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Review

A Review on the Characterization and Measurement of the Carbonaceous Fraction of Particulate Matter

Mauricio A. Correa-Ochoa [1], Roxana Bedoya [1], Luisa M. Gómez [1], David Aguiar [1], Carlos A. Palacio-Tobón [2] and Henry A. Colorado [3,*]

[1] Grupo de Investigación, Laboratorio de Monitoreo Ambiental G-LIMA, Universidad de Antioquia UdeA, Calle 70 N°. 52-21, Medellín 050010, Colombia
[2] Grupo Giga, Universidad de Antioquia UdeA, Calle 70 N°. 52-21, Medellín 050010, Colombia
[3] CCComposites Laboratory, Universidad de Antioquia UdeA, Calle 70 N°. 52-21, Medellín 050010, Colombia
* Correspondence: henry.colorado@udea.edu.co

Abstract: The carbonaceous particles represent a significant fraction in the particulate matter (PM) and are considered an environmental hazard due to their effects on climate and health. The main goal in this research is to identify and analyze the scope that have been achieved so far on the characterization and measurement of the carbonaceous fraction present in PM, a great contribution to global pollution and thus to the deterioration of public health. The ProKnow-C methodology was used to build a bibliographic portfolio and perform a bibliometric and systemic analysis of the information found in the chosen databases. The contribution of these carbonaceous compounds to PM is very significant, reaching values up to 50%. The most used methods for the determination of organic and elemental carbon are thermo-optical reflectance and transmittance. Positive Factorization models are used worldwide to determine potential sources of particulate matter emissions. Even though various studies have been developed to understand these carbonaceous substances, there are several limitations in the measurements and limited knowledge on the subject. The positive outcomes and future possibilities were analyzed as well.

Keywords: pollution; particulate matter; organic carbon; elemental carbon; characterization; measurements

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1. Introduction

Atmospheric pollution is a global problem that is closely related to the way in which man satisfies his needs and develops the everyday activities, which depend on industrial production, energy generation, and transportation, all of them generating atmospheric pollutants that deteriorate air quality [1]. A pollutant of interest in the deterioration of air quality is particulate matter (PM), also known as atmospheric aerosol. PM is defined as the suspension of fine solid or liquid particles, with a wide variety of anthropogenic and natural sources, whose presence in the atmosphere can be due to direct emissions or secondary formation from gaseous precursor species [2,3]. Particulate matter can be classified according to its origin, formation mechanism, chemical composition, and size. PM_{10} and $PM_{2.5}$ particles are those whose aerodynamic diameter is equal to or less than 10 µm and 2.5 µm, respectively [4]. This contaminant is the cause of various effects on human health, mainly generating pulmonary and cardiac effects. Exposure to PM not only significantly affects children and older adults, but especially people with lung and heart diseases [2].

Due to the various emissions sources, PM has a varied geochemical composition. Within the compounds of PM, carbon (organic and inorganic) is especially relevant, since various studies have found that it represents a significant percentage of its contents [5–7], especially black carbon, which is defined as an unwanted by-product of the incomplete combustion of fossil fuels and biomass, and encompasses a wide variety of carbonaceous

substances, from partially charred plant residues to highly graphitized soot [8]. Black carbon is a solid composed almost entirely of elemental carbon, which absorbs solar radiation at all wavelengths [9]. Brown carbon is another organic carbonaceous particle emitted in biomass burning processes able to absorb ultraviolet and visible solar radiation [10].

There are several methods and equipment for on-line and offline measurements of carbonaceous aerosols, which are used to know not only the optical properties but also the concentrations of these compounds. Generally, optical properties are tested by measuring the light absorption with spectrophotometers, aethalometers, absorbance analyzers, and more recently, using thermo-optical equipment [11]. One of the most widely used equipment is the aethalometer, which measures the attenuation of light passing through a filter on which the carbonaceous aerosol is deposited. This attenuation signal, together with the deposition area and the volume of air sampled, is used to determine parameters such as the absorption coefficient [12]. Thermo-optical processes are most used for off-line measurements, during these processes ambient air samples are collected on heat resistant filters and a small portion of the filter is subjected to temperature increases and stepwise changes of atmospheres (usually inert helium atmospheres and then helium/oxygen mixture) [13]. The carbon present in the PM sample undergoes a volatilization process and is oxidized to carbon dioxide (which can be determined by an infrared detector) or reduced to methane, quantified by a flame ionization detector [14]. Several temperature protocols exist for these methods, differing in the temperature set points used and the residence times at each temperature step [15]. Usually, the filter material used for the determination of these aerosols is quartz fiber, due to its resistance to high temperatures.

These carbonaceous aerosols have been considered an environmental problem because they affect human health and climate change. In terms of health effects, exposure to this substance can be associated with cardiovascular and respiratory diseases, cancer, and even, congenital malformations [16–19]. In the case of climate effects, elemental carbon, due to its special characteristic of strong absorption, contributes to the warming of the atmosphere and the darkening of the surface, disturbing or influencing the hydrological cycle through changes in variables such as latent heat, modifying circulation, and convection patterns [9]. Black Carbon is considered the second largest contributor to global warming after carbon dioxide [7]. On the other hand, organic carbon (OC) is a dispersal medium and exerts a negative climatic forcing influence [6].

Some studies have used the effective carbon ratio (ECR), which is an indication of atmospheric warming due to carbonaceous aerosols [19–21]. This concept was proposed by Safai, et al., in 2014 [22] to better associate carbonaceous atmospheric aerosols with climate change. This relationship is defined as ECR = Secondary Organic Carbon/(Primary Organic Carbon + Elemental carbon). Primary organic carbon and elemental carbon (POC and EC) are potential light absorbing species and therefore contribute to global warming. Secondary organic carbon (SOC) scatters solar radiation. High values ($\geq$0.7) of ECR indicate low POC and EC, leading to reduced atmospheric warming effects of combustion aerosols and increased radiation scattering properties. Low ECR values ($\leq$0.3) indicate high POC and EC concentrations and contribution to global warming.

Figure 1 shows typical images of critical polluted days during 2022 at Medellin, Colombia. Figure 1a shows a long-distance view of the valley, showing the pollution during the day hours. Figure 1b shows typical filters used for collecting samples. Figure 1c,d show PM emissions of fixed and mobile sources respectively.

This review article summarizes and analyses the current state of the art of the characterization and measurements of the carbonaceous fraction present in PM. Since this is a critical subject for both environment and human health, this research analyzes the gaps in knowledge, advantages, and opportunities of the current technologies, and draw plans and perspectives to have initiatives, research, and developments that contribute to the mitigation of such a global issue.

Figure 1. (**a**) Pollution in Aburrá Valley during a period of air quality episode management in 2022; (**b**) Particulate matter filters collected at monitoring stations in the Aburrá Valley; (**c**) Emissions from fixed sources; (**d**) Emissions from mobile sources.

2. Materials and Methods

The current study identifies and analyzes the scientific production available on research regarding the characterization and measurement of the carbonaceous fraction of particulate matter (PM), especially carbonaceous aerosols, such as brown carbon and black carbon. The methodology used was the Knowledge Development-Constructivist process, known as the ProKnow-C methodology. It consists of four phases or structural blocks [23,24]: (a) Selection of the bibliographic portfolio; (b) Bibliometric analysis; (c) Systemic analysis; and (d) Research questions. Figure 2 displays the methodology used in this research.

For the selection of the bibliographic portfolio, the topic of interest, keywords, and databases were established. The search commands, or equations, were built by combining the keywords and the Boolean operators. The delimitations were established, which included the type of document, language, and publication year, all this, according to the methodology established by Enssil in 2014. Thus, the search was limited only to scientific articles from the year 2013 in English and Spanish, but due to the large volume of information, another document selection filter was used from 2018 onwards.

The documents found were stored in the Mendeley bibliographic manager, obtaining an initial database that was later filtered to discard documents that were not related to the topic of interest. A bibliometric analysis was carried out on the already consolidated bibliographic portfolio, where characteristics of the entire set of documents such as authors, journals, keywords, and publication dates are identified, and thus, the representativeness of the documents was analyzed. Then, having the representative articles of the topic of interest, a complete reading of them was carried out to make a systemic analysis [24]. Table 1 summarizes the process carried out with the ProKnow-C methodology.

Figure 2. Process carried out with the ProKnow-C methodology.

Table 1. Search commands used to obtain the investigated information.

Command	Search Commands
1	"Determination" AND "Carbon Compounds" AND "Particulate Matter"
2	"Chemical Analysis" AND "Carbon Compounds" AND "Particulate Matter"
3	"Techniques" AND "Determination" AND "Carbon compounds" AND "Particulate matter"
4	"Techniques" AND "Chemical Analysis" AND "Carbon Compounds" AND "Particulate Matter"
5	"Carbon" AND "Air pollution" AND "Particulate Matter" AND "Emission sources"
6	"Characterization" AND "Carbon compounds" AND "Air pollution"
7	"Characterization" AND "Carbon compounds" AND "Air pollution" AND "Particulate Matter"
8	"Emission sources" AND "Carbon compounds" AND "Air pollution" AND "Particulate Matter"
9	("Carbon compounds" OR "Carbon") AND "PM10" AND "PM2.5" AND "Determination" AND "Techniques"
10	"Techniques" AND "Chemical Analysis" AND "Determination" AND "Carbon compounds" AND "Particulate matter" AND "Filters"
11	"Brown Carbon" AND "Black Carbon" AND "Particulate Matter"
12	"Brown Carbon" AND "Black Carbon" AND "Particulate Matter" AND "Water Soluble Organic Carbon"
13	"Brown Carbon" AND "Black Carbon" AND "Particulate Matter" AND "Water Soluble Organic Carbon" AND "Air Pollution"
14	"Water Soluble Organic Carbon" OR "Brown Carbon" OR "Black Carbon" AND "Characterization" AND "Air Pollution"
15	"BrC" AND "BC" AND "WSCO" AND "PM" AND "Chemical Analysis" AND "Air Quality"
16	"Water Soluble Organic Carbon" AND "Particulate Matter" AND "Air Pollution" AND ("Techniques" OR "Chemical Analysis")
17	"Water Soluble Organic Carbon" AND "Characterization" AND "Particulate Matter" AND "Air Pollution" AND ("Chemical Analysis" OR "Techniques")
18	"BrC" AND "BC" AND "WSCO" AND "PM" AND "Air Quality" AND ("Chemical Analysis" OR "Characterization" OR "Techniques")

3. Results

A total of 9 databases and 18 search commands were selected from the search, finding 3507 documents. Eliminating documents without data access, repeated, or unrelated to the subject, a total of 2456 articles were obtained. Subsequently, a consolidated of 853 representative articles were filtered. This value represents a large volume of information, and thus, the search was delimited from the year 2018 onwards, obtaining a total of 462 articles. From these, 146 were selected as representing the bibliometric matrix of the state of the art. Finally, 110 articles were targeted as corresponding to the systemic analysis of this search (Table 2).

Table 2. Compilation of results of the search from the current research.

Compilation of Results	
Raw articles	3507
Articles not repeated and with access	2456
Representative articles (2018 onwards)	462
Bibliographic portfolio	110

Figures 3 and 4 show which are the countries and journals with the highest number of articles related to the topic of characterization and measurement of carbon in PM, according to the selected articles. It is observed that India and China lead the scientific production related to this topic.

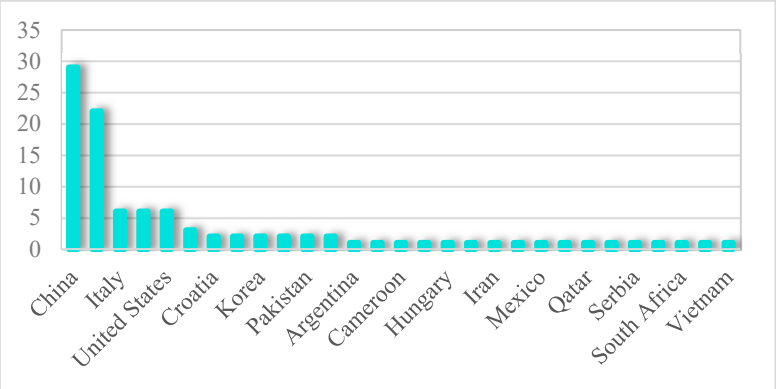

Figure 3. Number of Articles per country.

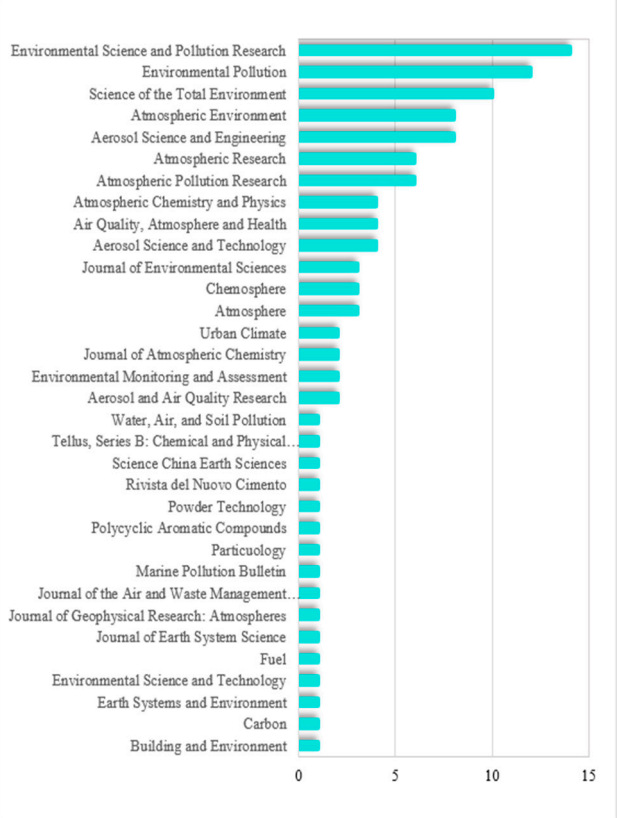

Figure 4. Number of Articles per Journal.

4. Discussion

4.1. Carbonaceous Fraction Present in Particulate Matter

Carbonaceous aerosols constitute representative fraction within the particulate matter (PM). These species are usually classified as organic and elemental carbon [6,25,26]. Some studies have determined that the contribution of this fraction to PM2.5 particulate matter can be 25% for organic carbon (OC) and 22% for elemental carbon [27]. Other studies mention that the carbonaceous fraction may represent 50% of the PM [28]. Buchunde et al., found that total carbon mass accounted for about 55% and 90% of $PM_{2.5}$ during winter and summer seasons, respectively. OC concentration contributed 42% (in winter) and 79% (in summer) to the $PM_{2.5}$ concentration, while EC concentration contributed about 13% (in winter) and 12% (in summer) of $PM_{2.5}$ [29]. Other authors such as Moretti et al., [17] have found that that carbonaceous compounds contribute between 20% and 35% of PM_{10} and between 20% and 45% of $PM_{2.5}$.

These carbonaceous particles mainly originate during the incomplete combustion processes of fossil fuels and biomass [30]. Elemental Carbon is considered as the fraction of carbon that does not volatilize at low temperature, with prolonged photochemical useful life, is generally classified as a primary pollutant; while the OC that represents the organic fraction of the carbonaceous material, can come from primary and secondary sources, the latter being the product of oxidation of volatile organic compounds that are present in the atmosphere during photochemical reactions [17,26,28,31]. Organic carbon encompasses organic compounds (aliphatic, aromatic compounds and acids), and it is hygroscopic, acting as a cloud condensation nucleus and a scattering system for the solar radiation. In contrast, elemental carbon is hydrophobic and efficiently absorbs solar radiation [32].

Within these two classifications, other components of interest can be found, such as black carbon, which encompasses a wide variety of carbonaceous substances and is an almost impure form of elemental carbon with structures very similar to graphite [8]. Some of the definitions of this component of PM have been based on its physical or chemical properties, since it is the fraction of total carbon that presents high absorption in a broad spectrum of visible and infrared wavelengths. Black carbon (BC) is frequently used for optical determination of the carbon content in the PM with attenuation or absorption measures. Black carbon aerosol measured by optical absorption methods is known as equivalent black carbon [33]. Measurements of the concentrations of this component are complex since it does not have a sufficiently clear chemical definition [28,34].

Another compound of interest that is part of the carbonaceous fraction of the particulate matter is brown carbon, which has a brownish or yellowish appearance and is made up mainly of carbonaceous organic compounds. It is generally associated with the burning of biomass, biofuels and has little or even no amount of elemental carbon [8,28]. Generally, carbonaceous aerosols are mostly composed of organic carbon (OC) reaching values up to 90% of the total carbon, so elemental carbon (EC) represents a low contribution, being of around 10% [35,36]. This OC can also be subdivided as primary organic carbon (POC), which is derived primarily from combustion activities, and secondary organic carbon (SOC), formed due to oxidation of gaseous precursors such as volatile organic species or through aging of POC in the atmosphere [29].

Water soluble organic carbon (WSOC) can contribute substantially to the mass of organic carbonaceous aerosols, as it can account for approximately 10–80% of organic carbon [37,38]. In addition, it can alter the hygroscopic properties of aerosols and affect global climate change because some of its components, for example, brown carbon and humic substances have light absorbing properties [39]. This compound generally has several sources such as primary emission from biomass burning, fossil fuel combustion, and photochemical oxidation of organic precursors of anthropogenic and biogenic origin [40]. Biomass burning is a major source of WSOC, so along with levoglucosan and potassium are considered good tracers of this emission source [30,41].

Table 3 summarizes some definitions and properties of carbonaceous species such as elemental carbon, organic carbon, black carbon, and brown carbon.

Table 3. Definitions and characteristics of some carbonaceous species.

Carbonaceous Specie	Definition	Emission Sources	Properties or Characteristics
EC [1]	Primary pollutant that originates from the incomplete combustion of carbon-based fuels. EC occurs in an inert state in the atmosphere; therefore, it can be a direct indicator of the degree of air pollution in urban areas [42,43]. It refers to the fraction of carbon that is oxidized in the combustion analysis above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere [10].	It is generated in the combustion of fossil fuels and the burning of biomass [20,44].	Ability to absorb solar radiation causes positive radiative forcing, generating impacts on climate change. It is ranked as the second most important contributor to global warming after CO_2 [43]. It is the fraction of TC carbon that does not volatilize at low temperatures, generally below 550 °C [28]. It plays an important role in reducing visibility [44]. It is highly refractive [29].
OC [2]	It can be divided into primary and secondary OC. Primary OC is emitted from biogenic and anthropogenic sources. Secondary OC is formed through chemical reaction of gaseous precursors, including volatile organic compounds [42,43].	The main anthropogenic sources of OC in the atmosphere are vehicle exhaust and combustion of fossil fuels and biomass [29]. Other sources may be the degradation of carbon-containing products (e.g., vegetation, windblown biological particles) [17]	It has an impact on climatic change due to its ability to absorb and scatter radiation [44]. It can act as cloud condensation nuclei [44]. It comprises a wide variety of organic compounds (aliphatic, aromatic and acid compounds) [22].
BC [3]	It is a kind of carbonaceous particle in the air that forms during combustion and is emitted when there is insufficient oxygen and heat available for the combustion process to completely burn the fuel [45]. BC is also operationally defined as the TC fraction that exhibits high absorption over a broad spectrum of visible and infrared wavelengths. The acronym BC is frequently used to identify the results of optical determination of carbon content in PM, as in the case of attenuation and/or absorption measurements [28].	Anthropogenic sources such as diesel engines and to a lesser extent gasoline engines. Utility generating units that use fossil fuels. Industrial boilers. Residential combustion sources (furnaces, fireplaces, wood stoves). Open biomass burning sources [8].	Black carbon is the most effective form or particulate matter, by mass, at absorbing solar energy [8]. BC can absorb a million times more energy than CO_2 [9]. A major climate warming pollutant in regions affected by combustion emissions [9]. BC originates as tiny spherules, ranging in size from 0.001 to 0.005 micrometers (μm), which aggregate to form larger particles (0.1 to 1 μm) [9].
BrC [4]	It is another product of incomplete combustion. BrC particles, referred to as brown carbon to reflect its characteristic brown appearance, are found in biomass and biofuel combustion soot and contain little or no elemental or black carbon [8]. BrC is a fraction of OC generally associated with biomass burning [28]. BrC can be directly emitted as a product of incomplete combustion, or it can be formed in the atmosphere as pollutants age [9].	Atmospheric BrC can come from biomass burning, coal combustion, secondary formation and vehicle emissions [46].	It contributes considerably to the absorption of the visible and ultraviolet regions of the light spectrum [46]. Is less efficient at capturing solar energy than BC [9]. It can be referred to as “tar balls” or “carbon spheres”, ranging in diameter from 0.03 to 0.5 μm [9]. The half-life of BrC in the atmosphere during biomass burning is 9 to 15 h, although it varies from case to case [47].

[1] EC: Elemental Carbon; [2] OC: Organic Carbon; [3] BC: Blac Carbon; [4] BrC: Brown Carbon.

As mentioned above, carbonaceous aerosols make up a large part of the particulate matter (PM). Below is Table 4 with some studies that have tried to determine the contribution of these components to the particulate matter.

Table 4. Contribution of the carbonaceous fraction to PM.

Percentage	Carbonaceous Aerosol	PM Size	Place	References
25%, 22% (KS Site) 35%, 8% (BG Site)	OC [1], EC [2] OC, EC	$PM_{2.5}$	Mumbai, India	[27]
41%, 53%	EC	TSP	Kathmandu Valley, Nepal	[48]
~30%	EC	$PM_{2.5}$	Changzhou, China	[49]
11.8%	Carbon compounds	$PM_{2.5}$	Nanchang subway, China	[50]
38% 27%, 11%	TC [3] OC, EC	$PM_{2.5}$	National Park in Bhopal, central India	[51]
42% (Winter) 79% (Summer) 13% (Winter) 12% (Summer) 55% (Winter) 90% (Summer)	OC OC EC EC TC TC	$PM_{2.5}$	Western Ghat Mountains, India	[29]
24.1% (2012) 22.4% (2013)	TC	$PM_{2.5}$	Debrecen, Hungary	[52]
13.81% 16.37% 1.16% 1.59%	OC OC EC EC	PM_{10} $PM_{2.5}$ PM_{10} $PM_{2.5}$	Monte Curcio, Italy	[17]
22.48% 9.16% 45.18%	OC EC TC	PM_1	Industrial area of Delhi, India	[53]
18.6% 20.6%	TC TC	PM_{10} $PM_{2.5}$	Eastern Himalaya, India	[54]
22.5%	TCA [4]	PM_{10}	Delhi, India	[19]
26.0% 28.9% 24.4%	TCA TCA TCA	TSP TSP TSP	Three Locations in Uttarakhand Himalaya, India	[55]
8.27 ± 5.00% 6.63 ± 4.49%	BC BC	$PM_{2.5}$ PM_{10}	Yaoundé, Cameroon	[56]
17.3% 16.2%	OC EC	$PM_{2.5}$ $PM_{2.5}$	Delhi, India	[57]
49.8%	TC	$PM_{2.5}$	Córdoba, Argentina	[58]
35.2% 26.6%	Carbonaceous species (OC + EC) Carbonaceous species (OC + EC)	$PM_{0.5–1.0}$ $PM_{2.5–10}$	Kuala Lumpur, Malasia	[59]
48% 26%	Carbonaceous species (OC + EC) Carbonaceous species (OC + EC)	PM_1 PM_{10}	Elche, Spain	[44]
42.5%	Carbonaceous species (OC + EC)	$PM_{2.5}$	Yibin, China	[46]
~33% ~40%	TC TC	PM_{10} PM_{10}	Rural station in southern Poland Urban station in southern Poland	[42]

Table 4. *Cont.*

Percentage	Carbonaceous Aerosol	PM Size	Place	References
12.8%, 2.4%	OC, EC	PM_{10}	Amsterdam (the Netherlands)	
9.8%, 2.4%	OC, EC	PM_{10}	Wijk aan Zee (the Netherlands)	
13.9%, 4.9%	OC, EC	PM_{10}	Antwerp (Belgium)	[20]
15.3%, 4.4%	OC, EC	PM_{10}	Leicester (United Kingdom)	
15.1%, 4.0%	OC, EC	PM_{10}	Lille (France)	
14.8%, 6.7%	OC, EC	$PM_{2.5}$	Wuhan, China	[60]
45–55%	Carbonaceous fraction	PM_{10}	Bogotá, Colombia	[61]
9.11–40.35%	TC	PM_1	Changchun, China	[62]

[1] OC: Organic Carbon; [2] EC: Elemental Carbon; [3] TC: Total Carbonaceous; [4] TCA: Total Carbonaceous Aerosols.

The variation in the concentrations of carbonaceous compounds such as EC and OC, and their contribution to PM can be attributed to different factors such as particle size, time of the year wind patterns, temperature, changes in boundary layer dynamics, geographical location, different human activities, intensity of vehicular traffic, and different types of industrial activities. For example, in the Delhi Industrial area, high OC and EC concentrations occurred in the post Monsoon season due to biomass burning emissions and contribution from fireworks of Diwali festival [53]. While, for the case of Changchun in the Northeast China, the highest OC and EC values were produced by a sandstorm [62]. Buchunde et al., [29] indicated that OC concentrations increased in the summer season, while EC concentrations occurred in the winter season. The significant contributions of OC to PM during the summer were attributed to increased photochemical production of OC through oxidation of certain volatile organic compounds. The sampling site being a high-altitude tropical station surrounded by forests and vegetation possesses high biogenic production of secondary particulate organics enhanced by photochemical processing due to seasonal high temperatures. Moretti et al., [17] indicated that in rural sites, OC concentration increases in warm periods, whereas, as for traffic and urban sites, seasonal trends of OC and EC reach the highest levels during winter. Unfavorable meteorological conditions for the dispersion of carbonaceous aerosols may prevail in winter, as low wind speed, atmospheric stability, and lower boundary layer height may increase OC and EC concentrations in the atmosphere [53].

4.2. Health Effects

PM is considered the fourth highest risk factor for human health and the greatest environmental hazards. In 2016, outdoor air pollution caused about 4.2 million premature deaths worldwide [63].The effects of PM exposure depend on their size and composition. Organic and elemental carbon concentrations present in PM have been associated with cardiovascular mortality and morbidity [16–18,64]. During the combustion or emissions of this carbonaceous fraction, toxic gases, volatile compounds, and hydrocarbons are generated, which are the cause of the deterioration of the respiratory and cardiovascular systems [19]. Premature death is also a consequence of exposure to the carbonaceous fraction, with estimations that every ten thousand premature deaths are caused by BC each year [65,66]. Forest fires are emission sources of these carbonaceous compounds as well, so exposure to these events has been associated with increased hospital admissions and respiratory, cardiovascular, and cerebrovascular symptoms in the general population [67]. But these are only one of the sources that people can be exposed to these pollutants. Indoor pollution is also an exposure event due to the fuels used for cooking. A study carried out in Colombia regarding the exposure to PM2.5 and black carbon of people with disabilities living in rural areas show that people with disabilities who spend most of the time at home can develop respiratory conditions or worsen current diseases such as hypertension or chronic obstructive pulmonary disease [68]. Traffic is another source of emission of carbonaceous particles, such as BC, and it has been associated, in addition to coronary

risks, to deterioration in cognitive abilities [69]. Inhalation of black carbon and primary organic aerosols (POC) generate oxidative stress and inflammation, leading to respiratory and cardiovascular diseases. Both BC and POC may contain primary ultrafine combustion particles that can carry harmful species such as polycyclic aromatic hydrocarbons [70].

In Delhi, India, a study showed that exposure to polycyclic aromatic hydrocarbons (PAHSs) bound to carbonaceous species of PM increased the risk of cancer. They exposed that if the population of Delhi inhales the concentrations found of PAHs throughout their lives, cancer cases could increase by 25 cases per million inhabitants [57]. These PAHs as components of OC, in addition to being carcinogenic, can be mutagenic and teratogenic, which represents a severe threat to human health [71]. Other studies have evaluated the risk of lung cancer (LCR) attributed to carbonaceous aerosol emission sources, where vehicle emissions and biomass burning contributed to a greater extent to LCR with 40.3% and 31.8% respectively [72].

4.3. Environment Effects

The carbonaceous fraction of the PM not only affects air quality, visibility, human health, but also has an adverse effect on the climate due to its optical properties. This is because it affects the radiative balance of the earth due to its ability to absorb light, causing heating of the atmosphere and light scattering, producing a cooling effect. In addition, it can influence the hydrological cycle through changes in variables such as latent heat and by modifying circulation and convection patterns [12,48].

Black carbon (BC), associated with elemental carbon (EC), is a strong absorber of visible light, making it a promoter of climate change, since after carbon dioxide, it is the second largest contributor to global warming due to positive radiative forcing it exerts [73]. On the other hand, organic carbon (OC) scatters light, although compounds such as brown carbon (BrC) that are part of OC could contribute to the light absorption process, but it does not do so in the entire visible UV spectrum as the BC, but rather at shorter wavelengths [12,74].

One of the effects of light absorption by carbonaceous aerosols is the darkening of the surface of glaciers due to the deposition of this pollutant, decreasing the planetary albedo and accelerating ice melting processes [28]. Figure 5 describes how the presence of carbonaceous aerosols like the black carbon (BC) emitted by various sources affects climatic processes in the environment.

4.4. Measurement Equipment/Techniques

Several studies that aim to determine the organic and elemental carbon present in PM have used quartz filters, because this is required by the equipment for the determination or quantification of these carbonaceous substances. The most commonly used equipment is the Carbon Analyzer DRI, 2001 as shown in Table 5. The principle of operation of this equipment is by means of reflectance and thermo-optical transmittance methods. This analytical technique is based on the conversion of the carbonaceous fraction through pyrolysis into methane. By means of reflectance or transmittance, the thermal evolution of the sample is followed when it is subjected to a change, ranging from room temperature to about 550 °C. In this range, devolatilization of the organic fraction is observed. At temperatures above 550 °C, devolatilization of the elemental carbon fraction is observed [75,76]. The most commonly used protocols for the quantification of organic and elemental carbon are the National Institute for Occupational Safety and Health (NIOSH) protocol, and the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol [26,77]. Currently, both Sunset and DRI carbon analyzers are instruments capable of operating with any thermal protocol [78].

The main difference between the two most common thermal protocols (NIOSH and IMPROVE) is the temperature regime used for the determination of organic and elemental carbon. With NIOSH, the temperature is raised to 870 °C for OC determination, whereas in IMPROVE, it is raised to 550 °C. This could mean that some of the carbon that is quantified as organic in NIOSH can be quantified as elemental with IMPROVE [79,80]. There is

another commonly used protocol developed by Cavalli et al., in order to decrease the variation of OC and EC measurements compared to the other protocols. This protocol is the European Supersites for Atmospheric Aerosol Research 2 (EUSAAR 2). It also differs in combustion temperatures, residence time at each temperature, atmospheric environment composition, and optical correction schemes [81,82].

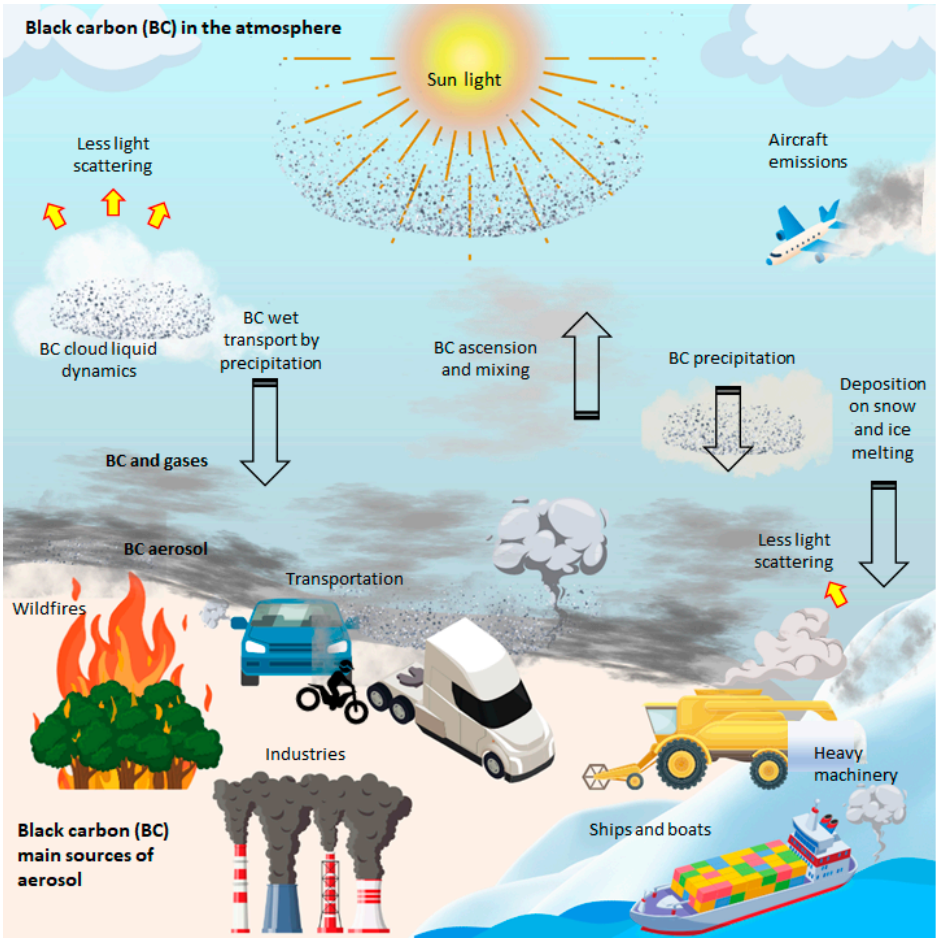

Figure 5. Description of Black Carbon climatic effects.

Other equipment used for the direct measurement of black carbon are multi-wavelength aethalometers, which are optical methods for the quantitative determination of carbon concentration [30,33]. In this case, the attenuation of the intensity of the light passing through the particulate matter filter is associated with an increase in the material collected.

Although in most of the literature reviewed in this investigation this equipment is the most used to perform quantifications or measurements of concentrations of the carbonaceous fraction in PM, there are other technologies that also allow this quantification, such as soot particle aerosol mass spectrometers, single particle soot photometers, multi-angle absorption photometers, and photoacoustic extinguishers [17,28,34].

Table 5. Equipment used for measurement or carbonaceous aerosols.

Equipment	Technique/Method	Protocol	Carbonaceous Aerosols	Filter	References
Sunset Carbon Analyzer	Thermal/Optical Reflectance	IMPROVE_A	OC, EC concentrations	Quartz fiber	[16,26,48,58,83–85]
Carbon Analyzer DRI, 2001	Thermal/Optical Reflectance	IMPROVE_A	OC, EC concentrations	Quartz fiber	[19,49,51,53–55,57,65,72,81,86–100]

Table 5. *Cont.*

Equipment	Technique/Method	Protocol	Carbonaceous Aerosols	Filter	References
Lab OC-EC Aerosol Analyzer	Thermo-Optical-Transmittance	NIOSH	OC/EC concentrations	Quartz fiber	[101,102]
Aethalometer (Magee Sci., Inc., USA, Model AE-33)	DualSpot Multi-wavelength absorption technique		BC concentrations	Quartz Fiber	[12,33,69,103–113]
OC-EC analyzer (DRI Model 2015)	Multiwavelength Thermal/Optical	IMPROVE_A	OC/EC concentrations	Quartz fiber	[27,50,74,114–118]
OC-EC analyzer (model 5 L, Sunset Laboratory Inc., Tigard, OR, USA)	Thermal Optical Transmittance	EUSAAR_2	OC/EC concentrations	Quartz fiber	[17,52,119–123]
EC-OC carbon analyzer (Model no-4F, Sunset laboratory Inc.)	Thermal Optical Transmittance	EUSAAR_2	OC/EC Concentrations	Quartz fiber	[124,125]
OC-EC analyzer	Thermal Optical Transmittance	NIOSH.1996	OC/EC concentrations	Quartz fiber	[126]
Aethalometer (Magee Scientific/Teledyne 633)	DualSpot Multi-wavelength absorption technique	- [1]	BC concentrations	-	[67]
Micro Aethalometer (AE51)	-	-	BC concentrations	-	[69,85,127,128]
Multiangle absorption photometer (MAAP, Thermo-Scientific, model 5012)	-	.	eBC concentrations	-	[17,125,129]
OC-EC analyzer from Sunset Laboratory (Model 4G)	Thermal Optical Transmittance	NIOSH 5040	OC/EC	Quartz Fiber	[32,117,130–132]
EEL M43D Smoke Stain Reflectometer (SSR)	-	-	BC concentrations	Nucleopore grease-coated and track-etched membrane filters	[56]
Dual-wavelength optical transmissometer (SootScan OT21, Magee Scientific	Thermal Optical	NIOSH	Bc concentrations Bc concentrations	Teflon filter papers Quartz Fiber	[15,133]
Sunset Laboratory Dual-Optical Carbonaceous Analyzer.	Thermal Optical	EUSAAR_2	OC/EC concentrations	Quartz fiber	[15,134]
Carbon analyzer (Sunset Laboratory)	Tthermal-Optical Transmittance	NIOSH870	OC/EC concentrations	Quartz fiber	[39,125,129,135–137]
Soot particle aerosol mass spectrometer (SP-AMS)	-	-	rBC	-	[138]

Table 5. *Cont.*

Equipment	Technique/Method	Protocol	Carbonaceous Aerosols	Filter	References
Seven-wavelength aethalometers (Model AE-31, Magee Scientific)	Multi-wavelength absorption technique	-	BC	-	[18,139]
OC-EC analyzer (model 5 L, Sunset Laboratory Inc.)	Thermal Optical Reflectance	IMPROVE_A	OC/EC concentrations	Quartz fiber	[66]
Elemental analyzer (Vario EL III)	-	-	OC/EC concentrations	-	
Dual-wavelength Aethalometer (Model AE22, Magee Scientific)	-	.	BC	-	[140]
Photometer Low-cost Aerosol Black Carbon Detector (ABCD)	-	-	BC concentrations	-	[141]

[1]—Dash: To indicate that the reference does not contain information on techniques/methods, protocols or filters used.

4.5. Identification of Emission Sources

Several studies have used the factorization matrix to identify sources of PM or the substances that make it up (Table 6), such as elemental and organic carbon [25,77,142–144]. This method is a bilinear statistical factor analysis model that does not need to know the profile of the emission source, unlike other methods that need it, such as chemical mass balance source-receptor models [6].

Table 6. Ratio between organic and elemental carbon determined in several articles.

Ratio OC/EC	PM Size	Place	Year	References
3.03 ± 1.47	$PM_{2.5}$	Kathmandu Valley, Nepal	2022	[48]
4.64 ± 1.73	TSP	Kathmandu Valley, Nepal	2022	[48]
1.5 ± 1.1	$PM_{2.5}$	Mumbai, India	2021	[27]
4.9 ± 2.7	$PM_{2.5}$	Mumbai, India	2021	[27]
>8.0	PM_{10}	Indo-Gangetic Plains of India.	2021	[119]
1.73 ± 0.48	$PM_{2.5}$–PM_{10}	Rangsit, Thailand (Wet Season).	2021	[83]
2.57 ± 0.67	$PM_{2.5}$–PM_{10}	Rangsit, Thailand (Dry Season).	2021	[83]
7.0–12.0	$PM_{2.5}$	Indo-Gangetic Plains of India (Winter)	2021	[83]
7.0–12.0	$PM_{2.5}$	Indo-Gangetic Plains of India (Winter)	2021	[124]
0.7–38.3	PM_{10}	Northern zone of Colombia	2022	[16]
1.8 ± 2.6	$PM_{2.5}$	Delhi, India	2021	[57]
2.9 ± 1.4	$PM_{2.5}$	Wuhan, China	2022	[60]

In the Metropolitan area of Costa Rica, Herrera Murillo et al., in 2013 [6], by means of the positive factorization matrix method, identified five main sources of organic and elemental carbon present in particulate matter $PM_{2.5}$. Gasoline vehicles, whose emissions contribute 10% of the concentration of $PM_{2.5}$, diesel vehicles that contribute 16%, rail traffic that contributes 4%, wood smoke that contributes 5% and industrial combustion with 9% contribution to the $PM_{2.5}$ mass concentration.

In Wuhan China, the positive factorization matrix (PMF) model was also used. There, 6 emission sources were identified. Secondary organic aerosols contributed 34.7% to $PM_{2.5}$ % concentrations; coal combustion accounted for 20.5%; industrial emissions contributed 19.6% and fugitive dust contributed 9.8%. The PMF analysis indicated that vehicle emissions contributed 10.5% to $PM_{2.5}$ mass, due to high proportions of POPs and EC. Finally, the analysis noted that there was an unidentified source that accounted for 4.9%, but could include industrial combustion, biomass, and other sources [60].

In central Japan, the positive factorization matrix model was used to evaluate the contribution of biomass burning (BB) to PM, OC and EC concentrations, in addition to the identification of $PM_{2.5}$ emission sources. The results indicated that Factor 1 was associated with biomass burning as a source of $PM_{2.5}$ particulate matter emission (it contributed 17% to the mass of this pollutant), since it indicated strong presence of levoglucosan and potassium, which are useful tracers of BB, in addition to presenting significant proportions of OC and EC (32% and 17%, respectively). PMF results also indicated that BB contributed significantly to $PM_{2.5}$, OC and EC at urban, suburban and background sites during the fall season [145].

In Colombia, this method has also been used to identify the contributions or contributions from various sources to PM. Silva et al., 2021 [25], carried out a study in the city of Barranquilla where was observed that the predominant sources of PM_{10} are attributed to civil works and resuspended soil with a contribution of 34.2% and marine aerosols with a contribution of 29.8%. In the case of $PM_{2.5}$, it was identified that the main sources are attributed to the burning of fuels and industrial emissions, with contributions of 36% and 23%, respectively. The relative abundances of EC and OC that is, the OC/EC ratio, are essential to assess the impact of carbonaceous species on climate forcing [29].

The OC/EC ratio is used to identify sources of carbonaceous aerosol emissions, since these ratios depend on fuel type, quantity, and combustion efficiency [59]. Generally, these ratios are calculated from data obtained from off-line or laboratory measurements. However, these data are comparable to Aerosol Organic/Black Carbon (AO/BC) ratios obtained from on-line measurements with instruments such as mass spectrometers [124]. Generally, high OC/EC levels (3–8) are associated with biomass combustion, while lower ratios are associated with fossil combustion (0.5–2) [83]. Other studies indicate that values between 0.7 to 2.4 are related to vehicle emissions, and values between 0.3 to 7.6 are related to biomass burning [48]. Other studies support that relatively low ratios reflect the significant impact of coal combustion as well as a high contribution from traffic emissions, while high values are associated with biomass burning or secondary organic aerosol (SOC) formation [27,86,146]. There are some authors who have defined OC/EC ratios for emission source determination as 1.0 to 4.2 for diesel or gasoline vehicle exhaust or fossil fuel combustion; 16.8–40.0 for wood combustion; 2.5–10.5 for residential coal smoke; and about 7.7 for biomass burning emission [59].

This ratio is also used to observe the aging of emissions [147]. After release into the atmosphere, emissions such as those from wood combustion are transformed into a complex process known as "atmospheric ageing" involving multiphase chemistry, leading to oxidation and functionalization of particulate and gaseous pollutants [148]. The concentration of organic aerosols emitted in wood combustion can be increased by a factor of two to three times due to the formation of secondary organic aerosols after less than 1.5 days of photochemical ageing [149,150]. Exhaust gases may contain large amounts of gaseous organic compounds, which can be precursors for the formation of secondary

organic aerosols due to atmospheric ageing, which changes the physical and chemical properties of the primary emission [151].

Some authors have identified that the high dominance of organic carbon and the potential formation of secondary organic aerosols (SOA) are also demonstrated by high values of the OC/EC ratio [42]. There are studies that mention that when OC/EC ratios are higher than 2.0, they indicate a possible SOA [6,20,152,153].

5. Summary

It is evident by multiple researches that the exposure to the carbon content present in particulate matter has a negative impact on human health, generally causing respiratory, cardiovascular, and carcinogenic problems. This aspect itself supports more research that could decrease these effects, such a deep knowledge of the characterization and measurement of the carbonaceous fraction of PM.

There are several methods that allow the determination and quantification of the carbonaceous fraction present in PM. Among the most widely used worldwide are the optical reflectance and the transmittance method used by Carbon Analyzer DRI 2001, whose detection method is the flame ionization detector. However, there are recent studies that show the existence of other equipment that perform measurements of these carbonaceous substances and that even seek to reduce the error in the measurements, such as the multi-angle photometer.

Statistical models such as the factorization matrix and principal component analysis are tools used elsewhere by the scientific community since they allow establishing the contribution of potential emission sources to the concentration of PM and the elements that compose it. In this detailed revision was observed that the subject of understanding the carbonaceous fraction in PM is a very significant topic almost in all countries, and it is of great interest to the scientific community given the volume of information found and the contemporaneity of the references. However, in developing countries there is not much scientific production on the characterization of carbonaceous compounds present in the particulate matter emitted. Therefore, it is necessary to develop studies to determine the composition of PM and identify possible sources of emissions of substances such as carbonaceous aerosols applicable elsewhere. These characterization studies allow a better understanding of local air pollution phenomena in places where air quality is an issue of great interest. An example of these is the Aburrá Valley in Medellin, Colombia, due to the critical pollution episodes that have occurred since 2016. In addition, these studies allow to specify measures and strategies for the plans formulated by the environmental authorities for the management of air quality for the benefit of human health and the environment.

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