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Characteristic Chemical Profile of Particulate Matter ($PM_{2.5}$)—A Comparative Study Between Two Periods, Case Study in Medellín, Colombia

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Abstract: Medellín, a densely populated city in the Colombian Andes, faces significant health and environmental risks due to poor air quality. This is linked to the atmospheric dynamics of the valley in which it is located (Aburrá Valley). The region is characterized by a narrow valley and one of the most polluted areas in South America. This is a comparative study of the chemical composition of $PM_{2.5}$ (particles with diameter less than 2.5 μm) in Medellín between two periods (2014–2015 and 2018–2019) in which temporal trends and emission sources were evaluated. $PM_{2.5}$ samples were collected from urban, suburban, and rural stations following standardized protocols and compositional analyses of metals (ICP-MS), ions (ion chromatography), and carbonaceous species (organic carbon (OC) and elemental carbon (EC) by thermo-optical methods) were performed. The results show a reduction in average $PM_{2.5}$ concentrations for the two periods (from 26.74 μg/m^3 to 20.10 μg/m^3 in urban areas), although levels are still above WHO guidelines. Urban stations showed higher $PM_{2.5}$ levels, with predominance of carbonaceous aerosols (Total Carbon—TC = OC + EC = 35–50% of $PM_{2.5}$ mass) and secondary ions (sulfate > nitrate, 13–14% of $PM_{2.5}$ mass). Rural areas showed lower $PM_{2.5}$ concentrations but elevated OC/EC ratios, suggesting the influence of biomass burning as a major emission source. Metals were found to occupy fractions of less than 10% of the $PM_{2.5}$ mass; however, they included important toxic species associated with respiratory and cardiovascular risks. This study highlights progress in reducing $PM_{2.5}$ levels in the region, which has been impacted by local policies but emphasizes current and future challenges related mainly to secondary aerosol formation and carbonaceous aerosol emissions.

Keywords: $PM_{2.5}$; characterization; urban valley; secondary aerosols; organic carbon

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1. Introduction

Air pollution is a major global concern, with an estimated 99% of the world's population living in areas that are exposed to high levels of pollution [1]. Air pollution is related to rapid economic and infrastructure growth, particularly in nations and urban areas experiencing rapid development. This phenomenon is primarily driven by increased resource consumption, which in turn leads to a greater quantity of emissions [2,3]. Urban areas are particularly susceptible to poor air quality, as emissions from both internal processes and external sources contribute to the deterioration of air quality [4,5].

The dynamics of atmospheric pollutants are influenced by atmospheric conditions, including factors such as wind speed and direction [6], as well as phenomena like thermal inversion [7]. Additionally, circulation patterns can lead to the accumulation of pollutants in specific areas [8,9], which is frequently observed in valleys or urban areas where the dispersion of these pollutants is more complex [10,11].

Due to its implications, particulate matter (PM) is one of the most widely studied atmospheric pollutants. Its presence can negatively influence several phenomena including cloud formation [12], the generation of acid rain [13], and the formation of secondary compounds by photochemical reactions [14]. These effects may involve the bioaccumulation of pollutants in plant species [15], soil [16], and water [17]. Additionally, the persistent presence of these pollutants in the atmosphere is associated with reduced visibility [18].

PM comes from both sources: natural (volcanic eruptions, suspension of the earth's crust, suspension of sea salts, among others) and anthropogenic (e.g., industrial processes, construction, burnings from agriculture, vehicular emissions) [19,20]. This pollutant is often transported over long distances [21] and remains suspended in the atmosphere, where it is altered or eliminated; thus, residence times can vary from a few days to several weeks [22].

The composition of PM is variable and depends on different factors such as the emission source [23], atmospheric conditions [24] or its origin (which is primary when it comes directly from the emission source and secondary when it is generated due to the interactions that pollutants face in the atmosphere with solar radiation and/or other pollutants [6,25]). It has been widely determined that the composition of PM is mainly given by the presence of ions (e.g., sulfate, nitrate, ammonium), metals (e.g., lead (Pb), copper (Cu), aluminum (Al)), carbon-derived compounds (black carbon (BC), organic carbon (OC), elemental carbon (EC)), minerals, and others, including biological material [26–29].

In terms of health, PM is capable of penetrating the lungs, posing a wide range of risks to humans, especially in relation to respiratory and cardiovascular diseases [30]. Particles with a diameter less than 2.5 μm ($PM_{2.5}$) can reach the alveolar region of the respiratory system, where gas exchange occurs—an essential function for overall system performance [31]. PM contains various chemical compounds that have adverse effects on human health [32]. For instance, Pb can damage the nervous and hematopoietic systems, resulting in impaired growth and mental function [33]. Elements such as cobalt (Co), chromium (Cr), arsenic (As), vanadium (V), iron (Fe), manganese (Mn), and nickel (Ni) present in ambient PM can generate reactive oxygen species, which inflame the respiratory tract and may even cause oxidative DNA damage [34]. On the other hand, a correlation has been identified between short-term exposure to elemental carbon (EC) and the relative risk of mortality from all causes, including cardiovascular and respiratory diseases [35], while organic carbon (OC) is considered a significant contributor to the cancer risk associated with air pollution [27]. Understanding the main chemical components found in PM is essential, as it enables the identification of specific emission sources—providing clarity for the development of regulations that support decontamination processes in urban areas [36].

PM is the primary pollutant of concern in the Aburrá Valley (AV)—a narrow valley in the northern Andes of South America where Medellín is the main city. Air pollution reaches high levels at various times, making the AV one of the continent's most polluted metropolitan regions [37]. A 2020 study of the metropolitan area [30] found that none of the AV's monitoring stations met World Health Organization (WHO) standards for $PM_{2.5}$. That study also estimated that $PM_{2.5}$-related deaths could increase by more than 150% between 2016 and 2030. High-pollution episodes have previously triggered citizen alerts and local interventions—such as bans on outdoor exercise and private vehicle use—to reduce exposure [38]. Previous studies have identified the main components of PM in Medellín. In 2011, researchers analyzed $PM_{2.5}$ and detected ions, metals, and carbonaceous species,

with average concentrations surpassing 30 μg/m^3 (three times the WHO's recommended limit) [39]. Later, a 2023 study used energy-dispersive X-ray spectroscopy (EDS) to identify metals in PM_{10} [40], and a 2024 analysis found that ions accounted for 26% of PM_{10} and metals for 3% [6]. Other studies have used different techniques to identify metals and other compounds in Medellín [36,41]. The chemical composition and characteristic profile of PM particles have also been identified in other Colombian cities, such as Bogotá [42,43], Manizales [44], and others [45,46]. In most cases, levels of contamination exceed the recommendations of the WHO and Colombian regulations. This study aimed to use various chemical characterization techniques to identify $PM_{2.5}$ composition profiles in Medellín and nearby cities, contrasting the effect of a set of policy regulations and social measures on air quality in the region. Two periods were analyzed to explain changes in $PM_{2.5}$ profiles over time and space: 2014–2015 and 2018–2019. Additionally, the study identified emission sources based on concentrations of carbonaceous species and the EC/OC ratio.

The compounds present in the pollutant were identified by chemical characterization of ions and metals using ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) techniques, respectively; for the characterization of OC and EC, we used thermal/optical reflectance (TOR) and thermal/optical transmittance (TOT). This information is valuable for understanding how the dynamics of air quality in the city have changed.

2. Materials and Methods

2.1. Site and Study Period

The site of study is Medellín, located in the AV, a narrow valley in Colombia between 6.0° and 6.5° N and −75.5° and −75.7° W. This city has an area of 376 km^2, where approximately 30% is urban, with a population of 2,612,958 inhabitants in 2022 [47,48].

Samples were taken in two periods. In the first period, 87 samples were collected at five different points, between October 2014 and June 2015. For the second period, 149 samples, distributed across four points, were collected between April 2019 and March 2020 (see Table 1). Full information about the station and periods can be found in the Supplementary Material (Table S1).

Table 1. Study periods, stations of study, and number of samples by station.

Period (p)	Station	Start Date	End Date	n	Location (W, N)
p1	Poblado fp [1]	October 2014	April 2015	25	75.577, 6.20897
	Laureles	December 2014	May 2015	25	75.591, 6.24169
	Robledo	January 2015	June 2015	25	75.592, 6.27388
	Santa Elena [2]	January 2015	January 2015	6	75.498, 6.23636
	Jardín [3]	June 2015	June 2015	6	75.815, 5.59751
p2	Girardota [3]	April 2019	May 2019	11	75.450, 6.37904
	Belén	April 2019	March 2020	118	75.612, 6.24321
	La Ye	April 2019	May 2019	10	75.550, 6.18254
	Poblado sp [1]	April 2019	May 2019	10	75.577, 6.20897

[1] Poblado is the only station used in both periods; fp: first period; sp: second period. [2] Santa Elena is a background area. [3] Those stations are outside Medellín and were used for comparison proposals.

Air quality sampling stations are affected by various factors that contribute to air pollution. The environmental authority classifies these stations based on their characteristics, which correspond to fully urbanized (urban) or mostly urbanized (suburban) areas. Urban Traffic Stations are located in fully urbanized zones, where pollution levels are mainly influenced by nearby traffic emissions. Urban Background Stations are positioned to measure pollution influenced by general air circulation rather than by specific roads or local sources.

Suburban Background Stations are installed in areas where urbanized spaces blend with non-urbanized ones. Rural Background Stations monitor air quality in rural regions, far from major local pollution sources, and are used to measure pollutants transported over long distances. Suburban Industrial Stations are placed in mixed urban and non-urban areas but are primarily affected by emissions from nearby industrial activities [49]. Figure 1 shows the location of these air quality stations in the AV and in Jardín, Antioquia.

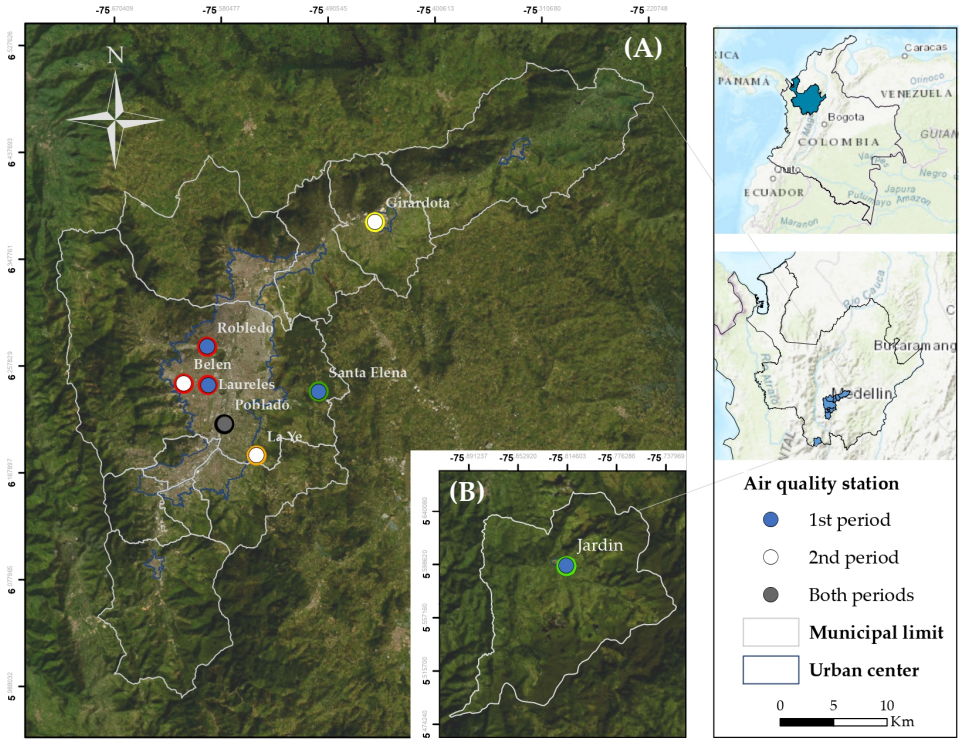

Figure 1. Location of air quality stations and study period in the (**A**) AV and (**B**) Jardín, Antioquia, Colombia. The halo represents the type of station: red—urban background station; orange—suburban background station; black—urban traffic; yellow—suburban industrial; green—rural background.

2.2. Sample Collection

Sample collection was carried out by applying reference method procedures implemented and confirmed by the GHYGAM Laboratory of the Jaime Isaza Cadavid Colombian Polytechnic, according to the guidelines of the Quality Assurance Instructions ID-MEA183, Sampling Instructions associated with its Management System accredited in accordance with the requirements of NTC ISO/IEC 17025 [50]. $PM_{2.5}$ samples were collected using low-vol equipment (16.7 L/min) according to international reference methods (CFR 40 Appendix L to Part 50—Reference Method for the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere [51]). Gravimetric analysis of filters and samples obtained from low-vol equipment was performed three consecutive times on a 0.001 mg resolution microbalance (Sartorius CPA26P, Sartorius AG, Göttingen, Germany), and for samples obtained from high-vol equipment, three consecutive times on an analytical balance with a 0.1 mg resolution (Radwag AS-220-X2, RADWAG, Radom, Poland). Samples were transported to the laboratory under a cold chain, ensuring a temperature equal to or less than 4 °C during transport and protected from light to prevent the loss of volatile and photosensitive compounds [52]. Once in the laboratory, the samples were subjected to final temperature and humidity conditioning for a minimum period of 24 h. Quartz filters (47 mm diameter and 0.3 µm pore size) were used.

2.3. Sample Analysis

Analytic procedures were executed at the Hygiene and Environmental Management Group (GHYGAM) Laboratory. For the chemical analysis, a 2.5 cm wide strip is cut from the quartz filter, starting at the edge of the deposition zone. To perform the extraction, the strip is segmented into smaller fractions (2.5 cm × 2.5 cm) and subjected to ultrasonic agitation in ultrapure water for 45 min. The content of metals in the collected $PM_{2.5}$ was determined by inductively coupled plasma mass spectrometry analysis (ICP-MS) on Thermo Scientific equipment model I CAP-RQ (Thermo Scientific, San Jose, CA, USA), using reference protocols and methods [53,54]. The concentration of ions sulfate ($SO_4{}^{2-}$), nitrite ($NO_3{}^{-}$), fluoride (F^{-}), and chloride (Cl^{-}) in $PM_{2.5}$ was determined by ion chromatography using the standard reference method [55] on Thermo Scientific equipment reference Dionex Aquion (Thermo Scientific, San Jose, CA, USA). The minimum detectable concentration will depend on each ion, volume of air collected and sampling time. Organic carbon (OC) and elemental carbon (EC) are analyzed in $PM_{2.5}$ ambient samples taken on quartz fiber filters by combustion with continuous temperature ramps in oxidizing and/or non-oxidizing atmospheres, thermal/optical reflectance (TOR), and thermal/optical transmittance. Thermal methods heat a portion of the sample continuously or stepwise under different atmospheres, with the detection of volatilized carbon and oxidized carbon coming out of the sample. With consistent standardization, these methods provide equivalent measurements of total carbon (TC = OC + EC) and define the split between OC and EC and their fractions, based on combinations of combustion temperatures, residence time at each temperature, the composition of the atmosphere surrounding the sample, and the light reflected or transmitted through the filter. OC and EC are determined by the NIOSH 5040 method, applying the experimental conditions established in the protocol [56] and using the Sunset Thermo-Optical Meter, ref 5L (Sunset Laboratory, Inc., Tigard, OR, USA).

To ensure the reliability of the results, quality control and assurance procedures were applied throughout the sampling and analysis process. This included the use of field and laboratory blanks, calibration of weighing equipment before and after each weighing session and adherence to standardized handling protocols to minimize contamination and variability. All procedures followed internal quality guidelines consistent with international best practices. To ensure information quality control, data traceability is maintained in compliance with standard operating procedures, documented formats, and codified instructions as per the GHYGAM Laboratory Master Document List. Internal audits are conducted to identify preventive and corrective actions, which are documented in activity reports and promptly communicated to project management. Special emphasis is placed on adherence to the NTC 17025 Standard for developing standardized procedures. These measures guarantee data quality and facilitate the identification and control of potential errors throughout all stages—including sample collection, handling, transportation, storage, packaging, and preservation.

2.4. Data Analysis

A descriptive statistical analysis was performed. Subsequently, we analyzed the data for each period to reconstruct the PM mass in each one by station and to compare the characteristic profile for each period. We used R Studio version 12.1 to determine the descriptive statistics and to perform normality analyses using the Shapiro–Wilk test for datasets larger than 50 observations and the Kolmogorov–Smirnov test to determine *p*-values. These tests allow us to assess whether a dataset follows a normal distribution ($p > 0.05$). We also analyzed the OC/EC ratio at each station with the aim of identifying sources of carbonaceous aerosol emissions [19].

3. Results

The metals were characterized (ordered from highest to lowest concentration) as follows: sodium (Na) > potassium (K) > silicon (Si) > calcium (Ca) > iron (Fe) > aluminum (Al) > zinc (Zn) > magnesium (Mg) > titanium (Ti) > copper (Cu) > barium (Ba) > lead (Pb) > manganese (Mn) > beryllium (Be) > cobalt (Co) > antimony (Sb) > chromium (Cr) > nickel (Ni) > silver (Ag) > molybdenum (Mo) > selenium (Se) > arsenic (As) > vanadium (V) > cadmium (Cd) > mercury (Hg); the anions SO_4^{2-} > NO_3^- > Cl^- > Fl^-; and the carbonaceous species OC and EC. Table 2 shows the average values of $PM_{2.5}$ composition at each station. Full data can be found in the Supplementary Material (Table S2).

Table 2. Mean concentration of the analyzed species.

p	Station	(μg/m³)				
		$PM_{2.5}$	**Metals**	**Anion**	**OC**	**EC**
p1	Poblado fp	27.690	2.379	3.874	7.889	7.974
	Laureles	25.290	0.346	3.974	5.938	5.250
	Robledo	27.247	1.123	3.953	9.426	9.674
	Santa Elena	8.053	0.180	1.135	0.726	0.898
	Jardín	14.435	0.295	2.874	2.781	1.238
p2	Girardota	16.716	1.141	2.258	6.826	3.970
	Belén	21.729	2.337	2.600	7.286	0.896
	La Ye	17.337	0.810	1.980	7.661	2.995
	Poblado sp	21.247	1.286	2.575	8.132	4.395

It can be seen that the urban background stations have the highest concentrations of $PM_{2.5}$, and these are even higher in the first period. In the second period, a decrease in the total concentration of $PM_{2.5}$ is observed; however, the levels of OC are higher in proportion, anions, metals, and EC also had a reduction between the first and second period. Figure 2 shows the characteristic composition of PM particles in each station and period, where it can be seen that the concentration of metals is considerably lower compared to the other components. In rural areas (Santa Elena and Jardín), the unidentified fraction occupies the largest part. It is also evident that EC and OC occupy a significant fraction of the $PM_{2.5}$ mass, especially in the second period, where OC takes greater prominence.

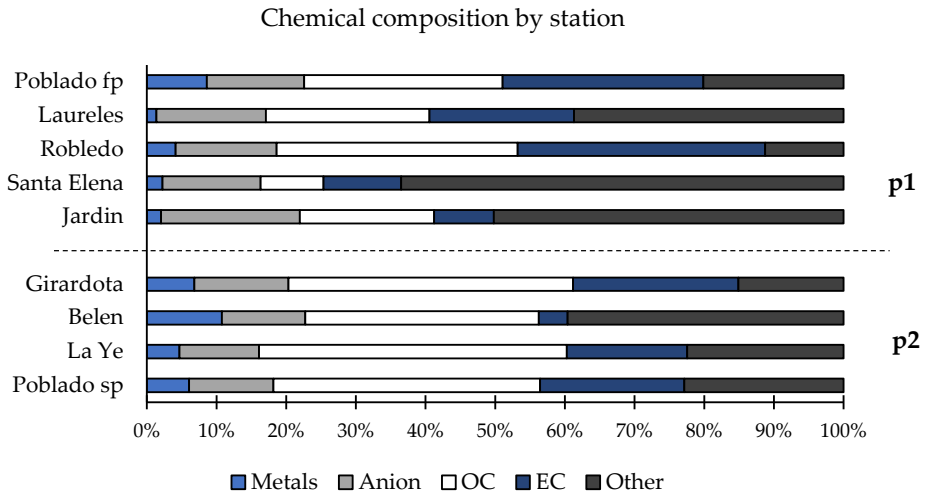

Figure 2. Characteristic chemical composition of each station during the studied periods.

Figure 2 shows the characteristic composition by station for each period.

The characteristic chemical composition of $PM_{2.5}$ in each station shows that the urban stations have similar behavior in both periods. The highest percentage of the sample not identified by the techniques used is found mainly in the rural areas of Santa Elena and Jardín. This fraction may refer to the compounds of minerals, biological matter, and cations [6,36,57]. On the other hand, it is noteworthy that the concentration of the characterized species has a similar proportionality in the rural areas, except for OC, which is higher in Jardín than in Santa Elena. Figures 3 and 4 show the characteristic profiles from the first and second period respectively, according to the mean concentration obtained at each sample point.

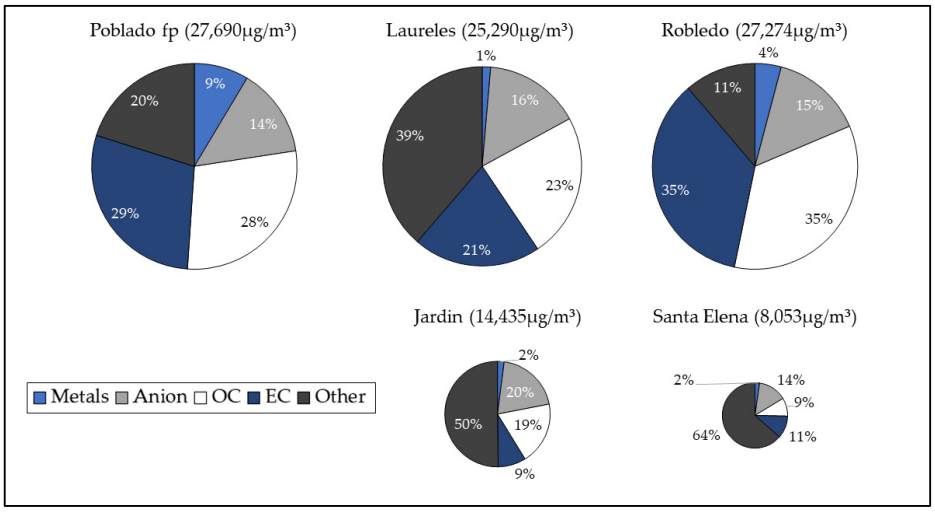

Figure 3. Particle chemical profile for the first period. $PM_{2.5}$ concentrations are shown in parentheses. The size (diameter) of the pie chart corresponds to the average concentration found at each station.

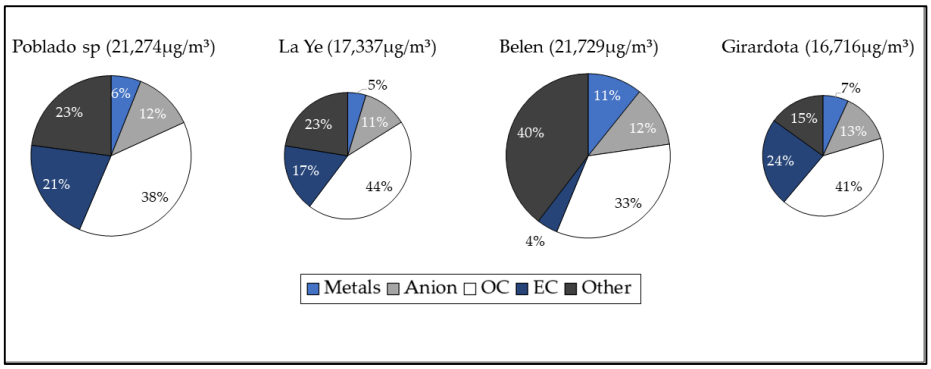

Figure 4. Particle chemical profile for the second period. $PM_{2.5}$ concentrations are shown in parentheses. The size (diameter) of the pie chart corresponds to the average concentration found at each station.

Figures 3 and 4 again show the influence of the study area and the reduction of contamination levels between periods. On the other hand, it can be seen that, at each sampling point, the anions occupy a similar mass composition percentage of about 13% of the total $PM_{2.5}$ mass. A similar pattern occurs with the concentrations of OC, which in urban areas range from 23% to 44%. It is also notable that the lowest levels of OC were found in rural areas. EC has similar proportions in the urban area in the first period (around 28% of the total $PM_{2.5}$ mass) and the rural area (around 10%). For the second period, there is evident similarity in the concentrations and proportion of EC, except in the Belén station, where this compound occupies only 4% of the total mass, well below the average data obtained in this study, possibly due to the specific conditions of the sampling area.

Regarding metals, it is clear that they occupied the lowest concentrations and percentage of $PM_{2.5}$ mass, including compounds characteristic of industrial sources, and which are also found in the earth's crust as Pb, Cd, Cr, As, Ni, among others. Metals remain dangerous even in low concentrations [58,59]. It is also important to note that at least 90% of the anion mass is composed of SO_4^{2-} in the Girardota, La Ye, Poblado (in both periods), Laureles, and Jardín stations, the highest percentage of SO_4^{2-} ion mass occupancy corresponds to Santa Elena (66%). Considering SO_4^{2-} and NO_3^- in the total anion mass, all sampling points exceed 93% of the total mass, which shows the importance of the formation of secondary compounds.

Figure 5 corresponds to the analysis of the carbonaceous aerosol fraction, showing TC and the OC/EC ratio, which is useful to identify the source of carbonaceous aerosols [60,61]. Figure 5 highlights the distinction between urban and rural areas in terms of composition and sources of carbonaceous aerosols. In the first period, urban sites (Robledo, Poblado fp, and Laureles) exhibit higher concentrations of OC and EC, probably due to emissions from traffic, industrial activities, and other combustion-related sources [62–64]. The OC/EC ratio at these locations remains relatively low, suggesting a greater influence of direct emissions from fossil fuel combustion [19,27]. In contrast, Santa Elena and Jardín, which are rural areas, show lower concentrations of carbonaceous species, although the OC/EC ratio in these areas is higher (particularly in Jardín), indicating a greater contribution from Secondary Organic Carbon (SOC) or biomass burning [19,27]. This suggests that the sources in these regions differ from urban areas, possibly involving natural emissions from vegetation and residential wood burning rather than fossil fuel combustion. During the second period, the overall TC concentration appears lower, with a more uniform distribution among the stations of Girardota, Belén, and La Ye. This decrease could be attributed to seasonal variations, meteorological factors, or emission control measures [65]. Despite this reduction, the OC/EC ratio remains variable, reinforcing the idea that different sources influence each location differently.

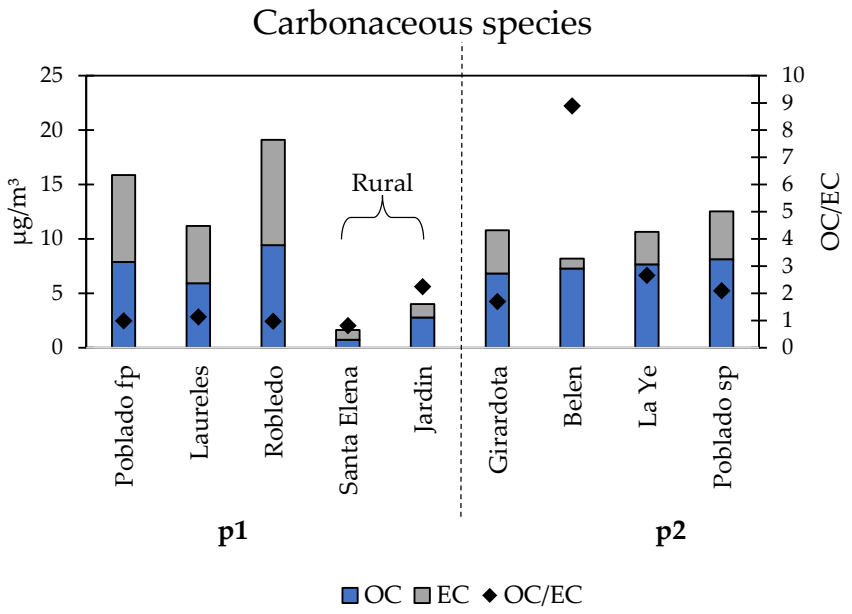

Figure 5. Carbonaceous species. The TC corresponds to the sum of the OC and EC columns.

4. Discussion

Between 2015 and 2020, the AV had significant milestones in terms of air quality management [66]. Among the representative achievements, it is important to mention the reduction in sulfur content in diesel from 50 ppm to 14 ppm and in gasoline from 300 ppm

to 145 ppm, which represents an improvement in fuel quality and, therefore, constitutes a reduction in polluting emissions [67,68].

In addition, the transportation sector in the AV promoted the modernization of the bus fleet, retiring 410 old vehicles and replacing them with cleaner technology units. As part of this transition toward sustainable mobility, the AV's mass transportation network was enhanced through several initiatives: the purchase of 20 train units for the Medellín Metro System in 2015, the beginning of operations of the Ayacucho Tramway, the integration of new articulated buses for the Metroplus system in 2016, and the launch of the Metroplus O line, composed of electric buses, in 2019.

At a strategic level, the environmental authorities of the AV implemented important environmental policies such as the formulation and adoption of the Operational Plan to Confront Critical Air Pollution Episodes (POECA) in 2016, (Metropolitan Agreement N°15), which was subsequently modified with Metropolitan Agreement 03 of 2019, Metropolitan Agreement 16 of 2020, and Metropolitan Agreement 01 of 2021 [69]. Taking into account that the 2015 goal of 25 $\mu g/m^3$ of $PM_{2.5}$ per year proposed in the 2010 Decontamination Plan was not met, the Comprehensive Air Quality Management Plan (PIGECA) was adopted in 2017, in which management strategies focused on the effective reduction of pollutants and significant improvements in air quality are proposed, as well as a goal of 23 $\mu g/m^3$ of $PM_{2.5}$ in 2030 [70].

Regarding the management of stationary sources, the environmental authority of the AV (AMVA) issued the Metropolitan Resolution 912 of 2017, which adopts measures that contribute to the development of a comprehensive management strategy of air quality in the jurisdiction of the metropolitan region of the AV, aimed at the measurement, prevention, reduction, and control of emissions of air pollutants generated in various facilities in the region. It addresses issues such as the possibility of implementing restrictions on the operation of emission sources during periods of atmospheric contingency and the mandatory implementation of an operation and maintenance logbook. As part of the implementation of this resolution, more than 1900 inspections of industrial stationary sources were carried out. Subsequently, in 2018, following the provisions established in Decree 1076 of 2015 [71], the Metropolitan Resolution 2231 [72] delimited two Urban Protected Air Zones (ZUAP) were delimited in the center of Medellín and south of the Aburrá Valley. These areas were identified as points where a considerable deterioration of air quality was recorded, and in which management, monitoring, and control measures were implemented to reduce the concentration of pollutants. Finally, in the same year, the Air Quality Pact was signed, with more than 150 public and private entities committing to reduce their emissions through concrete actions. While the effectiveness of these policies is still under evaluation, they demonstrate a commitment and present a positive outlook in this regard.

On the other hand, analysis of pollutant concentrations reveals that the highest levels were recorded during the first period, suggesting that factors such as meteorological conditions [73], emissions from specific sectors, or seasonal variations [74] could have contributed to the high concentrations. As expected, $PM_{2.5}$ concentrations in rural areas remained below those measured in urban areas; however, they were 1.4 times higher than the WHO recommendations (10 $\mu g/m^3$) for that time in Santa Elena [75]. Urban environments consistently present higher pollution levels due to traffic, industry, and other anthropogenic activities, as identified in previous studies in Colombia [76,77], Latin America [78,79], and the rest of the world [26,33,59].

The reduction in concentrations could be attributed to changes in environmental conditions, mitigation measures, or fluctuations in pollution sources. The observed decrease in $PM_{2.5}$ concentrations in urban areas is consistent with regional efforts to reduce emissions,

such as vehicle restrictions and renovation and industrial regulations. $PM_{2.5}$ levels remain 3–4 times higher than WHO guidelines (annual mean of 5 $\mu g/m^3$ [75]), underscoring persistent public health risks. However, these results are in line with the permissible levels of $PM_{2.5}$ established 2017 for the Colombian Environmental Ministry [80]. It is important to highlight the reduction in anion concentrations in urban areas. During the first period, the total anion concentration at the urban stations was 3.87 $\mu g/m^3$ in Poblado, 3.97 $\mu g/m^3$ in Laureles and 3.95 $\mu g/m^3$ in Robledo. During the second period, the concentration in Poblado dropped to 2.58 $\mu g/m^3$ (a 33% reduction), while in Belén it was 2.60 $\mu g/m^3$ and in La Ye it was 1.98 $\mu g/m^3$. Sulfate, which on average accounted for around 80% of the total anion mass, showed a 30% decrease in the urban area, falling from 3.45 $\mu g/m^3$ to 2.41 $\mu g/m^3$. This information can be found in Table S2.

Notably, the OC/EC ratios in rural areas (e.g., Jardín: OC/EC = 2.25) indicate the burning of biomass or biogenic secondary organic carbon, which contrasts with urban ratios (e.g., Robledo: OC/EC = 0.97), which reflect the combustion of fossil fuels [19,27]. However, the proportional increase in organic carbon (OC) during period 2 (e.g., 28.8% to 32.1% in Poblado) suggests higher contributions from secondary organic aerosols. This should be one of the sources that environmental authorities must pay attention to in this region, for example, although Laureles was not the area with the highest $PM_{2.5}$ levels, it recorded the highest concentrations of anions among all monitored sites. This could be related to aerosol transport dynamics. SO_4^{2-}, a tracer of secondary aerosols, constituted between 13% and 14% of the $PM_{2.5}$ mass at all sites, predominating >90% of the anion mass in urban areas. This highlights the role of secondary aerosol formation from SO_X (industrial/vehicular) and NO_X (traffic) precursors under the AV conditions [6]. The dominance of OC/EC (35–50% of $PM_{2.5}$ mass) calls for stricter controls on diesel vehicles [81,82].

In relation to the evidence on the general reduction of $PM_{2.5}$ pollution levels and its components, it is suggested that the implementation of public policies has had a significant influence. However, this statement should be treated with caution, since other important parameters, such as local climatology and the different atmospheric dynamics characteristic of the region (e.g., wet and dry seasons or ENSO oscillations), can influence the results, especially when analyzed over specific time periods. Nevertheless, some studies have indicated that policy implementations can strongly impact air quality in cities and countries, particularly when examined in relation to short- to medium-term effects (i.e., over a period of years). For example, China has introduced more restrictive policies since 2013, which have to some extent equalized the levels of various pollutants in urban and rural areas [83]. As shown, there has been an approximate 8% reduction in $PM_{2.5}$ concentrations in Beijing between 2014 and 2019 [84], Jinan experienced similar reductions between 2014 and 2021 [85]. There have also been more successful cases, such as in Hebei, where more aggressive policies reduced concentrations by up to 60% in certain periods [84]. Another example is Weifang, where reductions of almost 30% of $PM_{2.5}$ were achieved in certain areas of the city [86]. Many of these policies were directly aimed at controlling sulfur dioxide and industrial soot emissions [87]. Conversely, some policies affecting local traffic dynamics have led to reductions in certain urban areas of the Netherlands, despite less stringent restrictions being applied [88]. Another example of the influence of public policies is Thailand, where a 'zero burning' standard was introduced, reducing concentrations of atmospheric pollutants by half compared to previous years [89].

5. Conclusions

This study evaluated the characteristic chemical profile of $PM_{2.5}$ in two periods (2014–2015 and 2018–2019) in the AV, showing that the urban area has the highest concentration levels of the pollutant. The results suggest a reduction in the levels of this pollutant

between the periods; however, they are still above the WHO air quality guidelines. There is an increasing trend toward secondary formation species, such as SOC and SO_4^{2-} and NO_3^- anions. The carbonaceous species EC and OC occupy the highest proportion of $PM_{2.5}$ in this region, with the EC/OC ratio values suggesting biomass burning and secondary aerosols as important sources of atmospheric pollution in the AV. Although the concentration levels of metals are low, compounds that represent important health risks are still found.

The results show that the type of zone in which the stations are located has an important influence on the concentrations and components of $PM_{2.5}$. The policies and actions implemented to reduce the emission of pollutants in the AV go hand in hand with the reduction of pollutants evidenced; however, it is important to consider variables related to climatic variations (e.g., ENSO), meteorological conditions, or the dynamics of the valley.

The 4-year difference between periods limits the attribution of trends to specific policies or meteorological changes. However, for future work, it is suggested to evaluate how the meteorological parameters influence the concentrations of the pollutants and to apply methodologies for source apportionment with larger datasets. This will provide a better understanding of the behavior of air pollutants in Medellín and the AV, as well as tools for policymakers to take informed action.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su17125380/s1, Table S1: Detailed sampling collection information; Table S2: Detailed concentration species by station.

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