

UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

TÍTULO: DETERMINATION OF ATMOSPHERIC BLACK CARBON CONCENTRATION IN JURIQUILLA AND ALTZOMONI, MEXICO

Trabajo de titulación presentado como requisito para la obtención del título de Químico(a)

Autor:

Sandoval Collins Bruno Leonel

Tutor:

Ph. D. Sandra Hidalgo

Co-tutor: Ph. D. Harry Alvarez

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Resumen

La contaminación del aire es uno de los problemas ambientales más preocupantes que ha ganado importancia en todo el mundo. Los aerosoles carbonosos, como el carbono negro, contribuyen significativamente a la contaminación del aire causando impactos en el cambio climático y problemas en la salud pública. El objetivo principal de este estudio fue determinar la concentración de carbono negro presente en los aerosoles atmosféricos $(PM_{2.5})$ en Juriquilla y Altzomoni durante 2017. La concentración de carbono negro se determinó mediante el empleo de un extinctometro fotoacústico. Posteriormente, se llevó a cabo un procedimiento de validación para verificar la fiabilidad de los resultados, utilizando programas en "Matlab R2015B" y "RStudio". La concentración en Juriquilla muestra una variación de 0.5 - 1.49 $\mu g m^{-3}$ con un promedio anual de 0.623 $\mu g m^{-3}$. Por otra parte, Altzomoni mostró concentraciones más bajas con una variación de 0.34 - 0.71 $\mu g m^{-3}$, con un valor anual de 0.487 $\mu g m^{-3}$. Adicionalmente, se realizaron variaciones de tiempo para reconocer el comportamiento diario, semanal, mensual y estacional del carbono negro. De esta manera se pudo demostrar que existen variaciones de concentracion que dependen de las condiciones climaticas, como pueden ser la temperatura y precipitación. Esta investigación representa uno de los primeros estudios sobre el carbono negro en la región de Juriquilla y Altzomoni, lo que puede demostrar su importancia, ya que tiene una influencia considerable en el clima y la salud humana.

Palabras Claves: Carbono Negro, Contaminacion del Aire, Efectos en salud y medio ambiente, Extintometro Fotoacústico.

Abstract

Air pollution, one of the most concerning and widespread environmental issues, has gained importance in the world. The carbonaceous aerosols such as black carbon significantly contribute to air pollution, causing both public health concern and impacts to climate change. The main objective of this study was to determine black carbon concentration in the atmospheric aerosols $(PM_{2.5})$ in Juriquilla and Altzomoni during 2017. Black carbon concentration was evaluated by a photoacoustic extinction eter. Consequently, a validation procedure was carried out, to check the reliability of the results, using programs in "Matlab R2015B" and "RStudio." The concentration in Juriquilla shows a variation of 0.5 - 1.49 $\mu g m^{-3}$ with an annual average of 0.623 $\mu q m^{-3}$. Otherwise, Altzomoni showed lower concentrations with a variation of 0.34 - 0.71 $\mu g m^{-3}$, with an annual value of 0.487 $\mu g m^{-3}$. Besides, time variations were realized to recognize their daily, weekly, monthly, and seasonal behavior. Recognize the processes of formation and transportation of black carbon will contribute to the understanding and determination of the main emission sources and its behavior in the atmosphere. This investigation represents one of the first studies about black carbon in Juriquilla and Altzomoni region, which can demonstrate its importance since it has considerable influence on the climate and human health.

Keywords: Black Carbon, Air Pollution, Climatic and Health Effects, Photoacustic Excintometer.

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Chapter 1

Introduction

1.1 The atmosphere of the Earth

The atmosphere is a mix of gases with a considerable number of suspended particles, solids, and liquids (called aerosols). It is composed mainly of the gases N_2 (78%), O_2 (21%), and Ar(1%).¹ The atmospheric mass belongs almost 99 % to the first 30 km of height. Additionally, there are other gases, called trace gases, that are in a less of 1 % of the atmospheric mass. These trace gases play a crucial role in the radiative balance of the planet and the chemical properties of the atmosphere.¹ The abundance of trace gases has changed rapidly and remarkably in these last two decades.¹

Physicochemical characteristics of the atmosphere and the energetic balance of the Earth came from many processes of mass transfer and energy balance. The interchange between atmosphere, biosphere, and geosphere is realized by mechanical, chemical, caloric and electromagnetic forces.² The last effect came from solar radiation and is a unique force with an external energy source, which plays an essential role in the climate of the Earth climate. This energetic balance will be discussed in the "Aerosol" section, where the topic will be extended.

Atmosphere has non-homogeneous characteristics among layers.¹ Its properties do not only change with altitude, latitude, seasonal variation, and solar activities, also varies with pressure, temperature, composition, electrical properties, or magnetic conditions.¹ To understand these variations, the atmosphere layer is divided into five sub-layers in function of the temperature (Figure 1.1).



Figure 1.1: Atmosphere sub-layers division. Taken from Castellanos.³

The troposphere is divided into two layers: the atmospheric boundary layer (BL), which extends up to about 1 km in height (Figure 1.2), and the remaining kilometers are known as the free troposphere (FT). The movement of the air, in the boundary layer, is influenced by friction forces with the surface, and goes through turbulent diffusion, with a joint process of mechanical and thermal components.² Meanwhile, in the free troposphere, the surface influence is nullified. Also, the boundary layer concept is dynamic: its dimensions vary with the time of day and weather conditions. Its experimental determination is not simple: radiosonde profiles, radar, and others.² It is crucial to mention, regard air pollution that most sources of pollutants are located in the first meters of the troposphere, in which the friction forces due to the Earth's surface and its temperature profile plays an essential role in the dynamics of air masses and the processes of mixing pollutants.



Pollutants in the Atmospheric Boundary Layer

Figure 1.2: Description of boundary layer height.

1.2 Aerosols

Atmospheric aerosols are solid or liquid particles that are suspended in the atmosphere with radii from 0.001 to 100 μm (1 $\mu m = 1 \ge 10^{-6}m$), which have effects on health, ecosystems, and the environment climate.^{4–8}

1.2.1 Radiation and radiative balance of the Earth

To understand climate changes on Earth, it is necessary to know the role of solar forcing on Earth's atmosphere. Global warming can be understood considering the energy radiation, from the sun, that heats the Earth's atmosphere. Therefore, thermal radiation of the Earth, along with the atmosphere, is radiated into space.⁹

The average temperature of the Earth remains slightly constant, which tells us that the Earth and the atmosphere lose as much energy in the form of radiation to space as they receive through radiation from the sun.¹⁰ The amount of radiant energy coming in and out of the Earth is defined as energy balance or radiative balance. The atmosphere controls the amount of energy that reaches the Earth's surface and at the same time, controls the energy radiated by the Earth's surface that escapes into space.¹⁰

The radiative balance modifies the amount of energy present in the atmosphere.¹¹ This modification provokes positive and negative radiative energy or forcing balances. The forcing balance is expressed in units of Wm^{-2} , and results in positive values of balance referring that aerosols absorb radiation, which contributes to increasing the temperature of the surface of the Earth.¹¹ On the other hand, negative refers to the scattering radiation which favors cooling.¹¹ The absorption and scattering of energy by the Earth and atmosphere are almost completely responsible for the climate on both a global and local scale.¹

The absorption of solar radiation by aerosols is characterized by the conversion of the energy of the photons into the internal energy of the particle that is then re-emitted in the form of heat.¹² Scattering by aerosols can be considered as a set of four physical phenomena: reflection (photons bounce with an equal angle), scattering (photons go in different directions), refraction (course of the photons change a bit), and the diffraction (the photon beam doubles). However, considering these four scattering processes would be very difficult. For this reason, usually these are generalized, and we speak of scattering in a general way as the redirection of radiation concerning its trajectory of incidence.¹³



Figure 1.3: External factor and their estimated radiative forcing on the global climate system. Taken from IPCC.¹⁴

The effects caused by radiative forcing by greenhouse gases such as carbon dioxide and

troposphere ozone are well known, while in the case of black carbon and mineral material present in atmospheric aerosols is not well studied, as observed in Figure 1.3.

1.2.2 Classification of aerosols

There are a large number of pollutants in the atmosphere that has different impacts on the environment and human health.⁷ Among these pollutants are highlighted aerosols. Aerosols can be classified in many ways according to different criteria; the most common are described below:

1. Sources that emits particles

There are several ways to sort the sources of emission of a pollutant; one of the most common is to divide them into anthropogenic sources and natural sources.¹⁵ The anthropogenic sources include the emissions generated by the activities of man, while the natural ones are those natural phenomena where man does not intervene (Figure 1.4).

Anthropogenic sources are subdivided into fixed or stationary sources, area sources, and mobile sources, while natural sources are divided into biogenic and geographic origins. This classification serves as a basis to compile in an orderly manner the information of emissions.



Figure 1.4: Examples of aerosols according to their origin: A) Natural aerosols and B) anthropogenic aerosols. Taken from Pixabay.¹⁶

2. Particles according to their origin

Primary particles: are those that are emitted directly into the atmosphere by various anthropogenic sources (for example, the dark smoke that is observed in the escapes of cars and trucks, the dust of the streets).¹⁵

Secondary particles: these particles are formed in the atmosphere as a result of chemical reactions from the presence of gaseous materials (Figure 1.5), called precursors.¹⁵ The primary precursor gases of the particles are sulfur dioxide (SO_2) , nitrogen oxides (NO_X) , volatile organic compounds (VOC) and ammonia (NH_3) , which mainly form sulfate and nitrate particles, as well as secondary organic suspended particles derived from the photochemical oxidation of organic compounds.¹⁵



Figure 1.5: Primary and secondary aerosols formation. Taken from Lu.¹⁷

3. Particles according to size

Suspended particles are also classified by their size (see Figure 1.6), but since they have an infinity of shapes, it is not possible to characterize them with a single real geometric dimension. Therefore, the aerodynamic diameter is used as an indicator of the size of the particle; this indicator is equal to the diameter of a spherical particle of unit density that has the same terminal velocity as the considered particle, independent of its shape, size or density under existing temperature, pressure and humidity conditions.¹⁸ These particles are classified by total suspended particles (TSP) defined as the set of all particles from 0.001 to 100 μm . PM₁₀ are composed of particles that have an average aerodynamic diameter of less than 10 and 2.5 μm , called coarse particles. PM_{2.5} contains particles less than 2.5 μm and are called fine particles. Finally, PM₁ or ultrafine particles have a diameter of less than 1 μm (Figure 1.6). However, it is essential to clarify that given the shape of aerosols it is challenging to determine their geometrical diameter and to classify them, for this reason, for practical-comparative purposes we will work with the aerodynamic diameter definition. The aerodynamic diameter is defined as the diameter of a spherical particle equivalent with a density equal to 1 $g \, cm^{-3}$ that would have the same aerodynamic behavior in an air flow.¹⁸



Figure 1.6: Comparison of size of particle. Taken from IPCC.¹⁴

4. Finally, aerosols can be classified according to the formation mechanism; within this classification, we have nucleation, aitken, accumulation, and thick mode (see Figure 1.7).



Figure 1.7: Illustration of different modes in a typical atmospheric particle size distribution. Taken from Watson.¹⁹

- a) Nucleation mode (<0.02 μm): Both combustion sources and gas condensation emit these particles. Gaseous precursors capable of forming particles by homogeneous nucleation are H_2SO_4 , NH_3 and H_2O . Its maximum concentration in many particles ranges are between 5 - 15 μm . Their average lifetime is from hours, since they coagulate quickly reacting with other particles or increasing in size due to condensation.²⁰
- b) Aitken mode (0.02 0.1 μm): These particles have a primary and secondary origin (natural or anthropogenic). Coagulation or condensation processes generally form on secondary particles origin from those of nucleation modes. Carbon (soot) is a typical example of this mode.^{20,21}
- c) Accumulation mode (0.1 1 μm): In this mode, the highest density has been reported within the range of 150 to 250 nm. These particles are product of the coagulation of smaller particles emitted from the combustion sources, the condensation of volatile species, the gas-particle conversion and the fine particles of ground dust. The particles

grow because of reactions in the liquid phase that takes place in small drops of water inside the clouds. A 90% of sulfate forms in the atmosphere, as a consequence of the oxidation in the liquid phase of the sulfur dioxide in the clouds.^{20,21}

 d) Thick mode (> 1 μm): Most of these particles are formed by mechanical processes such as the erosion of the Earth's surface or the explosion of bubbles on the surface of the oceans.²⁰

1.2.3 Chemical composition of aerosols

The concentration, size distribution, and composition of atmospheric aerosol particles are temporally and spatially highly variable.¹⁵ The composition depends on the source of emission, mechanisms of formation, as well as the meteorology of the place.² In general, atmospheric aerosol particles principally contain compounds such as sulfates, nitrates, ammonium, organic material, crustal species, sea salt, metal oxides, hydrogen ions, and water.¹⁰ However, for fine particles, our study main focus in the particles size, the principal's compounds are: sulfates, nitrates, ammonium, carbon compounds, and certain transition metals.¹⁰

a) Sulfates: secondary compounds are generated as a product of the oxidation of SO_2 , which is emitted into the atmosphere through volcanic emissions, biogenic emissions, and fossil fuel combustion processes. Another important source is the unicellular algae, which emits dimethyl sulfide. Although sulfates has highest abundance sulfur component, there are occasions in which sulfuric acid is formed by the hydroxyl radical.²²

b) Nitrates: are secondary compounds formed from nitrogen oxides (NO_2 and NO), considered together as NO_X , whose primary source is the combustion of fuel by vehicles. This process emits both NO_2 and NO; however, NO is produced in a more significant proportion, which oxidizes the atmosphere and generates nitrogen dioxide. The precursor gases are also emitted through bacterial activity in the soil that causes the decomposition of nitrogen compounds, as well as volcanic activity and electric discharges. Like sulfur oxides and nitrogen oxides can form their corresponding acid by the presence of the hydroxyl radical.²²

c) Ammonia: is the most abundant and vital alkaline compound present in the atmosphere due

to its neutralizing role in the atmosphere through the formation of salts, mainly ammonium sulfate and ammonium nitrate. It is emitted into the atmosphere in the form of its precursor gas (NH_3) , in a gaseous state due to the decomposition of organic matter, and the burning of fossil fuels.²²

d) Carbon compounds: within this classification are included organic carbon (OC) and elemental carbon (EC), which represents more than 50 % of the mass concentration of the particulate material.²³ Its emission sources are of both biogenic and anthropogenic origin.

Organic carbon consists of a large amounts of organic compounds (aldehydes, alkanes, alkenes, ketones, etc.) produced from the condensation of volatile organic compounds emitted directly into the atmosphere by combustion processes such as emissions of vehicles and/or industrial processes, although they are also emitted by biogenic sources, mainly by vegetation.^{24,25} Due to, the large variety of compounds composition for organic carbon is classified into volatile and semi-volatile organic compounds, which have very different physical and chemical properties.^{25,26}

Elemental carbon is emitted directly to the atmosphere through an incomplete combustion process. Its structure is very similar to the impure graphite. Most elemental carbon particles are issued in a smaller size (0.2 μm in diameter). However, studies in the United States have shown that sometimes this EC exceeds its size.^{24,27} Elemental carbon is a substantially pure form of carbon, which is poorly combined with other elements such as hydrogen and oxygen.²⁸ It is usually used as a synonym of black carbon "BC," which is a solid form of carbon, with more than 60% of this element in mass.²⁹

1.3 Black carbon

Soot is a carbon particles resulting from the incomplete combustion of hydrocarbons. Its color is black, therefore its called "Black Carbon." BC is an unwanted byproduct from carbonaceous materials such as fossil fuels, or biomass.³⁰

1.3.1 General background on black carbon

BC is a common carbonaceous component of particulate matter (PM) which can interact with solar and terrestrial radiation. In the atmosphere, particularly in the boundary layer, black carbon is the major component of aerosols which strongly absorbs solar radiation.³⁰ As mentioned before this particulate particle is produced from incomplete combustion which can be produced by many emission sources such as industries or vehicles. On the other hand, it is also produced by natural sources, for example in open biomass burning.³¹

Nearly 90% of global BC emissions in 2009, come from three main sources (see Figure 1.8): Open biomass burning from forest fires and controlled agricultural fires (41%), fossil fuel combustion for on-road and non-road transportation (25%), and solid fuel combustion for cooking and residential heating (23%).^{31,32}



Figure 1.8: Global black carbon emission sources by sector. (Data are from [33])

The principal sources of air pollution in urban areas are due to transportation.³⁴ For example, Figure 1.9 shows the overall BC emission by its source realized in the United States. Air pollution is emphasized on diesel exhaust regarding transportation topic, when urban areas are in discussion, due to the higher levels of contamination than gasoline exhaust. This type of fuel is generated from petroleum sources which produce different concentration and

composition emission.³⁵ Biodiesel, for example, can produce lower overall PM emissions but slightly higher nitrogen oxide (NO_x) emissions compared to conventional diesel fuel (because of the higher oxygen content of the fuel).³⁶



Figure 1.9: United Stated black carbon emission sources by sector. (Data are from [31])

Despite the versatility and efficiency of diesel engines, diesel vehicles have historically had a higher PM and NO_x emissions. PM mass emissions are much lower in gasoline, natural gas, or liquefied petroleum gas engines.³⁶

Fortunately, there is possible to realize mathematical estimations of pollutant behaviors. Figure 1.10 shows an estimated percentage of BC emission from transport sources regarding the ten highest motorized countries. In the United States, for example, there is a decrease in BC emission since the USA is an industrialized country. The main reason for this behavior is the policy and advanced technology. On the other hand, China, with the highest population number, is estimated to be the best BC transmitter in 2050 despite the number of people using transportation.



Figure 1.10: Global black carbon emissions from transportation by region among top 10 motorized regions, 2000-2050. Taken from Minjares.³⁶

The overall particle size is around 0.5 μm . However, it can coat with another atmospheric material, which can form larger size particles from 0.1 to 1 μm of diameters (Figure 1.11). The ability of a higher size makes it possible to absorb and scatter more effectively the radiation emitted from the Earth or sun. This topic will be discussed properly in the few sections. The chemical composition of BC is mainly composed of nitrates, sulfates, ammonia, and sodium chloride.³⁷

Due to the small size and chemical composition of BC is considered a toxic atmospheric component. It has an impact on human health and the environment. The small size of BC provokes important negative effects on human health, because we can easily inhale it; and can affect directly or indirectly our pulmonary system and bronchi, also increments the risk of having respiratory infections.³⁴ On the other hand, the energy released, from absorption radiation as the heat, warms up the atmosphere, which might contribute to the acceleration of ice and snow melting. This will have a significant impact on global warming and climate change. BC absorbs energy million times more efficiently than CO_2 .³⁸



Figure 1.11: Particle aerodynamic diameter (μm) . Taken from Colbeck.³⁹

Another important characteristic of this pollutant is the lifetime. Many studies recognize the regional effect due to their short atmospheric residence. The lifetime of BC is about 4-12 days classifying it as a Short-Lived Climate Pollutant (SLCP).^{40,41} The main characteristic of SLCP is due to the short lifetime that has and the regional impacts on environment and health. Tropospheric ozone (O₃), methane (CH_4), hydrofluorocarbons (HFC) are also part of SLCP classification.⁴²

1.3.2 Absorption, scattering and extinction coefficients

Another essential characteristic of studying BC properties remains in their interaction with sunlight, which leads to different phenomena that occur in the atmosphere, such as visibility, air heating, cloud formation, etc.⁴³ To study this issue, it is necessary to understand the concept of some natural phenomena that occur in this interaction.

Absorption phenomenon

Absorption is produced when there exists a transfer of energy from radiation to an atmospheric material (aerosols). Each substance will absorb a series of radiation frequencies; it will not absorb all of them because it is specific. Due to this, the molecules transforms the atmosphere to an opaque medium of specific spectral ranges while offering absorption-free windows in other scales. When a parallel beam of light propagates through a uniform atmosphere, no scattering, its intensity decreases exponentially with "x" distance (Equation 1.1).⁴⁴

$$I = I_0 e^{-\sigma x} \tag{1.1}$$

where I_0 is the initial intensity, and σ is the extinction coefficient.

The black body is a transmitter and receiver of perfect energy.⁴⁴ The radiant energy emitted from the black body per unit area, time and wavelength range, tends to zero for very short and long wavelengths and presents a single maximum at a length of the wave that depends on the temperature. However, black body concept no such perfection description, since any body entirely absorbed energy. Despite the situation, this is solved by introducing the model of "gray body," whose behavior resembles the real masses. For the same, the absorptivity does not depend on the temperature of the external medium.⁴⁴ The relationship between the emitting power of any body and the absorption coefficient of a said body depends exclusively on the temperature (T).

Scattering phenomenon

Scattering is the reverse process of absorption. It is a physical process which a particle during its trajectory as an electromagnetic wave continuously extracts energy from the incident wave and radiates it in all directions.⁴⁵ In scattering, a particle absorbs a certain amount of incident energy, then emits at a stable angle centered on the particle, which is considered as a source point of the scattered energy. The scattering coefficient of light is the fraction of incident light that is scattered by the particles per unit of length traveled by the light beam. Scattering is a valuable optical property of aerosols, often called mass scattering efficiency, and is evaluated as the light scattering quotient of the particles divided by the mass concentration of particulate

matter. Sometimes the molar scattering efficiency is used, divided the molar concentration of a species of aerosol particles.⁴⁶ Within scattering, three mechanisms are considered:

- Mie scattering is observed when the diameters of the atmospheric particles are equal to the wavelength of the radiation and tend to influence the radiation of wavelengths more significant than those affected by rayleigh scattering (Figure 1.12).



Figure 1.12: Patterns of Rayleigh, Mie and Non-selective scattering. Taken from Alkholidi.⁴⁷

- Rayleigh scattering is a result of the interaction of radiation with aerosols and small particles, whose diameter is lower than the wavelength of the radiation with which they interact. These particles tend to scatter on shorter wavelengths; an example of this scattering is the blue color of the sky (Figure 1.13).



Figure 1.13: During broad daylight, the sky is blue due to rayleigh scattering.

- Non-selective scattering occurs when the diameters of the particles or aerosols that are produced by scattering are much higher than the wavelengths, whose interact. An example is the white color of clouds and fog (Figure 1.14).





Extinction phenomenon

In chemistry, the extinction coefficient (also called mass attenuation coefficient or mass absorption coefficient) defines how strongly a substance absorbs solar radiation at a specific wavelength.⁴⁵ On the other hand, in physics, the extinction coefficients are the imaginary part of a refractive index that is related to the absorption of light. It is usually called opacity and is associated with the degree of light that material passes through. When the light is mostly blocked, it is said that the material is opaque. If the flow of light that passes is quite large, the material is classified as translucent; and if the light passes through the material in its entirety, it is considered a material transparent. For technical applications, the transparency or opacity of infrared radiation, ultraviolet light, X-rays, and gamma rays is studied, and in each of them, its opacity function is characterized.

Atmospheric gases can affect the extinction coefficient because it depends on the phenomena of absorption and scattering. Scattering coefficient is essentially for rayleigh scattering, for which the frequency of the incident light does not change in the scattering process. This happens on gas molecules and smaller sizes than the wavelength of incident light; radius less than 0.1 μm . In this case, the aitken particles have great importance in this phenomenon.¹⁵ On the other hand, the contribution of rayleigh scattering to the reduction of atmospheric visibility is minimal compared to other aspects such as the Mie scattering.⁴⁹

1.3.3 Coating of BC particles and its effect on absorption

In the atmosphere, there is always a mixture of different types of particles. There exists a different classification of the particle air composition. If a particle is composed only of the material from which it was originally formed, it is called external mixture; while an internal mixture describes the opposite situation, in which the internal part of a particle is heterogeneous.⁵⁰ In particular, this term is usually applied to secondary particle formation, which the nucleus is the fundamental particle, which has been covered by a layer of another substance(s). It is important to clarify that this nucleus is not necessarily located in the center of the new particle.^{51,52}

Internal mixing usually occurs in the atmosphere, when BC particles collide with each other, forming larger particles.⁵¹ Then are coated with organic and inorganic compounds.^{53,54} This type of mixing also occurs with the particles emitted in the biomass burning, which contain BC in smaller quantities.⁵⁵ Although the primary emission classification of particles of BC sometimes adopts elongated "chain" shapes, it is common during the aging process for BC core to compact and become more spherical as the layer covering becomes thicker.^{51,55}

Internal mixing affects BC absorption due to the lens effect (lensing effect). This consists, when the radiation reaches the outer layer of the particle, deflected to the BC core, where it is absorbed.^{51,55} This means that internal mixing increases the absorption, therefore also black carbon.

Chapter 2

Problem statement

Black carbon particles has two main reasons to be studied. Climatic effects and health problems related to the exposure of BC.

2.0.1 Climatic effects of Black Carbon

Air pollution has many different definitions which explain the same, air affectation. However, a remarkable description from Seinfel and Pandis¹⁰ defined air pollution as the presence of one or more substances in the air at a concentration or duration above their natural levels, with the potential to produce an adverse effect. The significant air precursors pollution can be photochemical oxidants, sulfur dioxide (SO_2) , nitrogen oxides (NO_X) , carbon monoxide (CO), hazardous air pollutants (HAPs), mercury (Hg), lead (Pb), particulate matter (PM₁, PM_{2.5}, PM₁₀ and TSP) and organic carbon (OC).⁵⁶ It has been shown that particulate matter has effects on climate regarding buildings, clouds properties such as brightness, emissivity, and lifetimes; radiative balance therefore warming and climate change.^{4,36,57}

The origin of air pollution is mainly anthropogenic, which the essential sources are: industrial and combustion processes by automobiles. These sources generate an enormous amount of pollutants such as monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), sulfur dioxide (SO_2), black carbon (BC), sulfates (SO_4^{2-}), nitrates (NO_3^{-}), volatile organic compounds (VOCs) and others.⁵

Black carbon can improve those negative climate effects previously mentioned and the

atmosphere temperature. Principally, BC affects climate through its ability to absorb radiation from solar radiation (mostly), then is emitted on infrared radiation. According to previous research, BC is considered to be the second most important human emission pollutants in the present-day in terms of its climate-forcing.⁵⁸ It has been estimated that BC is responsible for 0.3 °C increments in atmospheric temperature.³² The radiative forcing of BC occurs by three ways effects: Direct forcing, when occurs a direct absorption of solar and terrestrial radiation; Albedo forcing of snow/ice; and indirect forcing, resulting in the effect of BC impact on clouds, including its lifetime, reflectivity and composition.^{32,58} The Intergovernmental Panel on Climate Change (IPCC) characterizes the direct effect as "the mechanism by which aerosols scatter and absorb shortwave and longwave radiation, thereby altering the radiative balance of the Earth-atmosphere system."⁵⁹

Additionally, BC contributes to changes on the hydrological cycles (reducing precipitation and evaporation process) and surface visibility, due to the direct absorption of sunlight radiation, therefore re-emit it into the atmosphere as heat.³² Furthermore, BC also absorb the sunlight energy that is reflected by the Earth's surface and clouds, reducing the amount of solar radiation reflected into space by the Earth-atmosphere system.⁶⁰ BC may be as important as CO_2 in causing a rapid loss of glaciers over the Himalayas and Tibet.^{60–62}

2.0.2 Health effects associated with exposure to black carbon

The emission of particles into the atmosphere is a relevant problem at present since air pollution has been associated with health problems in people.^{13,63} Those principal health problems are as allergies, poisoning, respiratory problems and affectation of organs.^{6–8,64} All these mentioned effects usually occur when the aerosols penetrate the lungs or bloodstream.

We already discussed the principal's source emission of BC, and one of them is transportation, specifically diesel exhaust engines. Diesel exhaust has been classified as a probable, likely, and reasonably anticipated human carcinogen by the International Agency for Research on Cancer, U.S. EPA, and U.S. National Toxicology Program, respectively, and regulated as a toxic air contaminant in California.³² Diesel emissions are a significant contributor to overall air pollution.³⁶

According to World Health Organization (WHO),⁶⁵ an estimated of 4.2 million premature

Health problems	Deaths percentage
Lung cancer	29%
Acute lower respiratory infection	17%
Stroke	24%
Ischaemic heart disease	25%
Chronic obstructive pulmonary disease	43~%

deaths globally are linked to ambient air pollution from outdoor emission. In Table, 2.1 shows the most related health complications with its corresponding death percentage.

Table 2.1: Worldwide death percentage due to health problems caused by air pollution. (Data are from [66])

Respiratory problems are the primary health complication due to air pollution because they can produce internal problems such as lungs and heart diseases. Worldwide, preliminary results of global atmospheric chemistry and transport modeling demonstrate that air pollution contamination, specifically anthropogenic sources, causes 2-3 million deaths due to cardiovascular and respiratory disease; and 150000 to 250000 deaths due to lung cancer each year.^{32,67} Additionally, 1.6 million deaths globally are attributable to exposure to indoor air pollution from solid fuel.^{32,67}

Depending on time exposure of air pollution, the risk of having a health problem can increase. The most common symptoms to prevent air pollution health problems are: irritation of eyes, nose, and throat, coughing, chest tightness and shortness of breath.⁶⁶

Chapter 3

Objectives

3.1 General objectives

The main objective of this work was to determine the black carbon particle concentration in the $PM_{2.5}$ atmospheric particles, through the physical properties of aerosols (absorption coefficient, Babs), in Juriquilla and Altzomoni (Mexico) using a photoacoustic extinctioneter.

3.2 Specific objectives

For the fulfillment of the main objective, the following specific objectives were formulated:

- a) Acquire knowledge and skills handling a photoacoustic extinctioneter (PAX).
- b) Determine the absorption coefficient to estimate black carbon concentration, for Juriquilla and Altzomoni.
- c) Quantify the content of the atmospheric black carbon concentration in Juriquilla and Altzomoni.
- d) Obtain the diurnal, weekly and monthly behavior of black carbon concentration present in the atmospheric aerosols PM_{2.5}.
- e) Compare the obtained results with previous reported studies in Mexico and other countries.

Chapter 4

Methodology

4.1 Sampling sites



Figure 4.1: Geographical area of sampling sites: Juriquilla and Altzomoni.

During the period from January 1 to December 31, 2017, a campaign was performed to measure the physical properties of aerosols, therefore to determine the concentration of black

carbon particles. The sampling sites are part of the University Network of Atmospheric Observatories (RUOA, by its initials in Spanish), which are Juriquilla and Altzomoni. The main reason for both selected sites was to be able to compare a growing city, which has industries, transportation, and other anthropogenic emissions (Juriquilla), with a free of anthropogenic emission (Altzomoni).

The atmospheric observatory of Juriquilla (JQRO) is located in the northwest of Santiago de Queretaro (Figure 4.1) within University Campus on the roof of the Multidisciplinary Teaching and Research Unit (20.7030°N, 100.4473°W) at 1 945 m above mean sea level. JQRO is characterized by academic buildings interspersed with vegetation, with small anthropogenic emissions near the sampling site (Figure 4.2). However, Juriquilla is a growing site due to the constructions new that are emerging. As a result, the population of the zone tends to increase through the years, leading to an increase in atmospheric pollution.



Figure 4.2: University Network of Atmospheric Observatory in Juriquilla.

The atmospheric observatory Altzomoni (ALTZ) is located approximately 60 km southeast of the center of Mexico City, 70 km northeast of Cuernavaca, and 50 km west of Puebla in the coordinates 19.1187°N, 99.6552°W at 3 985 m above mean sea level (Figure 4.1). The observatory is in the slopes of the Iztaccíhuatl volcano, within the Izta-Popo National Park and there are no significant local sources of anthropogenic contaminants. It is situated in the national park of Izta-Popo-Zoquiapan with only a single road nearby, that is principally used to bring weekend tourists to the park center and is approximately five km to the southeast of the research site(Figure 4.3).⁶⁸



Figure 4.3: University Network of Atmospheric Observatory in Altzomoni. Taken from RUOA.⁶⁹

4.2 Instrumentation

To measure the physical properties (absorption and scattering coefficient) and the concentration of black carbon present in atmospheric aerosols ($PM_{2.5}$), a photoacoustic extinctiometer was used (PAX, Figure 4.4). For this particular instrument the measured parameters are scattering (Bsca) and absorption coefficient (Babs); meanwhile, the derived parameters are black carbon, extinction coefficient, single scattering albedo (SSA) and dew point.



Figure 4.4: Photoacoustic Extinctiometer overview (PAX). Taken from Droplet Measurements Technologies.⁷⁰

The PAX uses a modulated diode laser at a wavelength of 1500 Hz, which simultaneously measure in-situ light absorption (Babs) and scattering (Bscat) of the aerosol particle (Figure 4.5). This sensor was evolved from the Photoacoustic Soot Spectrometer (PASS) developed at the University of Nevada^{71,72} and commercialized by Droplet Measurement Technologies.^{73–76} Additionally, PAX has 375, 405, 532 and 870 nm single wavelength versions which have identical measurement cells and differ only in a few optical components.⁷⁷ The PAX whose measurements are reported in the current study uses the 870 nm laser. It has an internal

vacuum pump that causes the instrument to suck air with a flow of $1 L min^{-1}$. Once the air flow enters the device, it is divided in two parts; one part goes to a nephelometer where the scattering is measured, while the other goes to a resonator where the absorption is calculated by a photoacoustic sensor (Figure 4.5).



Figure 4.5: Diagram showing the scattering (blue dashed region) and absorption (green dashed region) cells in the photoacoustic extinctioneter (PAX). Taken from Droplet Measurements Technologies.⁷⁰

The measurement of the absorption of light is done using photoacoustic technology, where the laser beam is directed through the flow of aerosols, which absorb this radiation and passes to an excited state, which is unstable. It requires the elimination of energy to return to its ground state. This energy emits in form of heat is transferred to the surrounding, producing pressure waves that can be detected easily with a sensitive microphone. The amplitude of the waves is proportional to the absorption coefficient. Meanwhile, to measure light scattering, the PAX has an integrated nephelometer, where at a lower concentration of particles present in the sample, the less light intensity is dispersed and at higher concentration more intensity of light arrives at the sensor. The intensity of light and the concentration of particles in the sample are proportional. The measurement of scattering responds to all types of particles present in the air, regardless of the chemical composition, the state or morphology.⁷⁰

The PAX was calibrated before and after the campaign according to the method recommended by Droplet Measurement Technologies⁷⁰ using ammonium sulfate particles and soot particles at high concentrations, following the procedure in the PAX Operator Manual.⁷⁸ Once the absorption coefficient is obtained, the black carbon concentration is calculated by using equation 4.1. A value of the mass absorption efficiency (MAC) = 4.74 was used to estimate black carbon concentrations at 870 nm, which was derived using the correction to the 7.5 value recommended by Bond and Bergstrom.⁵⁰ Only the particulate matter with a size less than 2.5 μm in aerodynamic diameter (PM_{2.5}) was measured, by setting the inlet of the PAX with PM_{2.5} cutoffs.

$$BC = \frac{Babs}{MAC} \tag{4.1}$$

Where, BC is the concentration of black carbon in $\mu g \ m^{-3}$, MAC is the mass absorption coefficient, and Babs is the value of the absorption coefficient in m^{-1} .

4.3 Validation measurements

To carry out the data analysis of the physical properties and the concentration of black carbon in atmospheric aerosols $PM_{2.5}$, it was necessary to perform the following validation data procedure:

- 1. Elimination of negative readings (less than zero)
- 2. Elimination of values equal to zero
- 3. Elimination of anomalous peaks

To apply the first and second filter, it was necessary to develop a program in the Matlab R2015B software in which the condition of eliminating data, was to assign values of BC concentration less than or equal to zero.

The third filter demanded two procedures. The first consisted of plotting the whole time series and observing the peaks in which the concentrations changed suddenly. There was no gradual increase of BC concentration, that was maintained for a considerable time (at less a couple of minutes) that could be associated with a specific emission phenomenon. The second procedure consisted in realize a scattering plot where the concentration values of each of the coefficients (scattering values) were plotted both on the "x" and "y" axis; however, these values were offset by one reading. The values for the "y" axis started at time two while those from the "x" axis started at time 1. This way could discard some readings that came out of the trend of the data. In Figure, 4.6 shows an example of the scattering plot was develop. It is worth mentioning that it was necessary to review the data that came out of the trend, if they could corresponded to a holiday or a rush time in which there are higher emissions of pollutants, the data was considered valid.

	А	В	С	D	E		F		G		Н	1
1	Bsca(1/Mm)	Bsca(1/Mm) [Offset]	Bsca(1/Mm) [Non-Offset]									
2	11.5813		11.5813	Scattering Coefficient Graph								
3	9.464742	11.5813	9.4647	45								
4	7.223415	9.4647	7.2234	40								
5	12.16813	7.2234	12.1681									
6	8.257953	12.1681	8.258	30 E			_	_		200	•	
7	13.36836	8.258	13.3684	<u>O</u> 25					6.26			
8	14.73364	13.3684	14.7336	Ę 20			of call		ans.			
9	23.08063	14.7336	23.0806	B 15	•			30				
10	19.73842	23.0806	19.7384	a 10	-	£ al	4					
11	25.14481	19.7384	25.1448	5								
12	21.39465	25.1448	21.3946	0	-	40	45				- 40	
13	20.6151	21.3946	20.6151	0	5	10	15	20	25 :	30 33	5 40	45
14	22.0145	20.6151	22.0145				Bsca	,1/m) [N	lon-Offset	1		
15	27.63024	22.0145	27.6302									
16	34.07963	27.6302	34.0796									
17	35.5369	34.0796	35.5369									
18	34.50906	35.5369	34.5091									
19	38.27183	34.5091	38.2718									
20	31.35327	38.2718	31.3533									
21	31.28283	31.3533	31.2828									
22	31.06414	31.2828	31.0641									
23	32.76516	31.0641	32.7652									
24	38.338	32.7652	38.338									
25	33.89516	38.338	33.8952									

Figure 4.6: Scattering plot example for validation procedures.

Once the data (validated) measured every 5 minutes, it was possible to realize the averages through the development of a program in the Matlab R2015B software and later plotted with mainly Open Air package of the R studio software.

Chapter 5

Results and discussion

During 2017 a meterelogical campaign was carried out in atmospheric observatory Juriquilla (UNAM) and atmospheric observatory Altzomoni (UNAM), to evaluate both the physical properties of $PM_{2.5}$ particles through quantification of absorption coefficient and the concentration of black carbon.

5.1 Annual black carbon behavior

The concentration of BC on Juriquilla (BCJU) and Altzomoni (BCAL) was performed for different time variations, to recognize their daily, weekly, monthly, and seasonal behavior. The annual concentration of both sites is shown in Figure 5.1. Juriquilla has an annual average value of 0.623 $\mu g m^{-3}$, while Altzomoni 0.487 $\mu g m^{-3}$. It is important to mention that during the months of August to September, the data was not collected, making impossible to describe BC concentration, this was due to the maintenance procedure of the PAX.



Figure 5.1: Concentration of black carbon through 2017, on Juriquilla (BCJU) and Altzomoni (BCAL).

In Figure 5.2 shows the monthly variation of black carbon during 2017, where the maximum month's concentration for Juriquilla were: January, May, and December; meanwhile for Altzomoni were: May, November, and December.



Figure 5.2: Monthly variation of black carbon on Juriquilla (Blue) and Altzomoni (Red).

The month of May it was a month belonging to the warm season in which a maximum concentration was obtained close to the months of January and December. During this month, the solar radiation reaching the Earth's surface is maximum, which causes photochemical reactions to occur with higher intensities. This leads to the oxidation of many organic compounds present in the atmosphere, which results in a higher absorption coefficient and, therefore, a higher concentration of black carbon.⁷⁹ It has also been proven that these particles are coated with a material that spreads radiation when there exist secondary particles, remaining the atmosphere, and are composed with BC nuclei.⁸⁰ This causes greater absorption due to the coating process and the BC core, which also produces higher readings of the absorption coefficient, therefore increasing black carbon concentration.



Figure 5.3: Diurnal variation of black carbon on Juriquilla (Blue) and Altzomoni (Red).

To identify the emission source and trends of BC, diurnal cycle plot was performed to show changes of BC by day for each place (Figure 5.3). The diurnal cycle concentration of BCJU shows two well defined time-periods (bimodal behavior). The first peak starts increasing from 07:00 h with a concentration of $1.4 \ \mu g m^{-3}$ and the second peak with 0.8 $\mu g m^{-3}$ at 19:00. The first peak is associated with the daily starting vehicular and industrial activities.^{77,81} On the other hand, the second peak is a consequence of the return from work activities, also vehicular and industrial activities. The difference in BC concentration is a clear indication of the different traffic density and the influence of industrial operations. In Altzomoni, since there is not a traffic or industrial impact, the diurnal graph shows a broad



peak in the afternoon. The peak of BCAL is at a 15:00 h with a concentration of 0.8 $\mu g m^{-3}$, influenced by external BC concentration emitted from surrounded cities as Mexico City.⁶⁸

Figure 5.4: Weekly variation of black carbon on Juriquilla (Blue) and Altzomoni (Red).

The Figure 5.4 shows a weekly cycle, to reconfirm the reliable data of the previous graphs. BCJU shows a tendency from Monday-Friday, with a peak at 07:00 h and 19:00 h. Meanwhile, Saturday and Sunday demonstrates a decrease in concentration associated with a reduction in traffic emissions, weekly work, and industrial activities. Nevertheless, on Saturday still shows the same tendency, but lower in concentration. The reason is that the Atmospheric Observatories of Juriquilla is situated at the university UNAM which still have classes on this day, influencing the level of BC. In Altzomoni, there is not a specific tendency, but it shows a maximum peak between 12:00-18:00 h from Monday to Friday. Moreover, on the weekend there is a diminished of 0.2-0.4 $\mu g m^{-3}$ which can be associated with a decrease of activities of the surrounded cities which affect the measure of BCAL.

5.2 Seasonal variability of black carbon

Considering the meteorological parameters (temperature and precipitation) reported by the $RUOA^{69}$ in 2017 at Juriquilla and Altzomoni, and the previous variation in concentration

through the different times of the year of BCJU and BCAL, BC study was divided into three seasons: dry hot season from March to May (S1); dry cold season from October to February (S2), while the period from June to September (S3) was considered a rainy season. Figure 5.5 shows the difference of BC in each season on Juriquilla and Altzomoni.

In the case of Juriquilla (Figure 5.5) it is observed that the behavior is very similar in the three seasons, however different maximum concentrations are appreciated, obtaining the highest value in the cold season. It is due to the ow height of the boundary layer that causes the contaminants to be in a smaller volume close to the surface. On the other hand, on the rainy season, the concentration is the lowest, which is to be expected since the wet deposition process occurs.



Figure 5.5: Seasonal variation of black carbon concentration on Juriquilla.

This behavior related to the height of the boundary layer has been proven in different part of the world, such is the case of France where the relation between the height of the boundary layer and the concentration of atmospheric aerosols was determined.⁸² The highest temperatures were on summer season ($12.2 \pm 2.9 \,^{\circ}$ C); meanwhile, winter has the lowest value ($1.7 \pm 1.8 \,^{\circ}$ C). Within this, winter season shows the lowest height of BL, resulting in a high concentration of aerosols.⁸²

Meanwhile, in Altzomoni (Figure 5.6), it is observed that the behavior of the diurnal seasonal cycle is the same with different maximum values as was found in Juriquilla. However,

the main difference in this sampling site is the maximum value obtained in the dry season. This behavior is because in this season the maximum height of the boundary layer is reached, therefore there is a significant transport from Mexico City to our sampling site in this season. This affirmation is confirmed observing the behavior in the cold dry season since there is not enough boundary layer height, resulting in a efficient transport from Mexico City to Altzomoni causing the concentration of BC to decrease. As previously discussed, the rainy season has the lowest BC concentration due to the process of deposition of moisture that occurs in the atmosphere provoking a decrease of contaminants (BC).⁸³



Figure 5.6: Seasonal variation of black carbon concentration on Altzomoni.

5.3 Comparison of black carbon concentrations with other studies

To determine if the results obtained are in the order of those reported studies, it was decided to compare results with different researches in Mexico and other countries. This comparison is made since as mentioned that air pollution is a major environmental health problem affecting people to developed and developing countries alike. According to the World Health Organisation (WHO),⁶⁵ the mortality in cities with high levels of pollution exceeds by 15–20 % that observed in relatively cleaner cities.⁸⁴

Sampling Site	Black Carbon [$\mu g m^{-3}$]	References
Metropolitan area of Chile	3.5 - 10.4	Artaxo et al. 1999
Helsinki, Finland	2.2 - 4.2	Viidanoja et al., 2002
Hong Kong, Japan	6.4	Ho et., 2004
Xi'an, China	5.0 - 10	Cao et., 2006
Los Angeles, USA	3.6 - 27.6	Faning et al., 2007
Juriquilla	0.5 - 1.49	This work
Altzomoni	0.34 - 0.71	This work

Table 5.1: Comparison of black carbon data concentration with world's most polluted cities.

In Table 5.1, we can observe the concentration of polluted cities around the world. It should be noted that the values obtained in the present work for the two sampling sites were lower than those reported for these large cities. One of the highest levels nowadays is China, specifically Xi'an. This particular city has a population more than 12 million.⁵⁶ For example, Figure 5.7 shows that Xi'an has a higher level of PM_{2.5} emission among other important cities such as Beijing and Shanghai, who has more population. Additionally, in the same Figure are Chinese national standards for air quality standards (WHO AQG, US NAAQS, WHO Interim Target 1,2 and 3; Chinese NAAQS). Those developed countries are out of the range for every Chinese standard.



Figure 5.7: Annual $PM_{2.5}$ levels ($\mu g m^{-3}$) in Beijing, Shanghai, Guangzhou, and Xi'an with the Chinese national standards and international air quality standards. Taken from IARC.⁵⁶

Table 5.2 shows the black carbon concentration from different studies in Mexico and our reported values. We can observe that our results were lower, indicating that the amount BC emission is higher for those sites in Mexico. If we compare meteorological parameters, demography, and economic aspects for each city, we can understand the differences in concentration for each place.

Sampling Site	Black Carbon [$\mu g m^{-3}$]	References
Chapultepec, C.D.M.X	3.4	Miranda et al., 1992
La Merced, C.D.M.X	4.5	Edgerton et al., 1999
Pedregal, C.D.M.X	2.9	Watson et al., 2001
C.D.M.X	3.4 - 30.2	Chow et al., 2001
CENICA, C.D.M.X	1.7 - 7.7	Salcedo et al., 2006
Centro, Guadalajara	1.3 - 8.7	Limon-Sanchez et al., 2011
Vallejo, C.D.M.X	2.2	Retama et al., 2015
Juriquilla	0.5 - 1.49	This work
Altzomoni	0.34 - 0.71	This work

Table 5.2: Comparison of black carbon data concentration with other studies in Mexico.

Chapter 6

6. Conclusion

Through this research, it was possible to observe the difference of BC concentration of a populated city (Juriquilla) and a rural place (Altzomoni). In Juriquilla its maximum concentration was January, May, and December. Its diurnal variation corresponds to a bimodal behavior showing two peaks, which belongs to starting activities (07:00 h) and returning of those activities (19:00 h). Additionally, a "weekend effect" is observed during all three seasons. The concentrations increase between workdays and decrease on weekends. Another characteristic is shown in the rainy season. This season shows the lowest concentration, as previously explained, due to the removal of the aerosol particles.

Altzomoni presented an unimodal behavior in the diurnal variation. A peak at (15:00 h) is exposed resulting from emissions of surrounded cities (Mexico City). As well as in Juriquilla, a "weekend effect" is presented for Altzomoni. The lowest concentration is shown on Saturday and Sunday; meanwhile, Monday to Friday demonstrates higher values of concentration. The seasonal variability demonstrates lower concentration in the rainy season, as expected.

According to the results obtained and previous studies, BC demonstrates a significant pollutant of the study, since there is a considerable influence on the environment and human health. Our reported values were much lower since the comparison of international sampling sites (Table 5.1) has different characteristics (demography, economics, geography, and others). Although in Mexico sampling sites, the concentrations were similar (Table 5.2).

Additionally, is essential to recognize the policy for this type of pollutant since there is no jurisdiction of BC in any country.³⁶ Regulate black carbon emission for transportation source

can be done by different strategies such as non-road diesel sources, heavy-duty diesel regulation, diesel emission reduction campaigns and many others. However, it is needed to establish policies for BC to cover climate legislation. Within this, we can effectively control black carbon. The Organisation for Economic Cooperation and Development (OECD) provides strategies for developing countries to address diesel emissions. Furthermore, make awareness to people of these environmental and health issues. As well as WHO,⁶⁶ which recommends, in order to reduce air pollution, to invest in energy-efficient power generation; improves domestic, industry and municipal waste management; make greener and more compact cities with energy-efficient buildings; built safe and affordable public transport systems; provide universal to clean, affordable fuels and technologies for cooking heating and lighting; and reduce agricultural waste incineration, forest fire and certain agro-forestry activities.⁶⁵

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