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Characterization and Source Apportionment of Ion and Metals in PM_{10} In an Urbanized Valley in The American Tropics Using Principal Component Analysis and Positive Matrix Factorization

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Abstract

The Metropolitan Region of the Aburrá Valley (MRAV) is an urbanized valley located in the central mountain range of the Andes of Colombia, with Medellin as the most important city of the region. Due to geography, economic trends, industrialization, and demography, air pollution has become one of the main problems in terms of health and the environment. The characterization of the ionic and metallic fraction of Particulate Matter (PM_{10}) was carried out following the standard procedures, using Ionic chromatography for the anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{-3} and SO_4^{-2}) and for cations (K^+, Na^+, Li^+, Mg^{+2}, Ca^{+2} and NH_4^+), as well as atomic absorption spectroscopy for the metals (Ni, Ba, Mn, Cu, Al, Cr, Zn, Fe). A total of 94 samples were collected in 10 different stations of the air quality network of the MRAV between December 2018 and October 2021. The results were statistically analyzed using receptor models: Principal Component Analysis (PCA) and the EPA Positive Matrix Factorization (PMF) to identify the main source of the pollutant. It was found that the average PM_{10} concentration of the collected samples was 40.65 $\mu g/m^3$, 43% of the data was over the standard established by the WHO (45$\mu g/m^3$). The contribution of ions was approximately 26% of the PM_{10} mass, with SO_4^{-2} occupying the largest fraction (approximately 12%), and Na^+, having the highest concentration among the cations. The metals corresponded to 3% of the total mass of PM_{10}, with Fe having the highest concentration. Through the statistical analysis, it was found that the results of both models have important similarities, identifying that the main emission sources of the pollutant in the MRAV are secondary aerosols (SA), biomass/waste burning (BB), soil/road dust (SD), vehicular emissions (VE), industrial emissions (IE), and mixed type contributions. The methods and results used in this case study for the particular geography of the valley are an important tool for understanding the effects of PM pollution in the local context and many regions worldwide.

Keywords: Air pollution; Source apportionment; Receptor models; PM_{10}; Urbanized valley.
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1. Introduction

Air pollution is a problem faced by communities around the world affecting the environment and public health. It has been associated with economic and industrial development, as well as population growth of urban centers.[1] Deteriorating air quality is a global concern, particularly in developing countries where pollutant levels regularly exceed safe limits. Particulate matter (PM) is a pollutant of non-specific physical and chemical composition, consisting of a combination of solid and/or liquid suspended particles[2] capable of being transported[3] and remaining for extended periods in the atmosphere.[4] PM has primary origin when its emission occurs directly from the source, and secondary origin when it occurs due to the transformations that the primary compounds face in the atmosphere.[5] PM is used as criteria to estimate air quality,[6] where the PM_{10} and $PM_{2.5}$ fractions (particles which an aerodynamic diameter less than 10 and 2.5µm respectively) are widely used.[7]

PM can be of anthropogenic origin[2,8] such as vehicular emissions,[9] industrial emissions, coal or fuel combustion, biomass burning,[10] and construction activities,[11] among others. It can reach the atmosphere by natural causes such as suspension of crustal matter,[12] sea salts,[13] and volcanic eruptions, and ash fly.[14,15] Hence, the chemical composition

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of PM is variable and will depend on different parameters like the emission source[8,16] or the meteorological conditions (temperature, atmospheric pressure, relative humidity, solar radiation, wind speed, precipitation, among others[17]). It has been found that among the main compounds of PM are ions, metals,[1] minerals,[3] biological material,[18] and carbon-derived compounds (such as polycyclic aromatic hydrocarbons (PAHs),[19] elemental carbon (EC),[20] and volatile organic compounds (VOC) [21]). Furthermore, particulate sizes less than 10 µm are able to absorb more toxic substances than coarser particles [22]. Cities have become the geographic focus for chemical emissions and resource expenditure, which has led to issues such as ecosystem degradation, biodiversity decline, and community health risks.[23,24]

Due to its size, PM_{10} particles can penetrate the lungs, and cause a large list of health problems affecting respiratory, cardiovascular and reproductive systems, and even causing premature deaths.[22,25] Numerous studies have recorded comorbidities related to air pollution.[7] such as those reported in 2019 by the WHO of about 4.2 million deaths related to PM.[26]

Some of the constituents of PM cause specific affectations, the trace elements are related to various issues such as memory loss, respiratory problems, throat and nose irritations, dermatitis, and lung cancer.[5] Heavy metals such as Cr, Ni, and Cd[27] are known for their carcinogenic potential.[28,29] In some areas where higher levels of Ni are found, a higher number of cases related to respiratory diseases have also been reported.[30] On the other hand, some elements classified by the International Agency for Research on Cancer (IARC) as non-carcinogenic (Cu, Mn, Zn) represent a health risk as they cause respiratory diseases even in low concentrations.[27] In environmental terms, PM contributes to haze which affects air quality, decreases visibility, generates acid rain, and impacts cloud formation,[22] which affects the heat exchanges with the atmosphere and could lead to global warming.[23] Additionally, it can affect the crops, especially in small and short cycle plants such as vegetables[2] and create a negative influence in the biosphere and the ecosystems.[11]

Several statistical techniques have been employed for the study of PM. The Receptor Models (RMs) are widely used[22] and consist of the application of multivariate statistics to identify the contribution of quantitative apportionment and identification of emission sources of air pollutants,[8,31] These models have been known to provide relevant information on emission sources for the development of effective and efficient air quality management plan.[31] Principal Component Analysis (PCA) is a well-established multivariate statistical analysis tool for the analysis of air pollutants[23,32] that seeks to reduce the complexity of a sample[5] by identifying several unrelated components (sources), that explain the variance of a sample. Another technique widely used for such analysis is Positive Matrix Factorization (PMF),[33] this model has been adopted by the Environmental Protection Agency of the United States (EPA) for source apportionment of atmospheric pollutants, it consists of the performing a factor analysis to estimate the contributions of pollutants to each source.[34,35] The sample data set is assumed to be influenced by linear combinations of the emission sources, PMF performs identifies the contributions of the pollutants to each of these sources.[11] This method is described in detail by Paatero and Tapper, 1994[36] and by Paatero, 1997.[37]

In the present study, the characterization of 94 samples of PM_{10} was carried out finding the metals nickel (Ni), cupper (Cu), aluminum (Al), chromium (Cr), zinc (Zn), and iron (Fe); the anions fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{-3}), and sulfate (SO_4^{-2}); and the cations sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{+2}), and calcium (Ca^{+2}). Additionally, source apportionment of the PM10 was performed using RMs: PCA and PMF. These chemical species are constituents of PM_{10} in the Metropolitan Region of the Aburrá Valley (MRAV), an urbanized valley located in the central mountain range of the Andes in Antioquia, Colombia. Medellin, one of the most important cities of Colombia and South America is located there. The combination of diverse anthropogenic emission sources with tropical climate and topographical conditions makes the MRAV one of the most polluted locations in Colombia.[38]

In this region, the study of atmospheric pollutants has taken on great importance; in 2016, levels of atmospheric pollutants were found well above those recommended by Colombian legislation.[25] Since that year, critical episodes have been faced due to the same problem. According to the National Administrative Department of Statistics, commonly referred to as DANE, in the city of Medellin, between 1980 and 2021, one person died every three hours from diseases related to chronic respiratory infections, cerebrovascular accidents, lung cancer, and diseases of the circulatory system, all of which are related to air pollution.[39,40] Furthermore, due to the economic and industrial development of the region, there has been a migration of residents from all over the country to the MRAV, leading to the massification of public transport, an increase in the number of vehicles, and organized and unplanned urbanism expansion. This has caused the urban region to grow in a disorderly manner by occupying spaces such as slopes, ravines, and natural parks[25,38,39] This Valley is surrounded by large mountains on all sides, so emissions can remain trapped much longer than in other geographical areas, which really worsens atmospheric pollution and all its consequences on the environment, Additionally, significant thermo-dependent diffusion processes at ground level have been reported to cause important variations of atmospheric boundary layers, affecting atmospheric stability conditions in the region and making the dispersion of pollutants more difficult.[38] PM exposure potentially increases in settlements located in narrow valleys where local conditions do not allow for adequate diffusion.[38]

The aim of this study is to characterize the composition of PM_{10} in the (MRAV), and to identify its emission sources using Receptor Models (RMs): PCA and PMF. A deep understanding of PM$_{10}$ composition and emission sources in Medellín and the MRAV could lead to improvements for the region in terms of public health and the environment and could help to develop more efficient air quality management plans, as well, it could help for the understanding of the air pollutants in regions with similar topographies, demography and/or PM pollution rates.

2. Methodology

2.1 Sampling site and evaluation time

The Metropolitan Region of the Aburrá Valley (MRAV) is located in the middle of the central mountain range of the Andes, ranges between 6.0° and 6.5° N and -75.5° and -75.7° W.[25] It is the most important subregion of Antioquia, Colombia, covering an area of 1157 km^2, with 70.5% being rural and 29.5% urban.[25] Its topography is irregular.[40] with altitudes ranging from 1130 m to 3120 m above sea level.[25] The MRAV is the second-largest urban concentration in the country. The region is comprised of the municipalities of Caldas, La Estrella, Sabaneta, Envigado, Itagüí, Bello, Copacabana, Barbosa, Girardota, and Medellín. The MRAV is one of the most important regions in Colombia and Latin America in terms of industry, education, and culture, attracting more people from other parts of Colombia, with an increasing trend over more than a century.[25] This has led to an increase in the vehicular fleet, industries, and constructions, contributing to the emission of atmospheric pollutants and worsening public health.

The study of air pollution has taken great relevance in the region because of the pollution issues. The urban area of the MRAV is monitored through air quality stations that measure the concentration of the main atmospheric pollutants in specific areas. In previous years, the concentrations of air pollutants have exceeded the levels established by national regulations in the city of Medellin and the MRAV.[41] In 2017, a red alert was declared for air pollution which caused a series of restrictions that changed the rhythm of life of its inhabitants. It is increasingly common to establish preventive and/or restrictive measures in the region when air pollution levels reach critical values. Analyzing the physical and chemical characteristics of air pollutants is the first step to solve problems related to contamination, such as the need to improve car mobility, emission control, enforcement of standards, and adjustment of measurement criteria, among others.[42]

Ten (10) monitoring stations that are part of the air quality network of the MRAV were employed to collect the PM$_{10}$ samples, they are located (from south to north) in the municipalities of Caldas (1), La Estrella (2,3), Itagüí (4,5), Medellín (6,7,8), Copacabana (9) and Barbosa (10) (Fig. 1).

The sampling points are affected by different factors that contribute to air pollution, the environmental authority classifies air quality stations according to their characteristics, which can be in fully urbanized (urban) or mostly urbanized (suburban) areas. In Urban Traffic Stations (UTS), the level of pollution measured is determined mainly by emissions from nearby traffic. In Urban Industrial Stations (UIS), the pollution level is mainly influenced by industrial emissions. In Urban Background Stations (UBS), the pollution levels are not influenced by a specific source, same as in the Suburban Background Stations (SBS). Urban Mesoscale Trend Stations (UMTS) are stations located at a height above 15m above ground level.[43] For example, in the stations (1) and (6) are points where many vehicles converge daily, while the station (4), is located near brick factories, which are known for their large pollution contribution.[44,45] On the other hand, stations (1) and (7) are located in residential zones, near to factories and main roads. Table 1 summarizes the information concerning the characteristics of the stations.

A total of 94 samples were collected during 20 different dates between December 2018 and October 2021. At stations (7) and (8), a Graseby Andersen/GMW Model 1200 High-Volume Air Sampler, the remaining stations used a Tish Environmental Model TE-6070 PM$_{10}$ High-Volume Air Sampler, while ambient particulate matter was being deposited onto a filter tape sample spot. The dynamic filter loading was measured continuously, the equipment operated for 24 hours at a flow rate of 1.13m^3/min. The filters used were Whatman® 1851-865 QM-A brand quartz fiber filters of dimensions 20 cm × 25 cm and porosity of 2.2 µm, following the reference methods: RFPS-0202-141 and RFPS-1287-063 (US EPA CFR,

Table 1. Characteristics of the air quality stations in the MRAV.

ID	Name	Type	Location	Elevation (m)	Coordinates (WGS 1984)	
					Latitude	Longitude
1	CAL-JOAR	UBS	Caldas	1772	6°05'30.9"	75°38'04.7"
2	SUR-TRAF	UTS	La Estrella	1502	6°09'08.3"	75°37'39.0"
3	EST-MAGO	UIS	La Estrella	1766	6°09'39.3"	75°38'42.0"
4	ITA-POGO	UIS	Itagui	1702	6°11'23.6"	75°36'38.2"
5	ITA-PTAR	UMTS	Itagui	1542	6°11'37.1"	75°35'29.7"
6	MED-PJIC	UTS	Medellin	1546	6°12'32.3"	75°34'40.0"
7	MED-MIRA	SBS	Medellin	1618	6°13'47.9"	75°32'57.1"
8	MED-CORA	UMTS	Medellin	1514	6°15'09.0"	75°35'09.9"
9	COP-HSMA	SBS	Copacabana	1406	6°21'09.8"	75°30'29.6"
10	BAR-HSVP	SBS	Barbosa	1294	6°26'21.0"	75°20'10.8"

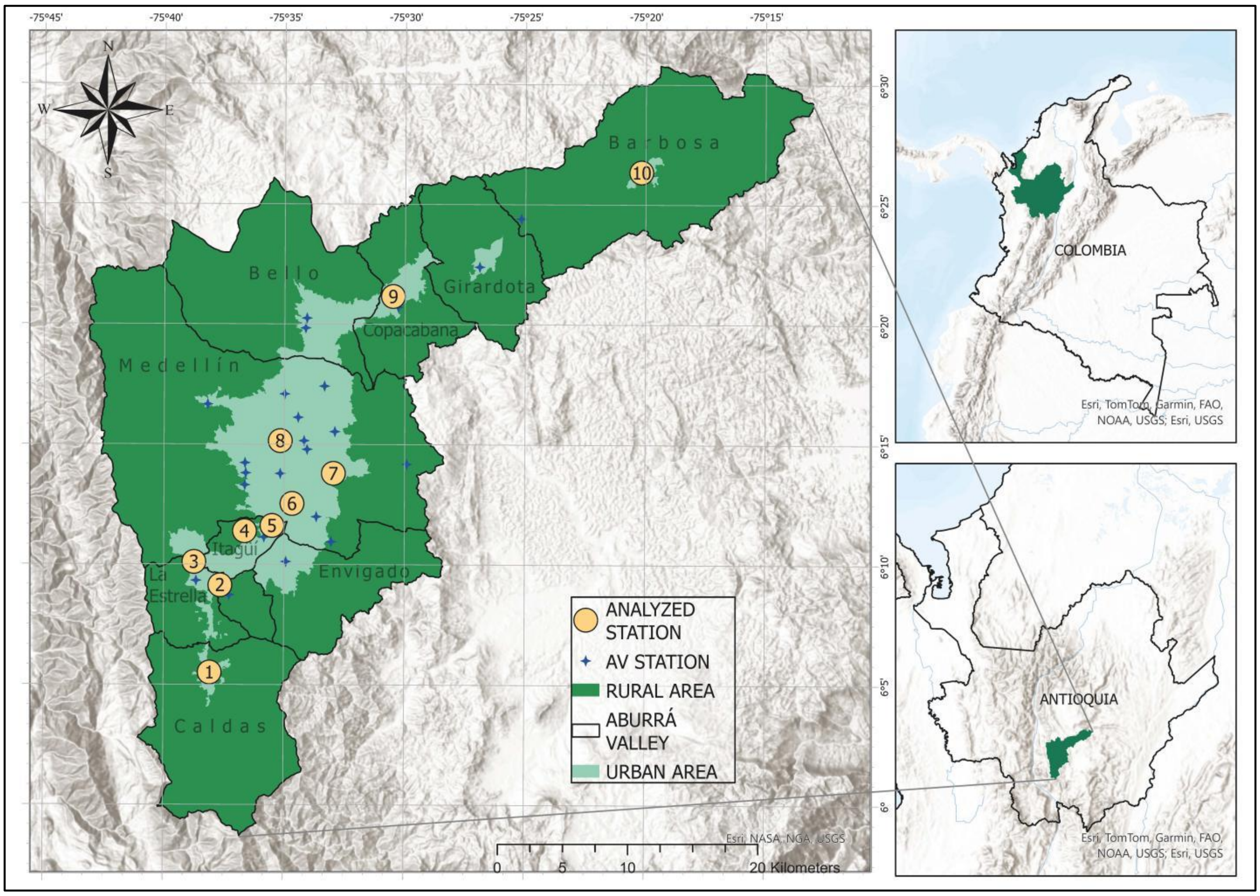


Fig. 1 Sampling site location in the Aburrá Valley (AV), Colombia.

Title 40, Chapter I, Subchapter C, Part 50, Appendix J. High Volume).[46]

2.2 Chemical analysis

The samples were analyzed at the Environmental Studies Laboratory of the University of Antioquia (LEA) (NTC ISO 17025) to determine their ion and metal contents using ion chromatography and atomic absorption spectrometry techniques, respectively. To determine the concentration of the ions, a Dionex Ion Chromatograph, Model ICS-1100 (with AS22 anion column, Dionex Ion Pac TM CS14RFIC cation column and Dionex Ion Pac TM CG14 RFIC column guard) was used to determine the anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{-3}, SO_4^{-2}) following the procedures established by the SM 4110B method.[47] For the cations (Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2}) followed the procedures established by the American Society for Testing Materials (ASTM) D6919.[48] The metals (Ba, Ni, Mn, Cu, Al, Cr, Zn, Fe) were characterized using an atomic absorption spectrophotometer (Thermo Electron Corporation Model A.A S4 series GE712311) following the procedure established by the United States Environmental Protection Agency US EPA IO 3.1.[49]

In ionic chromatography, the interactions of analytes in the sample with the stationary phase occur through Coulomb interactions. The stationary phase has ionic functional groups on its surface that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation exchange chromatography and anion exchange chromatography. When an aliquot of the sample is injected into the ion chromatograph, it is transported by the eluent (which in turn helps to separate the sample ions) through the guard column and the analytical column. The separated anions and cations are directed through an ion suppressor, which continuously suppresses the conductivity of the eluent and improves the analyte response. In the suppressor, the separated anions are converted into their highly conductive acid forms, while the conductivity of the eluent decreases significantly. The separated anions in their acidic forms are measured by a conductivity detector which gives the total concentration of the chemical species in the sample. In atomic absorption spectroscopy, the metal undergoes excitation to an excited or ground state, enabling it to absorb radiation emitted by a hollow cathode lamp. The absorbed energy is proportional to the metal concentration in the sample, facilitating precise quantification through the equipment.

For the elemental analysis, the PM_{10} sample fractions are stored in new paper envelopes, with the filter folded inward to ensure that the sampled portion remains within the fold, avoiding contact with the sampled area during manipulation, where a fraction of the quartz fiber filter equivalent to 10% of its total area is cut. To perform ion analysis, it is necessary to obtain an aqueous sample containing them. Therefore, the ions need to be solubilized. For this purpose, the filter fraction is cut into smaller pieces and placed into Falcon tubes. Then, 40 mL of ultrapure water is added, and the mixture is manually agitated for 1 minute. The samples are subjected to ultrasound for 1 hour, ensuring that the filter pieces are fully submerged and the tube is properly sealed. The sample is agitated again, and approximately 10 mL are taken for filtration using a 0.2 µm pore size acrodisc filter. Subsequently, the equipment performs the ionic analysis of the sample. On the other hand, to perform the sample extraction for metal analysis, the filter fraction is cut into smaller pieces and transferred to a 250 mL Erlenmeyer flask. Then, 12.5 ml of an acid solution of nitric acid and hydrochloric acid HNO_3: HCl (5.55%: 16.75%) is added. The sample is heated at 90 °C for one hour. Subsequently, 5 ml of HNO_3 are added to ensure the solubility of the metals and then, heated again at 90 °C for 30 min. Once the digestion is completed, it is allowed to cool for 30 min., distilled water is added to avoid losing the sample that is stuck to the walls of the flask. Finally, 12.5 mL of the solution are filtered through 0.45 µm pore size acrodisc filter, and the elemental analysis is carried out by the atomic absorption equipment. All the procedures are described in detail in the reference methods.

2.3 Source apportionment analysis

2.3.1 Principal component analysis (PCA)

PCA is a statistical tool that enables to identification patterns in the data, allowing to determine their differences and similarities.[34] from the analysis of the correlation matrix,[50] is an exploratory tool used to investigate structure in multivariate data sets by combining factor analysis with multi-linear regression to quantify the contributions of various particulate sources.[8] PCA is a valuable multivariate statistical tool, which reduces the dimensionality of large data sets. By systematic analysis of the correlation between all variables, PCA extract new variables, that have most of the information about the data.[11] PM_{10} composition was analyzed by PCA, in which variables with missing data over 50% were not considered for the analysis of the receptor models, finding under this criterion that the omitted variables for the source detection were NO_2^-, F^-, Ni, Cr and Ba. Subsequently, an analysis of the correlation matrix was performed using Spearman correlations, therefore, variables that do not represent a significant correlation ($\rho<0.5$) with any other variable are not considered for the analysis (under this criterion, the variable Cu was not considered). Spearman ρ correlation index is calculated as follows:

$$\rho = 1 - \frac{6\Sigma\, d_i^2}{n(n^2-1)} \tag{1}$$

where d_i is the difference between the two ranks of each observation and n, the number of observations. Once the correlation matrix has been analyzed. The first step of the PCA consists of standardizing the concentration data.[7]

$$Z_{ij} = \frac{C_{ij} - \mathbb{C}_j}{\sigma_j} \tag{2}$$

where Z_{ij} is the standardized value; C_{ij} is the number of the sample i by concentration of the chemical specie j; $\mathbb{C}_j$ is the arithmetic mean concentration of the chemical specie, and σ_j is the standard deviation.

PCA reduces the dimension of the original data matrix by generating new variables that correspond to a linear combination of the original variables.[51] This new set of variables are known as Principal Components (PCs). The PCA aims to solve the equation:

$$X = \lambda_1 + \lambda_2 + \cdots \lambda_n \tag{3}$$

where X is the total variance of the data, λ is the variance of each PC, and it's calculated through the eigen vectors and the concentration of each C_{ij}, the PCs can be interpreted as emission sources,[7,52] The strength of the PCA is that it is based on the evolution of data collected in specific sites.[11] In this study, were considered the number of PCs that covered the 81.4% of the total variance of the data. To run the analyses, R software version 4.3.0. was used.

2.3.2 Positive matrix factorization (PMF)

PMF is a technique that consists of factor analysis,[53] allowing to identification several factors, the contribution of the components to the factors, and the contribution of each factor to each sample.[8] The PMF assumes that in the results will not present values that contribute negatively to an emission source.[35] It is a widely used technique to perform PM source estimation.[35,53] PMF decomposes the original data matrix into two matrices, a contribution matrix and a factor profile matrix, and the interpretation of the emission sources is performed by the user.[35] PMF requires an uncertainty matrix[35] that assigns an uncertainty value to each species and sample. The uncertainty data set is calculated through the detection limit (DL) of the method as follows: [53,54]

$$U_{ij} = \left(0.05C_{ij}\right) + DL_j \tag{4}$$

where U_{ij} is the uncertain value, and DL_j is the detection limit of the method by chemical species. The speciated sample data set is assumed to be influenced by linear combinations of origin of sources emissions, which is distributed as factor contributions by PMF. P sources are affecting a receptor and linear combinations of contribution, affected by the factor contributions g and the factor profiles f. By using constraints and the associated adjusted uncertainty, the PMF model minimizes the Q function, which identifies if the model has reliable values and its results can be interpreted as emission sources,[35] it is written as**:**

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m} \frac{[C_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}]^2}{[U_{ij}]^2} \tag{5}$$

In the current investigation, the analyses were performed with the EPA PMF 5.0 software, following the considerations of the EPA 5.0 user guide. In which a set of 14 chemical species were analyzed in a total of 94 samples.

3. Results

3.1 Overview of the data

The average PM_{10} and chemical species concentrations are shown in Table 2. PM_{10} were found ranging from 6.9µg/m^3 to 72.8µg/m^3 with an average value of 40.6 µg/m^3 ± 14.5µg/m^3, this value is close to the WHO limit (45 µg/m^3),[55] 43% of the

Table 2. Summary statistics for the chemical species.

Specie	Average (µg.m3)	Standard dev. (µg.m3)	Minimum (µg.m3)	Maximum (µg.m3)
PM10	40.65	14.52	6.97	72.82
Sulphate	4.74	2.17	0.03	8.74
Sodium	1.36	1.16	0.20	4.09
Nitrate	0.99	0.59	0.05	3.18
Phosphate	0.86	1.03	0.03	3.93
Ammonium	0.79	0.69	0.04	2.35
Potassium	0.70	0.36	0.19	2.07
Calcium	0.52	0.30	>0.03	1.61
Iron	0.47	0.29	>0.07	2.12
Aluminum	0.30	0.19	>0.06	0.82
Magnesium	0.18	0.15	>0.03	0.54
Chloride	0.11	0.09	>0.01	0.77
Zinc	0.09	0.13	>0.01	0.40
Cupper	0.03	0.02	>0.01	0.12
Fluoride	0.03	0.07	>0.01	0.60
Barium	0.02	0.02	>0.02	0.09
Chromium	0.02	0.07	>0.01	0.53
Manganese	0.01	0.02	>0.01	0.11
Nickel	0.01	0.01	>0.01	0.05
Nitrite	0.01	0.01	>0.01	0.04

PM_{10} concentration data exceeded this threshold, like those values reported by Pereira in 2019 where 40% of the samples (n = 12) went above that limit in a study conducted in Medellin.[56] The average concentration of PM_{10} matches the data reported by Gómez-Peláez ($49 \mu g/m^3$) in the period 2010-2017 for the MRAV.[41] Ramos also reported similar values of PM_{10} concentration (Ranging from 37 to $45.7 \mu g/m^3$) in the region.[38]

The metals with the highest concentration were iron, followed by aluminum, the lowest concentrations were nickel and chromium (however, these metals are dangerous even in low concentrations).[28,29] As for the anions, sulfate and nitrate were the most concentrated, while the least concentrated were fluoride and nitrite. The cations that presented the highest concentration were sodium and ammonium. The contribution of ions is approximately 26% of the PM mass, comparable to the results reported by Jain, 2018 (30%),[8] Sharma, 2014 (23%)[57] and Ram, 2011 (25%).[58] The mass occupied by metals corresponds to 3%, like data reported by Correa, 2023,[1] indicating that the fraction of metals in PM occupies between 1-5% of the PM composition.

Table 3 shows the coefficient of the Spearman correlation ρ. The variables mainly correlated ($\rho > 0.75$) were PM_{10}-Sulfate ($\rho = 0.76$) (Fig. 2a), Sulfate-Ammonium ($\rho = 0.79$) (Fig. 2b) and Magnesium-Calcium ($\rho = 0.76$) (Fig. 2c). The high correlation PM_{10}-Sulfate is explained as sulfate is the major contributor to the mass of PM (Approximately 12%). PM_{10}, often harbors sulphate particles sourced from industrial activities, vehicle emissions, construction, and natural phenomena like dust and sea spray. These sulphate particles result from the oxidation of their precursor gases released by industrial processes, formed through atmospheric oxidation reactions, sulphate. Wind currents facilitate the long-distance transport of PM_{10} and its associated sulphate particles, leading to correlated pollution levels in affected regions. Seasonal variations in emissions, atmospheric conditions, and meteorological factors also influence the concentrations of both PM_{10} and sulphate.[8,23]

The relationship Sulfate-Ammonium suggests that its formation occurs due to atmospheric interactions of secondary aerosols (SA),[32,34] as sulfate and ammonium are formed mainly for the interaction of the precursor gases (NH_3 and SO_X respectively), such as the reaction of H_2SO_4 with NH_3 that can lead to the formation of $(NH_4)_2(SO_4)$ and NH_4HSO_4.[34] Sulphate and ammonium share common anthropogenic sources, including industrial activities, agriculture, and transportation. Given their similar sizes and properties, sulphate and ammonium particles are often transported together in the atmosphere by wind patterns and stability, resulting in correlated concentrations. Their seasonal variability is influenced by factors such as temperature, humidity, among others.[34] At last, Magnesium-Calcium are species of similar characteristics that are present in different sources, as can be the crustal material, dust suspension, or road dust,[59] sourced from phenomena like dust resuspension, soil erosion, agricultural activities, and sea spray. These elements, abundant in the Earth's crust, travel to the atmosphere through natural processes and human actions. Atmospheric calcium and magnesium can undergo reactions with acidic compounds such as sulfuric acid, forming salts like $CaSO_4$ and $MgSO_4$. These reactions aid in neutralizing acidic species and contribute to atmospheric particle formation. Wind-driven

Table 3. Spearman correlation for the selected species.

PM_{10}	Cl^-	NO_3^-	PO_4^{-3}	SO_4^{-3}	Na+	NH_4^+	K^+	Mg^{+2}	Ca^{+2}	Cu	Al	Cr	Zn	Fe
1.00														
0.23	1.00													
0.61	0.54	1.00												
0.19	0.34	0.64	1.00											
0.76	0.24	0.59	0.27	1.00										
0.53	0.19	0.71	0.68	0.63	1.00									
0.51	0.30	0.41	0.26	0.79	0.35	1.00								
0.65	0.18	0.32	0.00	0.53	0.19	0.30	1.00							
0.50	0.55	0.55	0.35	0.47	0.31	0.46	0.39	1.00						
0.56	0.53	0.54	0.18	0.58	0.22	0.57	0.50	0.76	1.00					
0.16	0.01	0.11	0.07	0.09	0.12	-0.16	0.19	0.06	0.04	1.00				
0.44	-0.05	0.20	-0.08	0.37	0.28	-0.02	0.44	0.09	0.18	0.18	1.00			
-0.06	0.02	0.02	0.22	-0.15	0.08	-0.29	0.23	-0.06	-0.16	0.26	0.09	1.00		
0.53	0.30	0.52	0.17	0.52	0.37	0.33	0.46	0.41	0.52	0.29	0.47	-0.09	1.00	
0.45	0.05	0.25	0.02	0.37	0.16	0.13	0.51	0.28	0.39	0.31	0.61	0.39	0.49	1.00

transport mechanisms, including dust storms and circulation patterns, facilitate the long-distance dispersion of calcium and magnesium-rich particles, leading to correlated concentrations.[7,34]

3.2 PCA and PMF analysis

Results can be interpreted from the perspective of previous studies, the working hypothesis and the actual conditions of the study area, the findings and their implications must be analyzed in the broadest context possible. We found five different emission sources for the PM_{10} in the MRAV, these are: secondary aerosols (SA), biomass/waste burning (BB), soil/road dust (SD), vehicular emissions (VE), and industrial emissions (IE). The results suggest that in the MRAV occurs mixtures between secondary aerosols with emissions from SD and IE. Table 4 shows the results of the PCA, while 4b shows the results of the PMF analysis. The loading value that allows to identify which species contributes to the different sources is shown, following the description of each source.

Table 4. Loadings of PCA analysis.

Specie	PC1	PC2	PC3	PC4	PC5
	SA	BB	SA/SD	VE	SD
PM10	0.369	0.131	-0.054	0.112	-0.307
Nitrate	0.372	-0.254	0.001	-0.038	0.028
Sulphate	0.380	0.075	0.035	0.316	-0.270
Phosphate	0.121	-0.575	-0.235	0.110	0.021
Sodium	0.186	-0.529	-0.291	0.056	-0.100
Potassium	0.228	0.369	-0.160	-0.050	-0.092
Iron	0.176	0.289	-0.428	0.043	0.258
Ammonium	0.326	0.011	0.362	0.307	-0.172
Aluminum	0.180	0.246	-0.528	-0.050	-0.141
Chloride	0.181	-0.006	0.300	-0.625	-0.461
Zinc	0.249	-0.095	-0.144	-0.614	0.233
Magnesium	0.318	-0.029	0.302	0.040	0.430
Calcium	0.338	0.111	0.190	-0.015	0.496

3.2.1 Secondary aerosols (SA)

The presence of sulphate, nitrate, and ammonium compounds in the atmosphere, is mainly due to the reactions of their precursor gases (SO_X, NO_X, NH_3).[8,23] These emissions can be natural or anthropogenic origin,[32,34] and they also can reach the atmosphere as a mixture of different combustion sources. According to some studies, the presence of sulfate in the atmosphere is mainly due to the oxidation of SO_2,[60] which comes from the burning of fuels containing sulfur such as diesel,[61] coal,[23] or natural gas,[62] as well as from oil refining and from diverse production activities. SO_2 is also emitted by chemical and metal industries which use sulfur compounds for calcination and smelting of materials such as copper, lead, zinc, and nickel.[62] Wood burning is another important source of this gas.[62] On the other hand, this gas reaches the atmosphere by natural causes, mainly geothermal emissions from volcanic activities and sulfur springs, sea salt aerosols, and biogenic emissions from the sea and land.[62] Previously, the environmental authority of the MRAV has performed the characterization of SO_X, finding that its emissions are mainly associated with vehicular and industrial sources.[63] Industrial processes,[64] biomass burning, and fossil fuel combustion.[31,59] have been identified as emission sources of nitrate and ammonium precursor gases[31,59] mainly in urban environments[65] when pollution levels are high.[65] Toro,[66] who previously studied the influence of NOx in the MRAV, determined the importance of reducing these emissions since they negatively influence the formation of secondary aerosols and VOCs.

3.2.2 Biomass/ waste burning (BB)

This factor contributes in several ways to the formation of PM,[59] as it is rich in various components due to the heterogeneity of the compounds that are burned. This source usually refers to fires, waste burning, and controlled burns for agriculture.[59] It has been determined that K^+ is one of the main components that reach the atmosphere due to biomass

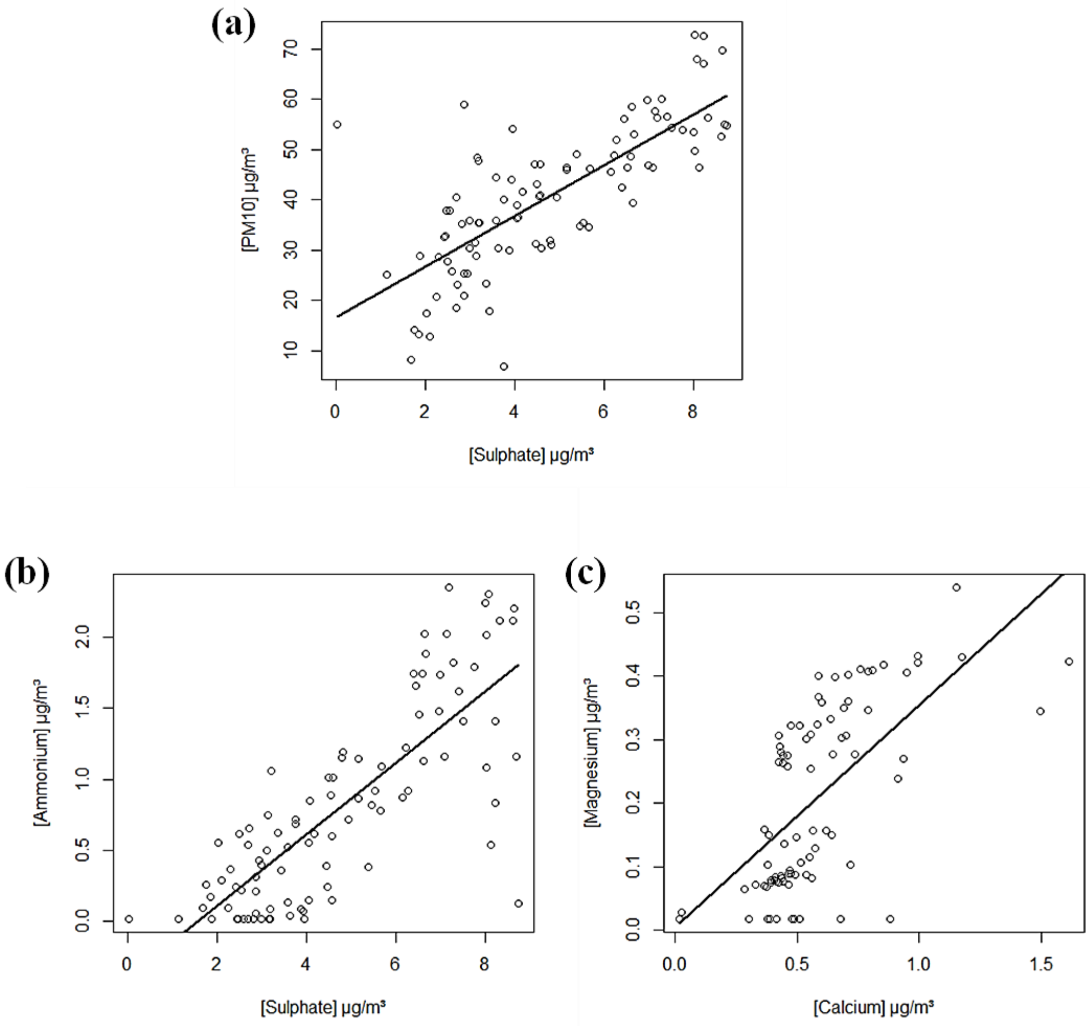


Fig. 2 High correlated variables, a) Sulphate-PM$_{10}$, b) Sulphate-Ammonium and c) Calcium-Magnesium.

Table 5. Loadings of PMF analysis.

Specie	F1	F2	F3	F4	F5
	SA/IE	BB	SA/SD	VE	SD
PM10	0.325	0.107	0.256	0.036	0.276
Phosphate	0.093	0.840	0.067	0.000	0.000
Sodium	0.266	0.599	0.017	0.088	0.030
Chloride	0.117	0.110	0.567	0.002	0.204
Nitrate	0.039	0.237	0.542	0.058	0.124
Ammonium	0.447	0.003	0.550	0.000	0.000
Magnesium	0.094	0.020	0.698	0.065	0.123
Calcium	0.068	0.001	0.623	0.022	0.286
Sulphate	0.466	0.111	0.233	0.028	0.162
Potassium	0.344	0.065	0.249	0.005	0.337
Aluminum	0.302	0.130	0.037	0.062	0.469
Iron	0.203	0.064	0.047	0.000	0.686
Zinc	0.074	0.003	0.100	0.823	0.000

combustion.[59] K^+ is used as a tracer for biomass burning[67] although it can be considered for other emission sources, however, the relationship with phosphate, widely used in fertilizers, enables a more reliable association to this source, as phosphate also stands out in the emissions generated by burning waste.[68] Sea salts are widely considered the sodium main source; however, it is also considered that Na^+ comes from anthropogenic activities as oil combustion, coal combustion and car exhaust. Nevertheless, the main source of Na^+ in urban air is the refuse incineration,[69] which suggest the biomass and waste burning. The Environmental Authority of the MRAV determined in its prevention plan declaration that vegetation fires near and far from the valley are the external factor that most affects air quality in the region, and thus, surveillance operations have been reinforced for possible burns and fires.[70]

3.2.3 Soil suspended dust (SD)

Mineral elements naturally occur in the earth crust. However, human activities have introduced high loads of these constituents in the environment, making it difficult to differentiate natural and anthropogenic contribution.[71] Soil dust and road dust are often considered to be the most influencing sources of airborne particulates in some cities.[59] Dust is characterized by elements abundant in the earth's crust rocks and the soil,[72] Calcium and magnesium are markers of mineral dust.[7,67,73] These elements are major constituents of airborne soil and road dust and generally contribute to coarse aerosols.[34] Aluminum and Iron also serve as markers of origin of this source, since these components are quite abundant[51] and can be converted into particles that can be transported by the air,[53] deposited again and resuspended.[74] The presence of iron and aluminum can occur in the atmosphere naturally and anthropogenically, for example, the composition of pavement is characterized by the presence of these two metals.[59] Al and Fe can be emitted from modern catalytic converters as well as abrasion of brake pads[51] and other composite materials of fleet.

3.2.4 Vehicle emissions (VE)

This is a source category that includes different kinds of emissions from several vehicle types. In addition to primary PM emissions from exhaust, and the emissions of organic and inorganic gaseous PM precursors from the combustion of fuels and lubricants, vehicles emit significant amounts of particles through the wear of brake linings, clutch, and tires.[72] Fine zinc particles can be generated from vehicle brake wear, and tire wear can also release small amounts of zinc in particulate form as well. Different studies have classified the presence of chloride about other metals as a source of vehicle emissions.[5,75] For instance, the emissions of chloride are attributed to the tailpipe emissions of two-stroke engines in which zinc is used as a fuel additive.[5] In the MRAV, vehicle emissions are relevant because in recent years the number of vehicles has increased significantly.[25] The Environmental Authority of the MRAV is implementing several actions aimed at managing public mobility in a more efficient, clean, and accessible way, thus contributing to the reduction of pollutant emissions generated by motor vehicles.[70]

3.2.5 Industrial emission (IE)

Industrial emissions are typically heterogeneous because these are emissions associated with very different manufacturing processes, such as petrochemical, metallurgical, ceramics, and pharmaceutical industries. A large growth in industrial activities is normally accompanied by increases in population.[2,59] A series of markers species have been used to identify emissions coming from industrial sources, such as Cu, Cr, Al and Ni. The location of the stations is influenced by the presence of industries in the sector, for example, the station (4) is located at an area known to have many of the brick companies from the city. On the other hand, the station (3) is near to ceramics, painting, electromechanical and chemical industries. The presence of sulfate and ammonium in combination with other metals such as aluminum, are also often used as tracers of industrial emissions. Like the automotive parts, the growth of settlements in the valley is also evident.[39] Aguiar[25] previously have reported the growth of emissions from stationary sources in the region, which has very significant consequences in the human health, the environment, the health system, and the production and economics as well.

3.2.6 Mixed type contributions

The results obtained for the PM_{10} component clustering in the MRAV, suggest the mixing of emissions coming for SA with other emission sources, mainly with SD and IE. The presence of mixed sources of air pollution is due to a combination of factors and human activities that generate air pollutants such those released for many of industries present in the region (manufacturing, construction, services, *etc.*), or the different chemical and photochemical reactions that can generate sulfate, ammonium, and nitrate precursor gases with suspended compounds already present in the atmosphere.

3.3 Comparison of the models

The PC1 (Table 4) identified by the PCA analysis corresponds to SA, which occupies 38% of the variance and is mainly explained by the variables sulfate and nitrate. However, SA also have influence in the PC3, appearing as a mixture with SD, where ammonium is grouped with iron and aluminum. By the other hand, in the PMF analysis, SA appear in the F1 in combination with IE, explaining the relation between ammonium and sulfate with potassium and aluminum to enable a reliable association to this source. F1 explains the 32% of the variance. SA also appears in the F3 (17% of variance) (Table 5) in combination with SD as nitrate and ammonium are related with chloride, magnesium, and calcium. Different studies conducted by RMs have associated the SA source with the combination of nitrate, sulphate, and ammonium, as those reported by Jain, 2018 in Delhi, India using PCA, PMF and UNMIX.[8] Contini in Lecce, Italy, found similar results using PCA,[32] while other studies conducted by PCA and/or PMF have obtained similar results to the association of this chemical species.[5,34,76,77] For the MRAV, Ramos, 2023 associated the presence of compounds of Sulphur and Nitrate with the source SA.[38]

Table 6 summarizes the results of the receptor models; the following is the comparison of the remaining sources according with the results of the models.

Table 6. Summary of the receptor models results.

Source	PCA	Source	PMF
SA	Nitrate, Sulphate	SA/IE	Ammonium, Sulphate, Potassium, Aluminum
BB	Phosphate, Sodium, Potassium	BB	Phosphate, Sodium
SA/SD	Iron, Ammonium, Aluminum	SA/SD	Chloride, Nitrate, Ammonium, Magnesium, Calcium
SD	Magnesium, Calcium	SD	Potassium, Aluminum, Iron
VE	Chloride, Zinc	VE	Zinc

The PC2 (BB), includes the compounds phosphate, sodium, and potassium, and corresponds to 17% of the total variance of the sample, comparable with the results of the PMF analysis (F2), in which phosphate, sodium, and in a little proportion potassium are grouped, aiming the association of the same specific source in both models. F2 explains 25% of the variance. Studies conducted using RMs have associated these chemical species with the source BB.[31,59,78,79]

For the PC3 was found a mixed contribution of SD/SA, explaining 12% of the variance of the sample, linking iron and aluminum with ammonium. SD/SA was also identified as a source in the PMF analysis (F3) linking chloride, nitrate and ammonium with magnesium and calcium. It is important to note that in the PC3, the greatest influence is given by the characteristic compounds of SD, while in the F2, the compounds coming from SA are of greater importance, in the local context, Ramos associated the presence of Al, Mg, Ca with re-suspended powder and Fe with quarries (rocks and clays).[38]

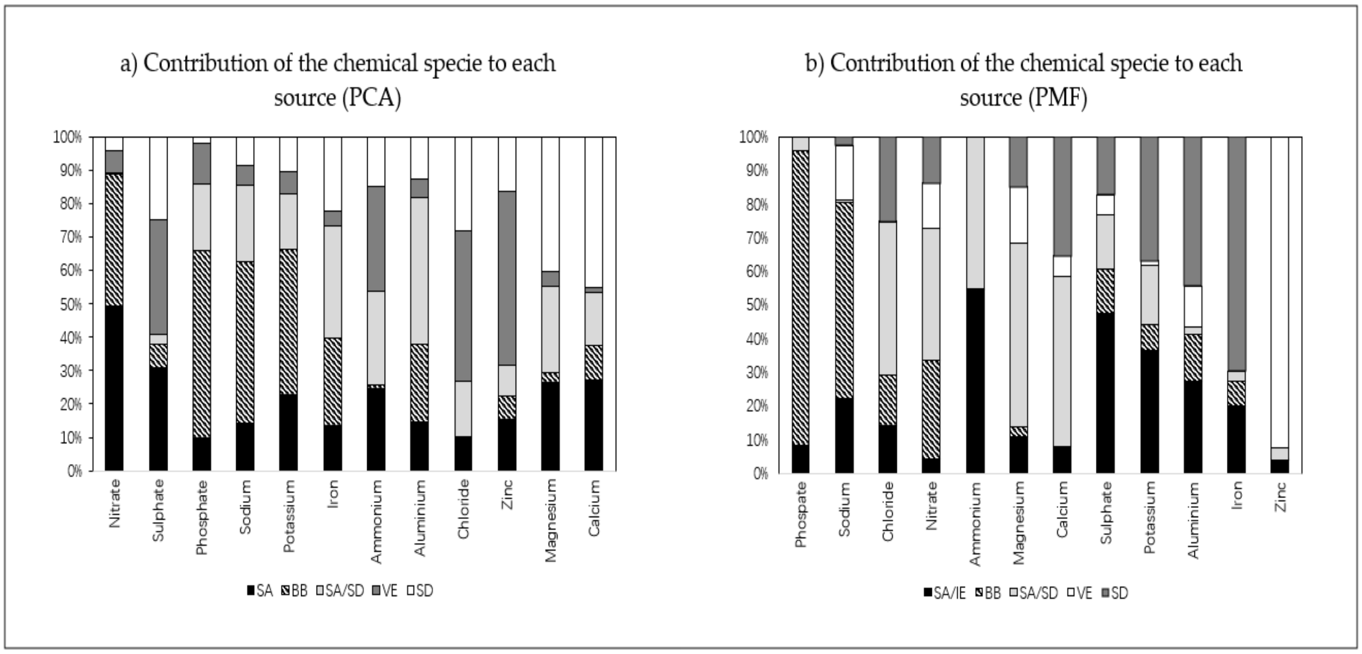
SD is the PC4, it accounts the 7% of the total variance, including calcium and magnesium. These compounds are widely known for being part of the earth crust, same as the compounds detected for the PMF in the F4 (Accounting 17% of variance) for that source (K, Al, Fe). On the other hand, PMF was identified a second mixed type contribution (F3), in which the combination of SA and IE have been obtained. IE was not identified as a source in the PCA, the mixing between sulphate and ammonium with metals like potassium and aluminum suggest emission generated by different industries. Different studies have concluded that the presence of these species have common origin.[68,78,79] For the MRVA: magnesium, calcium, potassium, aluminum, and iron were found to coming from re-suspended powder and quarries.[38] Zn and Cl^- compose the PC5 (6.5% of the total variance), identified as VE for their characteristics, as Zn is an important marker of VE it's also relevant in the PMF analysis in which Zn is the main component of the source (F5 with the 8% of the total variance). Numerous studies in different locations associate the presence of Zinc with VE as those reported in Los Angeles,[7] Delhi,[34] or Buenos Aires,[80] among others.[22,28,59] Chloride is also associated with that source.[5,78,81] In the local context, presence of Zn has been associated with tire wear.[38]

It's important to note that through the PMF all the emission sources proposed for the MRAV were detected, while PCA did not identified a source that could be enterally associated with industrial emissions. Figs. 3a and 3b shows the comparison of the influence of the chemical species in each source in the PCA and PMF analysis, respectively.

4. Discussion

The outcomes of both models effectively elucidate the identified sources within the MRAV. Fig. 4 delineates the proportion of data variance attributed to each source across both models. Remarkably, the SA source emerges as predominant, underscoring the high comparability of results.

The results obtained for PM_{10} in the analyzed region, show similarities with respect to other urbanized regions of Colombia. For example, a similar study conducted in the city of Bogotá, which is characterized by its high altitude and cool mountain climate, recorded an average concentration of 37.5 µg/m³.[77] Another study in Bogotá reported a concentration of 45.5 µg/m³.[75]. In contrast, in Barranquilla, a coastal city


a) Contribution of the chemical specie to each source (PCA)

b) Contribution of the chemical specie to each source (PMF)

Fig. 3 a) Contribution of the chemical species to the sources (PCA analysis), b) Contribution of the chemical species to the sources (PMF analysis).

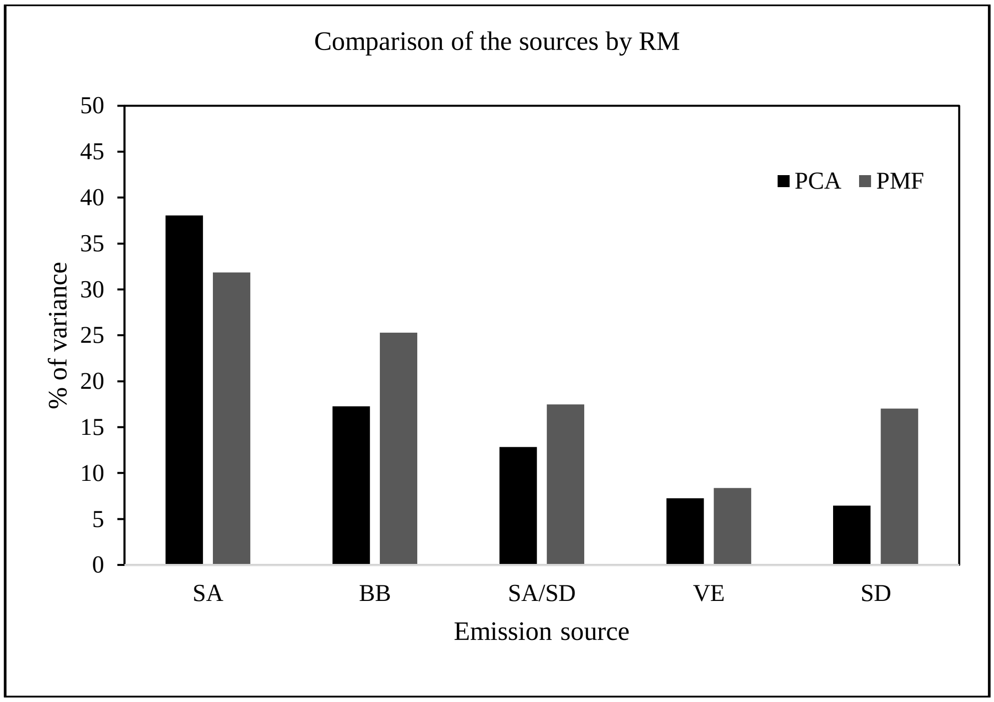


Fig. 4 Comparison of the source apportionment of the models PCA and PMF (*In PMF the source corresponds to SA/IE).

characterized by high humidity and higher temperatures, an average of 45.8 μg/m³ was found.[82] Data suggests that, despite geographic and climatic differences between cities, all face similar air quality challenges, underscoring the importance of implementing effective pollution control measures throughout the country.

The results show that PM_{10} levels are close to the maximum permissible by WHO and Colombian regulations, a clear signal that stricter regulatory measures are needed to reduce pollutant emissions. These data could support proposals to strengthen environmental regulations and set lower limits for emissions from identified sources. Knowing the major sources of PM emissions is valuable information for developing specific control strategies, for instance could be implemented in industries and vehicles, such as the use of clean and renewable energy can be promoted. Information on the spatial distribution of emission sources can influence urban planning and the location of industries, residential areas, and traffic routes. Low emission zones or green areas can be established to mitigate the effects of air pollution in the most affected areas.

To effectively address PM_{10} pollution in the valley, a multi-faceted approach is essential, that includes the implementation of stringent air quality management policies with the aim of regulating emissions from the sources identified, alongside setting emission standards, enforcing regulations, and promoting cleaner technologies. Furthermore, integrating air quality considerations into urban planning is crucial, promoting the establishment of green spaces, pedestrian zones, and sustainable transportation options to reduce vehicle emissions. Public health initiatives are vital to raise awareness about the health impacts of PM_{10} and atmospheric pollutants exposure and provide guidance on minimizing exposure, including educational campaigns, health advisories with greater reach and impact before, during and after high pollution episodes, and ensuring access to healthcare services for vulnerable populations. Collaborative governance among local governments, environmental agencies, industry, and community groups is essential to develop comprehensive strategies for pollution reduction, involving monitoring programs, data sharing initiatives, and coordinated efforts to address cross-boundary pollution sources.

In the subsequent studies, the focus must be towards comparing the obtained results with health and comorbidity datasets, with the aim to elucidate potential correlations between air quality patterns and health outcomes, providing valuable insights for public health interventions and policy formulation. Additionally, the exploration of alternative statistical methodologies, such as cluster analysis, which enable the identification of spatial patterns and similarities among monitoring stations. At last, engaging in international cooperation and knowledge exchange to learn from successful strategies implemented in other regions facing similar challenges is imperative, involving participation in global initiatives, sharing best practices, and collaborating on research projects to address common environmental concerns.

5. Conclusions

The receptor models yielded similar sources, identifying that the main sources of PM_{10} in the MRAV are Secondary Aerosols (SA), Biomass Burning (BB), Soil/road Dust (SD), Vehicular Emission (VE) and Industrial Emission (IE) which are relevant to the different problems faced by the MRAV in terms of atmospheric pollution, each model shows grouping forms that in contrast to what has been studied at the local and global levels allow establishing precise emission sources.

Among the characterized compounds, SA occupies the largest proportion of the PM_{10} mass in the MRAV, the characteristics of the study area promotes the combination and transformation of these chemical species (sulphate, nitrate, ammonium) with the species that are typical of other emission sources.

Sulfate occupies the largest mass fraction of PM_{10}, and thus, evaluating the impacts generated by this pollutant is fundamental to understand how this chemical specie affects the environment and mainly people's health.

The environmental authority has taken different initiatives to prevent the emissions generated by the different types of sources. The receptor models provide the possibility to directly identify the most important factors and to act on the prevention and mitigation of the factors causing the emissions. Identifying areas where further research is needed, such as understanding the temporal-spatial behavior of the pollutants and the interactions between different emission sources may provide additional information to develop more effective air pollution control strategies.

The results from this investigation increase awareness of the health risks associated with air pollution to the local population and encourage participation in initiatives to reduce emissions at Medellin, the MRAV, and other similar cities not only in Colombia, but elsewhere. This could include campaigns focused to understand the importance of encouraging more sustainable consumption practices, promoting public transportation, and reducing the use of internal combustion vehicles, among others.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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