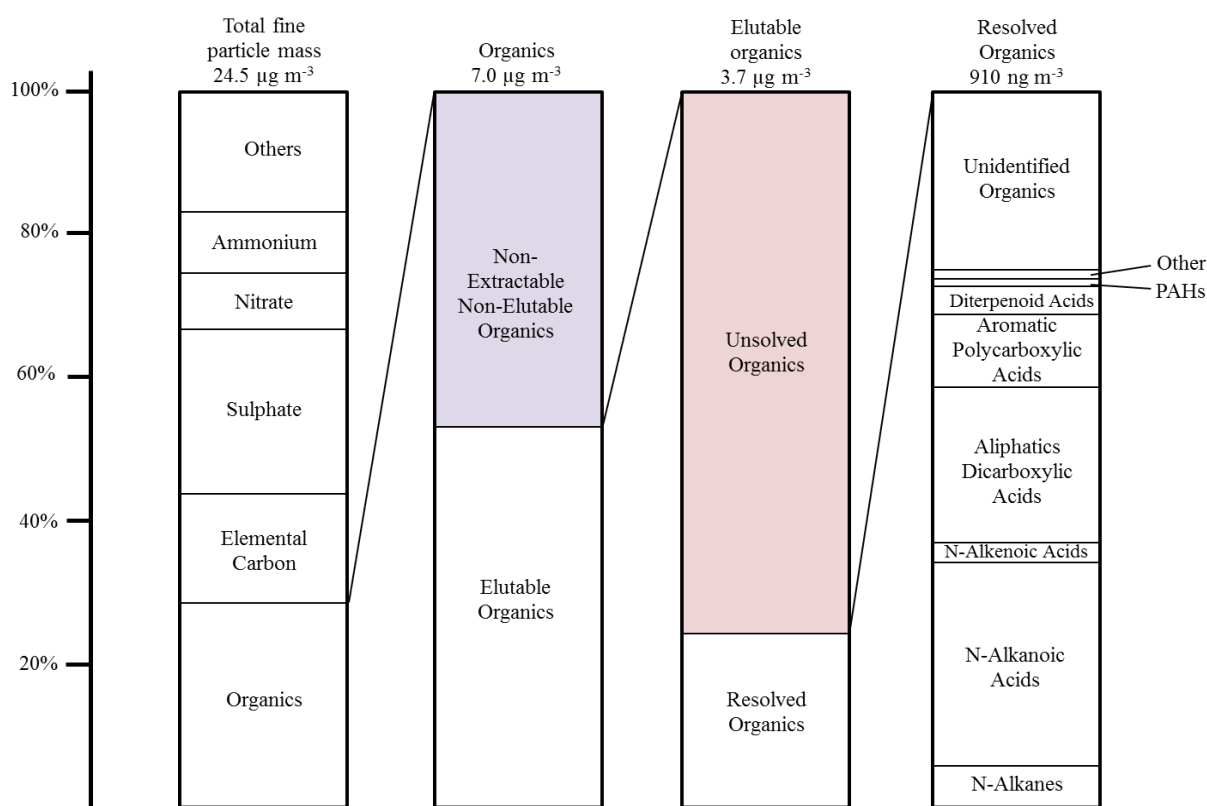
Condensation

Condensation is the partition of species between the gas phase and the particle phase as a result of the difference in ambient concentrations and equilibrium. However, due to the similarity between the size of the nanometric particles and the gas molecules the condensation to new particles is best determined by the collision rate between the gas molecules and the particles (Lehtinen and Kulmala, 2002). Most condensation models do not consider the diffusion effects of the molecules of the particles through the air. Though, for condensation to nanoparticles, since the gas dimensions are similar to those of the particles, ignoring the diffusion of the particles through the air can lead to an overestimation of the rate of condensation (Holmes, 2007). Gas phase diffusion is the first step for condensing low and semi-volatile organic vapors into existing particles. The gas phase diffusion correction factor describes the influence of gas phase diffusion (Pöschl, 2011). Therefore, it is an important parameter in the formation and growth of SOA (Pierce et al., 2011; Riipinen et al., 2011).

2.1.3 PM composition

The chemical components found in the particles are very diverse and depend mainly on both the emitting source and the mechanism of particle formation. Since the coarse, fine and ultrafine particles are generated through different processes, it is expected that each of these PM groups will have a unique composition of chemical species, allowing inferences about the sources and processes of formation. The formation of coarse particles through mechanical processes such as wind and erosion results in the abundance of inorganic species that derive from sand, soil and marine salt present in large particles. Common elements found in the Earth's crust may contribute to the chemical composition of coarse particles. Crushed limestone is a common material used on paved roads; it is a major source of calcium in large particles (Finlayson-Pitts and Pitts, 2000). Sulphates and organics are prominent compounds present in the ultrafine particles due to their formation by homogenous nucleation. In addition to inorganic species such as nitrates and ammonium, the chemical composition of the fine particles also comprises sulfates and organic polar species, derived from the fine particles that may arise from the coagulation of ultrafine particles. Organic species are a substantial fraction of fine particulate matter ranging from 20-90% of the mass of particles in the troposphere (Kanakidou et al., 2005). 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, elemental carbon and traces of metals. As far as organic matter is concerned, only a small percentage can be characterized. In Figure 8.4, a percentage relationship scheme is presented, illustrating the fraction concerning total carbon.

Figure 8.4 Mass balance applied to the fraction of organic matter contained in fine particles ($<2 \mu\text{m}$ aerodynamic diameter) and its relation to other components



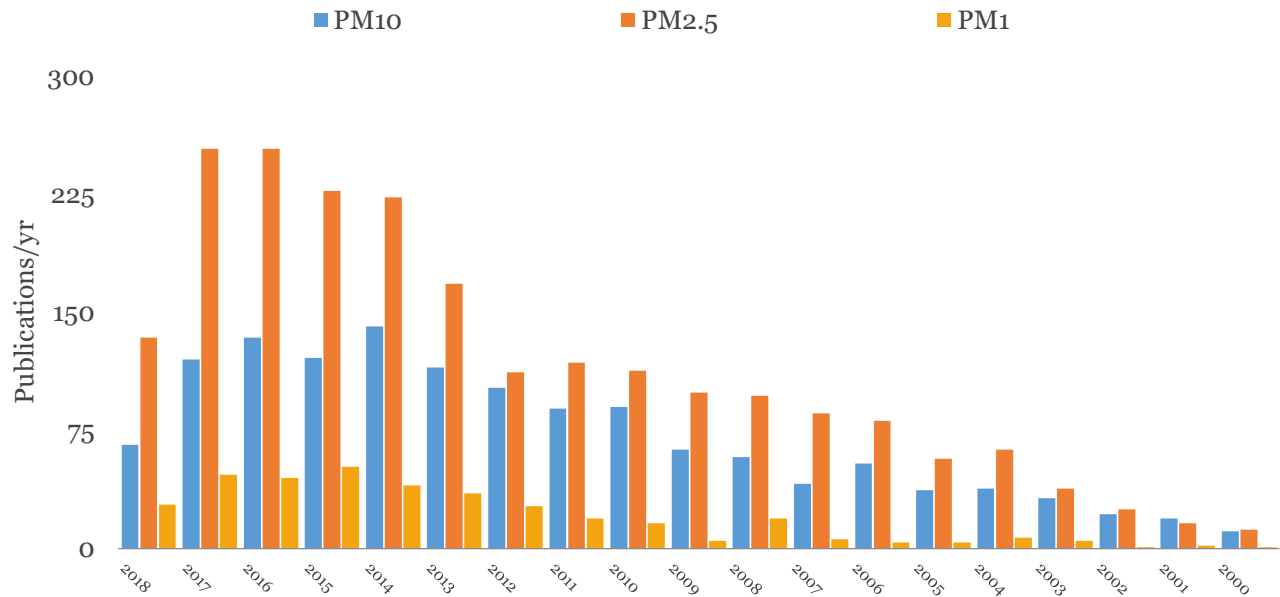
Source: Rogge et al., 1993

2.1.4 Previous research of PM_{10}

It has been established that PM_{10} are a better indicator of roadside emissions compared to $\text{PM}_{2.5}$. Also, PM_{10} are more cytotoxic for penetrating deeper into the respiratory system. Currently, several studies about PM_{10} concentrations have been published (Ariola et al., 2006; Godec et al., 2012; Gomišček et al., 2004; Pérez et al., 2008; Perrone et al., 2013; Spindler et al., 2004, 2013), however, compared to the information generated with coarse particle sizes ($> \text{PM}_{10}$) are scarce. Viana et al. (2008) reviewed publications in Europe focusing on PM and their sources over 18 years (1987-2005); and concluded that the contribution of origin detail requires characterization of specific tracers and chemical profiles for fine PM ($\leq \text{PM}_{10}$). Therefore, it is expected that the sources and profiles for each fraction will be different in the contribution of specific anthropogenic emissions, quantification of natural sources, identification of biomass combustion sources, nitrate components, etc.

More recent studies such as that of Hu et al. (2016) report high concentrations of PM_{10} in Beijing in the range of $60\text{--}85 \mu\text{g m}^{-3}$, of which it is estimated that 82% of the concentration of the mass of PM_{10} is composed of secondary species, where 62% is a secondary inorganic aerosol and 20% is a secondary organic aerosol. Valotto et al. (2014) indicate a total mass of PM_{10} in Italy of $27 \mu\text{g m}^{-3}$ in addition to a characterization of 16 elements (Fe, Mn, Zn, K, S, Mg, among others). Similarly, Perrone et al. (2013) report concentrations of a total mass of PM_{10} in $15 \pm 5 \mu\text{g m}^{-3}$ and characterization of ions, organic carbon and elemental carbon. Spindler et al. (2013) analyzed the mass of particles, ions, organic carbon and elemental carbon for PM_{10} in Germany and their difference according to the movement of the air masses, finding concentrations between 17 and $34 \mu\text{g m}^{-3}$ of SE to NW.

On the other hand, Agudelo-Castañeda et al. (2014) in one of the few studies oriented to the organic composition of PM_{10} and its health risk, reports polycyclic aromatic hydrocarbons (PAHs) levels for two sampling sites in Brazil, with concentrations of $\Sigma_{16}\text{PAHs}$ of 1.57 and 3.05 ng m^{-3} for summer and winter respectively. Similarly, Křůmal et al. (2013) analyzed 16 PAHs and 4 hopanes in PM_{10} at two sampling sites in the Czech Republic. In winter reports $\Sigma_{16}\text{PAHs}$ of 22.2 ng m^{-3} (in 2009) and 39.8 ng m^{-3} (in 2010); in summer 5.01 ng m^{-3} (in 2009) and 1.68 ng m^{-3} (in 2010). According to the above, it is evident that it requires information focused on the organic characterization of PM_{10} that would contribute to elucidate transformation mechanisms, atmospheric processes, and health in the population.

Figure 8.5 Reported sources contribution studies for PM₁ (2000-2018)

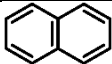
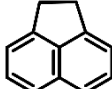
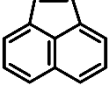
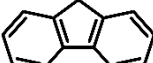
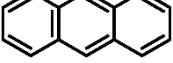
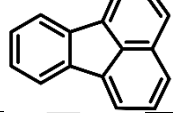
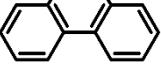
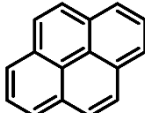
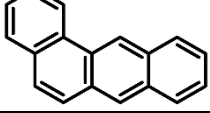
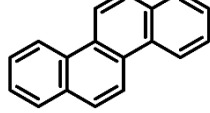
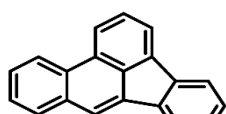
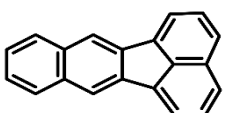
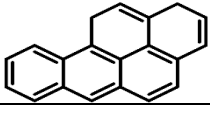
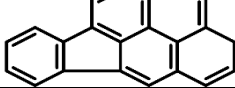
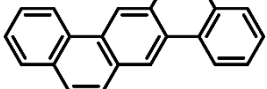
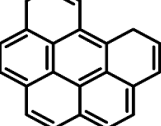
2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of various complex organic compounds, consisting of carbon and hydrogen together with two or more fused benzene rings (Ravindra et al., 2008). In the atmosphere, PAHs can be present in the gas phase, in case of PAH with high volatility ($P_v > 13$ mmHg). In particle phase, they are adsorbed/absorbed to the surfaces of fine particles; or they may be distributed between the two phases as shown in Table 1.1 (Finlayson-Pitts and Pitts, 2000). High molecular weight compounds are considered those are having 5 or 6 rings and are mainly found in the solid phase associated with the particulate matter; while the 4 ring PAHs may be in the gaseous phase and particle phase, Table 1.2 shows their properties.

Table 8.1 Forms of PAHs present in the atmosphere

PAHs	Acronym	Gas/Particle distribution
Naphthalene	Nap	Gas
Acenaphthene	Ace	Gas
Acenaphthylene	Acy	Gas
Fluorene	Fl	Gas
Anthracene	Ant	Gas/Particle
Fluoranthene	Flu	Gas/Particle
Phenanthrene	Phe	Gas/Particle
Pyrene	Pyr	Gas/Particle
Benzo[<i>a</i>]anthracene	BaA	Particle
Chrysene	Chr	Particle
Benzo[<i>b</i>]fluoranthene	BbF	Particle
Benzo[<i>k</i>]fluoranthene	BkF	Particle
Benzo[<i>a</i>]pyrene	BaP	Particle
Indeno[1,2,3- <i>cd</i>]pyrene	Ind	Particle
Dibenz[<i>a,h</i>]anthracene	Dib	Particle
Benzo[<i>g,h,i</i>]perylene	BghiP	Particle

Table 8.2 Physico-chemical properties of U.S. EPA priority PAHs

PAHs	Molecular formula	Structure	Molecular weight (g mol ⁻¹)	Vapor pressure of the supercooled liquid $p^{\circ}L$ at 298 K (Pa)	τ_{total} (h)*
Nap	C ₁₀ H ₈		128	38	13
Ace	C ₁₂ H ₁₀		154	1.7	5
Acy	C ₁₂ H ₈		152	2.6	1
Fl	C ₁₃ H ₁₀		166	0.54	21
Ant	C ₁₄ H ₁₀		178	5.9x10 ⁻²	2
Flu	C ₁₆ H ₁₀		202	6.8x10 ⁻³	14-25
Phe	C ₁₄ H ₁₀		178	0.10	9
Pyr	C ₁₆ H ₁₀		202	4.2x10 ⁻³	5-6
BaA	C ₁₈ H ₁₂		228	3.8x10 ⁻⁴	3-11
Chr	C ₁₈ H ₁₂		228	1.3x10 ⁻⁴	9-27
BbF	C ₂₀ H ₁₂		252	1.0x10 ⁻⁵	34 to >330
BkF	C ₂₀ H ₁₂		252	7.8x10 ⁻⁶	8-21
BaP	C ₂₀ H ₁₂		252	7.9x10 ⁻⁶	2-5
Ind	C ₂₂ H ₁₂		276	6.6x10 ⁻⁷	6-9
Dib	C ₂₂ H ₁₄		278	9.5x10 ⁻⁸	34 to >330
BghiP	C ₂₂ H ₁₂		276	4.6x10 ⁻⁷	5

High molecular weight PAHs are expected to require more time to partition to coarse particles than low molecular weight PAHs so that high molecular weight PAHs can be found mainly in the fine fraction (Duan et al., 2007). Also, fine particles have a higher organic carbon content and higher surface area; fine particles may, therefore, have higher PAH adsorption than coarse particles (Sheu et al., 1997).

On the other hand, the highest concentrations of PAHs occur in winter, a seasonal tendency possibly caused by the increase of adsorption of these substances at lower temperatures.

The reduction of PAHs concentration associated with PM₁ is related to the mechanisms of particle removal, such as dry and wet deposition. Wet deposition refers to the removal of rain or snow, and dry deposition refers to sedimentation and inertial impaction.

However, PAHs can be decomposed by photodegradation, chemical reactions with pollutants in the urban environment or the gas-particle partition. Photodegradation is the main chemical decomposition mechanism for PAHs of 4 to 6 rings associated with particulate matter (Finlayson-Pitts and Pitts, 2000).

While decomposition processes for PAH in the gas phase involve photolysis ($\lambda \geq 290$ nm); daytime reaction with hydroxyl radicals ($\cdot\text{OH}$), reactions with ozone (O_3), reactions with nitrate radicals (NO_3) at night and reactions of basic species with acids (HNO_3 or H_2SO_4 formed of NO_x and SO_x emissions) (Neilson, 1998).

2.2.1 Source identification

PAHs are typical components of incomplete combustion in automobiles that use gasoline and diesel and are emitted mainly to ambient air from vehicle exhausts and other sources of combustion as products of incomplete combustion (Ayers and Gillett, 1980; Spracklen et al., 2006). PAHs emissions can also arise from environmental tobacco smoke and biomass burning (Curtius, 2006; Marti et al., 1997).

It is estimated that about 90% of total PAH comes from incomplete combustion processes (Neilson, 1998). Some PAHs have been suggested as indicators of certain processes that release PAHs into the environment. These PAHs are known as sources, markers, tracers, or signatures. Concentration profiles and their relationships can be used to determine the contribution of different sources to concentrations in ambient air (Ravindra et al., 2008).

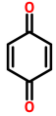
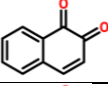

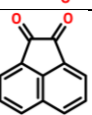
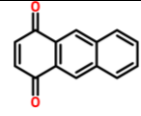
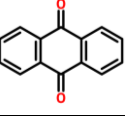
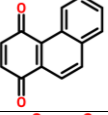
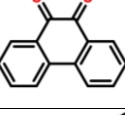
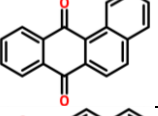
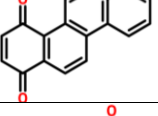
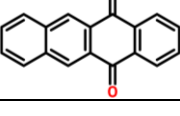
2.3 Quinones

Quinones are a class of organic molecules derived from aromatic species, which consist of a ring structure including two double bonds of carbonyl groups, located relatively in "ortho" (adjacent) or "para" positions.

Using as a criterion the type of aromatic system, quinones are classified as benzoquinones, naphthoquinones, anthraquinones and phenanthrenequinones. Quinones such 1,4-benzoquinone (1,4-BQ), 1,2-naphthoquinone (1,2-NQ), 1,4-naphthoquinone (1,4-NQ), 9,10-phenanthrenequinone (9,10-PQ) and 9,10-anthraquinone (9,10-AQ) are the most volatile, reactive and abundant in the atmosphere and are identified as environmental pollutants.

The most important physicochemical properties of quinones are shown in Table 1.3. Quinones are generally characterized by having higher molecular weights and lower vapor pressures compared to their precursor PAHs. These properties are important for the understanding of the behavior of quinones, both in the environment (e.g. partition between the gas and particulate phase) and in the human body (e.g. absorption and bioaccumulation) since those chemical properties allow them to interact with biological targets by forming covalent bonds and acting as transfer agents of electrons in the oxidation-reduction reactions (Sousa et al., 2016).

Table 8.3 Physico-chemical properties of selected quinones

Quinone	Molecular formula	Structure	Molecular weight (g mol ⁻¹)	Vapor pressure of the supercooled liquid $p^{\circ}L$ at 298 K (Pa)
1,4-Benzoquinone	C ₆ H ₄ O ₂		108	9.47x10 ²
1,2-Naphthoquinone	C ₁₀ H ₆ O ₂		158	2.44x10 ⁻¹
1,4-Naphthoquinone	C ₁₀ H ₆ O ₂		158	0.10
1,2-Acenaphthenequinone	C ₁₂ H ₆ O ₂		182	1.73x10 ⁻²
1,4-Anthraquinone	C ₁₄ H ₈ O ₂		208	1.1x10 ⁻⁴
9,10-Anthraquinone	C ₁₄ H ₈ O ₂		208	9.29x10 ⁻⁴
1,4-Phenanthrenequinone	C ₁₄ H ₈ O ₂		208	1.1x10 ⁻⁴
9,10-Phenanthrenequinone	C ₁₄ H ₈ O ₂		208	3.0x10 ⁻³
1,2-Benzoantraquinone	C ₁₈ H ₁₀ O ₂		258	5.65x10 ⁻⁷
1,4-Chrysenequinone	C ₁₈ H ₁₀ O ₂		258	5.51x10 ⁻⁸
5,12-Naphthacenequinone	C ₁₈ H ₁₀ O ₂		258	5.65x10 ⁻⁷

It has been demonstrated the presence of quinones in ambient air (Alam et al., 2013; Delgado-Saborit et al., 2013; Eiguren-Fernandez et al., 2008a, 2008b; Valavanidis et al., 2006). However, their potential health risks, their sources, and atmospheric concentrations have not been fully understood. Sources of these species may be primary or secondary (McWhinney et al., 2013). The secondary quinones can be products of the oxidation of PAHs, such as naphthalene, phenanthrene and anthracene through the reaction with oxidants in gas phase, which will generate their corresponding species (naphthoquinone, phenanthrenequinone and anthraquinone). Some sources identified are a) emission of diesel exhaust (Kulmala et al., 2001; Lazar et al., 1999; O'Dowd et al., 2002), and b) atmospheric formation in situ by reactions initiated by radicals and precursor PAHs (Sasaki et al., 1998) or photolysis of nitro-PAH (Cozzi and Cadorin, 1972; Otto and Fissan, 1999). It is expected that the formation of photochemical oxidants from precursor emissions is limited to daylight hours (usually during midday), since chemical reactions in the atmosphere are driven by sunlight. It has been shown that 1,4-naphthoquinone is formed from hydroxyl radical ([•]OH) and nitrate radical (NO₃) by initial reactions. With naphthalene in yields of 1-2% (Sasaki et al., 1998) and photolysis of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene leads to the formation of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone, respectively, with yields of ~ 20% (Cozzi and Cadorin, 1972; Otto and Fissan, 1999).

Quinones contribute to the adverse health effects caused by PM because they produce reactive oxygen species (ROS) due to their high redox potential (Li et al., 2012), which is a pathological factor of many diseases such as asthma, cardiovascular diseases, Alzheimer's, atherosclerosis, diabetes and neuromotor diseases (Finlayson-Pitts and Pitts, 2000; Kanakidou et al., 2005). Recently, Gurbani et al. (2013) conducted a study that establishes a connection between damage in the DNA of human lung cells and changes in the metabolism of exposure to quinone in PM that may lead the development of cancer.

2.3.1 Quinones in airborne

The presence of aromatic quinones in the atmosphere has been widely documented; different studies have identified and determined their concentrations in ambient air in urban and suburban areas. Bayona et al. (1994) studied the relationship between PAHs sources in PM and the seasonal variability of oxygenated mutagens (aromatic ketones, quinones, lactones, and aldehydes), concluding that these compounds have a greater contribution to atmospheric transformation processes than their parents (PAHs) and than primary emissions from combustion processes. Allen et al. (1997) reported concentrations of four quinones (1,4-naphthoquinone, phenanthrenequinone, 5,12-naphthacenoquinone, and benzo[a]pyrene-6,12-dione) in Boston, Massachusetts. Likewise, Cho et al. (2004) confirm the presence of 1,2-naphthoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, and 9,10-phenanthrenequinone in PM_{2.5} samples in different rural and urban communities in Los Angeles, California. Researchers such as Chung et al. (2006) quantified the mass of twelve quinones in total suspended particle samples and their ability to generate ROS through chemical assays with dithiothreitol (DDT) in Fresno, California. Valavanidis et al. (2006) determined the presence of five quinones in samples of PM₁₀ and PM_{2.1} particles in the Athens metropolitan area. Most studies on the presence of quinones in ambient air indicate that the burning of fuels emits them. But less are those that have focused on establishing and describing the processes that guide their formation in the atmosphere, explaining the relationship with their precursors and understand the role of their physicochemical properties, the processes of transport of pollutants in urban areas with high vehicular traffic and meteorological conditions. Recently Lee et al. (2015) observed in laboratory chambers, under controlled conditions, the gas phase reactions of naphthalene and phenanthrene with $\cdot\text{OH}$ radicals, suggesting the formation of quinones through oxidation processes. Similarly, some studies have attempted to demonstrate the contribution of PAHs derivatives in the atmosphere by quantifying the relative level of compounds originating from atmospheric transformation processes. Wang et al., (2007) suggest that gas phase diurnal reactions with $\cdot\text{OH}$ radicals and nocturnal NO₃ radicals are significant sources for the formation of 9,10-phenanthrenequinone in the atmosphere. Eiguren-Fernandez et al. (2008b) found a significant increase in the concentration of phenanthrenequinone according to the movement of the air mass throughout its trajectory, suggesting the presence of photochemical reactions that contribute to the environmental levels of phenanthrenequinone. It was determined and estimated that about 90% of phenanthrenequinone in Los Angeles originates from photochemical reactions during atmospheric transport. Eiguren-Fernandez et al. (2008a) report the presence of quinones in the gas phase and particle with greater distribution towards the gas phase, which represents a significant fraction of the total levels of quinones. Also, it suggests that temperature determines its distribution and deposition mechanisms and therefore the relative concentrations of quinones in the gas and particle phase. While Kojima et al. (2010) found that the percentage contribution of oxy-PAH (including 9,10-anthraquinone) by the atmospheric formation at windy sites ranges from 9-72%, depending on the compound and the season, with a secondary contribution observed in the summer. These findings demonstrate that a considerable fraction of the aromatic quinones detected in the particulate matter and the gas phase of urban areas is caused by atmospheric reactions favored by the photochemical susceptibility of PAHs and the presence of oxygenated chemical species originated through oxidation and reduction processes. Important factors have been found to influence the emission rates of PAHs and oxy-PAHs, meteorological parameters such as the height of the air mixing layer, wind speed, and direction, which is influenced by dilution levels, and the degree of gas-particle fractionation for PAHs and oxy-PAHs (Kojima et al., 2010).

In spite of the valuable information provided by the distribution of quinones between the gas phase and PM, the studies for quinones in the gas phase are still scarce. The gas phase is a crucial route in which a series of reactions are triggered and which may help to establish the relative contribution of quinones in both phases. Thus, it is necessary to contemplate the evaluation of the gas-particle partition behavior (Eisele and McMurry, 1997; Wang et al., 2006) to reduce the uncertainty in the identification of the specific contribution of sources.

3. Conclusions

The growing extent of pollution of the environment as a result of human activities has highlighted the need for a broad set of legislative and regulatory measures. However, reliable and relevant data on the levels of air pollutants in the environment are necessary for designing effective environmental protection policies with the objective of regulating each pollutant since the human body is at a variety of air pollutants at once, in a complex mixture and thereby minimize adverse effects on public health. It is considered that among the most toxic pollutants are the organic ones, such as PAHs. Their atmospheric and photochemical reactions are important because; a) individual PAHs can be removed from the atmosphere as a result of chemical reactions and b) derived products from PAHs may be more hazardous to human health than the PAHs themselves, such as quinones. The quinones have gained large attention recently because these can increase the concentration of reactive oxygen species (ROS) within the human body, which may cause significant damage to lipids, proteins and DNA. It has been established that most quinones are mainly secondary products, however, due to the challenges afore mentioned, studies of the transformation of PAHs in closed chambers under variable UV radiation and in the presence of oxidizing species to detect secondary products and conducting short time samplings (4 or 6 h) of quinones and PAHs to determine trends and occurrence are necessary in order to better assess the origin of the quinones ambient levels observed in urban areas.

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