Chapter 6 Evaluation of the heavy metal's levels in PM10 particles in air of an urban site of Leon City, in the cold dry climatic season 2018

Capítulo 6 Evaluación de los niveles de metales pesados en partículas PM10 en aire de un sitio urbano de la Ciudad de León, en la temporada climática seca fría 2018

CERON-BRETON, Julia Griselda†*´, CERON-BRETON, Rosa María´, LARA-SEVERINO, Reyna del Carmen´´ and MARTÍNEZ-MORALES, Stephanie´´´

´Universidad Autónoma del Carmen, Faculty of Chemistry, Mexico.
´´Universidad Autónoma del Carmen, Faculty of Health Sciences, Mexico.
´´´Instituto Potosino de Investigación Científica y Tecnológica, Post-Graduate Studies in Geo-Sciences, Mexico.

ID 1st Author: *Julia Griselda, Ceron-Breton* / **ORC ID:** 0000-0003-1551-7988, **CVU CONACYT ID:** 122903

ID 1st Co-author: *Rosa María, Ceron-Breton* / **ORC ID:** 0000-0001-8647-022X, **CVU CONACYT ID:** 30106

ID 2nd Co-author: *Reyna del Carmen, Lara-Severino* / **ORC ID:** 0000-0001-6173-0187, **CVU CONACYT ID:** 357254

ID 3rd Co-author: *Stephanie, Martínez-Morales* / **ORC ID:** 0000-0003-3465-7644, **CVU CONACYT ID:** 849451

DOI: 10.35429/H.2021.16.85.106

J. Ceron, R. Ceron, R. Lara and S. Martínez

* jceronbreton@gmail.com

A. Marroquín, J. Olivares, D. Ventura, L. Cruz. (Coord.) CIERMMI Women in Science TXVI Engineering and Technology. Handbooks-©ECORFAN-México, Querétaro, 2021.

Abstract

This work reports the levels of atmospheric particles concentrations PM10 and their content of trace metals (Cd, Co, Cu, Fe and Zn) collected in an urban site of Leon City, Guanajuato during the cold dry climatic season 2018. The analysis for heavy metals determination in the collected particulates were carried out by Atomic Absorption Spectrophotometry (AA). The elemental and morphological analysis of the particulates were carried out by scanning electronic microscopy with energy dispersive spectroscopy (SEM-EDS). Fe was the more abundant metal (1.50 µg m^{-3}), followed in order of importance by Zn (0.65 µg m^{-3}), due to these metals are abundant in the crustal. In minor proportions were found Cu (0.09 µg m^{-3}), Cd (0.28 µg m^{-3}) and Co (0.11 µg m^{-3}). Enrichment Factors analysis showed that all the analyzed metals were highly influenced by anthropogenic activity. Bi-variate and multivariate analysis confirm the anthropogenic origin of Cd, Cu and Zn. SEM-EDS analysis demonstrated Fe was the dominant metal and it was possible to relate the morphology of particulates with their elemental content and their emission sources.

PM10, Heavy metals, Leon

Resumen

El presente trabajo reporta los niveles de concentración de partículas atmosféricas PM10 y su contenido de metales traza (Cd, Co, Cu, Fe y Zn) colectadas en un sitio urbano de la ciudad de León, Guanajuato durante la temporada de seca fría 2018. Los análisis para la determinación de los metales pesados en las partículas colectadas se realizaron mediante Absorción Atómica (AA). El análisis elemental y morfológico de las partículas se llevó a cabo mediante microscopía electrónica de barrido con espectroscopia de energía dispersiva (SEM-EDS). Fe fue el metal más abundante (1.50 µg m^{-3}), seguido en orden de importancia por Zn (0.65 µg m^{-3}), debido a que estos metales abundan en la corteza terrestre. En menores proporciones se encontraron Cu (0.09 µg m^{-3}), Cd (0.28 µg m^{-3}) y Co (0.11 µg m^{-3}). Los Factores de enriquecimiento mostraron que todos los metales analizados fueron altamente influenciados por la actividad antropogénica. Los análisis bi-variado y multivariado confirmaron el origen antropogénico de Cd, Cu y Zn. El análisis SEM/EDS confirmó que Fe fue el metal dominante y fue posible relacionar la morfología de las partículas con su contenido elemental y sus fuentes de emisión.

PM10, Metales pesados, León

6.1 Introduction

Currently, air quality degradation represents a serious threat to human health and ecosystems (Molina L. & Molina N., 2004). Clean air is a basic right for human well-being (SEMARNAT, 2012). According to the World Health Organization (WHO), air pollution cause 2 millions of premature deaths a year in the whole world (WHO, 2006). This mortality index is due to exposure to fine particulates of aerodynamic diameter les or equal than 10 microns (PM10), which may cause cardiovascular and respiratory diseases and cancer (WHO, Air Quality and Health).

Air pollutants may exist in gas phase or in particulate form. Particulate matter is a mixture of liquid and solid particles, organic and inorganic substances, which are suspended in the air. Atmospheric particles can be emitted by a wide variety of sources of natural or anthropogenic origin. Regarding the formation mechanisms, the particles can be emitted as such to the atmosphere (primary) or be generated by chemical reactions (secondary particles). These chemical reactions can consist of the interaction between precursor gases in the atmosphere to form a new particle by condensation, or between a gas and an atmospheric particle to give rise to a new aerosol by adsorption or coagulation (Warneck, 1999). The composition of the particulate material is very varied and we can find, among its main components, sulfates, nitrates, ammonia, sodium chloride, coal, mineral dust, metallic ash and water, as well as certain metals such as As, Cd, Fe, Zn, Cr, Cu, Al, V, Ni and P (Wichman & Peters, 2000).

Atmospheric particles are also classified according to their size and, in the field of air quality, we speak of PM10 particles, which would be the largest, whose theoretical aerodynamic diameter would be less than or equal to 10 µm (microns of meter = millionth of a meter) and fine particles known as PM2.5 whose diameter is less than or equal to 2.5 µm.

This type of pollutant can cause serious effects in human health not only due to its mass concentration but also due to its chemical constitution, and may also contain viruses, bacteria, spores, etc. While PM10 particles are retained in the respiratory tract, producing effects at the respiratory system level, minor particles, such as PM 2.5, have the ability to pass into the bloodstream and can potentially damage any organ or system (INSAG, 2019).

Heavy metals are one of the most harmful constituents of atmospheric particles, due to the toxicity that they represent. Heavy metals have a high density (greater than 4 g / cm^3), mass and atomic weight above 20, and are toxic in low concentrations. Some of these elements are: cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), cadmium (Cd), lead (Pb), zinc (Zn) (Concon, 2009). The risks caused by heavy metals in the atmosphere are manifested when their absorption and accumulation in animal tissues exceeds certain limits; however there are metals that are toxic even at low concentrations, such as: Pb, Cd, As and Hg (OSHA). In the PM10 fraction, there are 75 to 90% metals such as: Cu, Cd, Ni, Zn and Pb, which implies that there is a high percentage of risk and probability of generating serious damage to the exposed organism (Báez et al., 2001). On the other hand, there are also some pollutants that have been designated as main pollutants or criteria, which include PM10 and PM2.5 particles, sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen oxide (NO_2), volatile organic compounds (VOC), and ozone (O_3). They are called “criteria air pollutants” because they are regulated by national and international regulations or standards that establish the maximum permissible limits in ambient air. These pollutants are the most common and ubiquitous in urban centers, where the population is concentrated. The knowledge of the concentration levels of the criteria air pollutants makes it possible to assess air quality in large urban centers and to develop public policies and strategies to protect the health of the population (Henry & Heinke, 1999). In Mexico, maximum permissible levels for PM10 particles in ambient air are regulated in the Mexican Official Standard NOM-025-SAA1-2014, published in the DOF on August 20, 2014. This standard establishes limits of 75 µg m^{-3} average 24 hours and 40 µg m^{-3} annual average.

Mexico has long faced air quality problems in its main metropolitan areas, registering an increase in hospital admissions and mortality related to air pollution in the Valley of Mexico. In addition to the local effects associated with poor air quality on people's health, there are also effects at the regional level, such as the impact on forests and aquatic ecosystems due to acid rain or even globally, such as climate change and the reduction of the thickness of the stratospheric ozone layer, being more obvious these effects in Antarctica. The Bajío area in Guanajuato is one of the commercial and industrial areas more developed in the country, so urban and population growth has increased in recent years, resulting in a deterioration in air quality, especially in the City of Leon, which constitutes the commercial operations center of the Bajío. In the emissions inventory of the State of Guanajuato 2016, it was estimated that the area sources are those that have the main contribution to the emissions of PM10, PM2.5 and NH_3, contributing 84.69%, 78.85% and 98.60% respectively of the total emitted. On the other hand, mobile sources contribute significantly to CO and NO_X emissions, generating 80.74% and 40.05% of the total of these pollutants, respectively; while, in the case of stationary sources, these contribute to almost all SO_2 emissions, with a contribution of 91.68%. In the particular case of VOCs, area sources and natural sources generate 48.45% and 39.95% of the total emissions, respectively.

Therefore, atmospheric monitoring is one of the main indicators of air quality, and in the State of Guanajuato, this monitoring process has been carried out for several years through the State Air Quality Information System, allowing citizens, companies, organizations and institutions, to obtain information on the environment and air quality regarding criteria pollutants and greenhouse gases. This information is generated by the Ministry of the Environment and Territorial Planning through programs and regulations, as well as strategic management instruments, seeking to improve the dissemination of knowledge for the improvement of air quality in the State of Guanajuato and well-being of its citizens. (SEICA, 2019). However, the continuous monitoring of particulate matter (PM10 and PM2.5) is only carried out considering the mass composition of the particles without chemical speciation of its content, hence, the levels of toxic agents such as heavy metals associated with the particles is unknown. Therefore, the effects on health that these pollutants could have on the exposed population is unknown too. For this reason, the present research work evaluated the atmospheric concentrations of the criteria pollutants, the gravimetric concentrations of PM10 particles and their content of trace metals (Zn, Cd, Fe, Cu, Co) in the ambient air of an urban site of the city of Leon, Guanajuato, evaluating the elemental composition, morphology and compliance with current applicable regulations.

This work also provides objective and reliable information about the behavior of the monitored pollutants that may be of help to government institutions to generate and / or update plans that mitigate the health risk to which the population in the study site could be exposed.

The general objective of this study was to evaluate the atmospheric levels of trace heavy metals in PM10 particles, their origin and their relationship with criteria pollutants, as well as their impact on health at a site in the city of Leon, Guanajuato during the cold dry climatic season 2018. The gravimetric concentration of suspended PM10 particles and the concentration of trace metals in trace ambient air (Zn, Cd, Fe, Cu, Co) were determined by atomic absorption spectrophotometry. In addition, the morphology of the particles and its elemental composition was studied by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). The influence of the winds at the local level on the concentrations of the pollutants measured was analyzed by means of an analysis of wind roses and the influence of the winds at the regional level on the concentrations of the atmospheric pollutants measured was studied by calculating the air mass trajectories using the NOAA HYSPLIT model. The probable sources of the measured pollutants were inferred from the results of the meteorological and statistical analysis (Pearson's correlation matrix and Principal Component Analysis). Finally, the health risk of PM10 particles and their heavy metal content were evaluated considering carcinogenic and non-carcinogenic risk.

This chapter is structured as follows: The first section provides the Introduction to the research work, Background Section (Section 1) gives information on the study of atmospheric particle levels and their trace metal content registered by other researchers around the world. Section 2 provides the study methodology, considering both the collection methods of PM10 particles, the analysis for the determination of heavy metals by atomic absorption spectrophotometry and SEM-EDS technique used to study the elemental characterization and morphology of the particles. A description of the method used for the meteorological analysis is also provided, which made it possible to determine the influence of local and regional winds on the levels of the measured atmospheric particles, as well as the identification of possible sources contributing to the levels of this pollutant. This section also provides descriptive information on the statistical tools and analysis applied to the data to determine the relationships between the measured air pollutants and the meteorological variables recorded (bi-varied and multivariate analysis: principal component analysis). This section also describes the method used for the evaluation of health risk considering both the cancer risk coefficient in the life time and the non-cancer risk coefficient (risk of contracting diseases other than cancer: cardiovascular and respiratory diseases) due to inhalation of trace metals contained in PM10 particles. Section 3 shows the results of the study, considering the concentration levels of both the PM10 particles and their trace metal content, the exceedances of current national and international regulations, the possible sources contributing to the levels of the pollutants measured and its location, based on statistical analysis and meteorological analysis. An analysis of enrichment factors is also carried out in order to determine which metals had a greater enrichment from anthropogenic sources and which metals were more influenced by the earth's crust. This section also shows the results of the health risk assessment for inhalation of these pollutants. Finally, section 4 provides the conclusions of the study, as well as the recommendations for future work.

6.2 Background

Heavy metal contamination is a current issue in both the environmental and public health areas, mainly due to the negative impact on public perception.

In several cities around the world the chemical characterization of the particulate material has been studied and one of the biggest concerns is always the content of metals in particles due to their toxicity (Molina et al. 2021; López Ayala, 2021). In Ecuador, cities such as Quito (Zalakeviciute et al., 2019) and Cuenca (Zegarra et al., 2020) reported content of metals in PM10, such as Cd (2.9 µg m^{-3}), Cu (1.06 µg m^{-3}), Fe (0.229 µg m^{-3}) and Zn (1.99 µg m^{-3}. One of the countries known for its high concentration of atmospheric pollutants is Thailand, where metal content in particles has also been reported, as it was shown by a study carried out in the city of Phitsanulok (Srithawirat et al., 2016) where the health risk assessment revealed that the carcinogenic effects of heavy metals are just below the maximum allowable values, which could pose a cancer risk for the site's population.

In southwestern Italy (Contini et al., 2014) low PM10 values of 34.4 µg m^{-3} were reported with metal content such as Cu (0.012 µg m^{-3}), Fe (0.229 µg $m^{-3)}$ and Zn (0.023 µg m^{-3}). In Havana, Cuba, Cruz and Valdivia (2017) found PM10 values of 39.5 (µg m^{-3}) with high concentrations of Cd (7.74 µg m^{-3}), Cu (100.31 µg m^{-3}) and low values for Zn (0.655 µg m^{-3}).

In Mexico, some studies have also been carried out on particulate matter and their heavy metals content in several cities such as Cananea, Sonora where it was found that the air quality during the study period was always from bad to regular with very few days with a good condition of air quality. In Puebla (Morales et al., 2014) reported PM10 concentrations of 55.9 µg m^{-3} with a trace metal content such as Cd (0.005 µg m^{-3}), Co (0.002 µg m^{-3}), Cu (0.09 µg m^{-3}) and Fe (1.203 µg m^{-3}). Morton and collaborators reported in 2021 for Mexico City, a PM10 concentration of 40.7 µg m^{-3}, with mean concentrations for Cd, Co and Cu of 1.5 µg m^{-3}, 0.5 µg m^{-3} and 123.6 µg m^{-3} respectively. In Tampico, Tamaulipas the concentrations for PM10 were 23.44 µg m^{-3} with concentrations of 0.033 µg m^{-3}, 0.236 µg m^{-3}, 0.04 µg m^{-3} for metals such as Cu, Fe and Zn respectively (Flores et al., 2015).

6.3 Methodology

6.3.1 Study Area

The city of Leon is located in the north of the state of Guanajuato, at an altitude of 1,798 meters above sea level, limiting to the north with San Felipe; to the east with Guanajuato and Silao; to the south with Silao, Romita, and San Francisco del Rincón; and to the west with Purísima del Rincón and the State of Jalisco. The urban sampling site was located within the Medicine Faculty facilities at 20. 13º North Latitude and 101.68º West Latitude, in the downtown. Leon is a Mexican city, head of the homonymous municipality, located in the State of Guanajuato. According to the interest survey carried out by the National Institute of Statistics and Geography (INEGI, 2015), it has a population of 1,578,626 inhabitants, which makes it the most populated town in the state of Guanajuato. The Leon Metropolitan Area is classified within the group 2 of CONAPO Metropolitan Zones Ranking that corresponds to "Metropolitan Zones and cities with more than 1 million and less than 4 million inhabitants" together with the Metropolitan Area of the Toluca Valley, Tijuana and Ciudad Juarez. Therefore, the urban and industrial development in the area has resulted in population growth and the need for services, as well as an increase in transportation vehicles resulting in a degraded air quality. The Institute of Ecology of Guanajuato State has an atmospheric monitoring network, measuring the criteria air pollutants and reporting emissions inventories since 2006. The study site is located within one of the stations of this network, (Station of the Faculty of Medicine), at 21.133 ° N and 101.68 ° W.

6.3.2 PM10 Sampling

The air sampler used was the Airmetrics miniVol TAS which is a portable sampler for suspended particles and non-reactive gases (Figure 6.1). This device was developed by the Environmental Protection Agency (EPA) and the Lane Regional Air Protection Agency in an effort to address the need for portable air pollution sampling technology. The sampling technique used by the miniVol is a modification of the PM10 reference method described in the United States Code of Federal Regulations (40 CFR part 50, appendix J). The sampling was carried out during the cold dry climatic season 2018 (January 05 to 12, 2018). The sampler was placed at the measurement site, where it was assembled, adjusted, and its correct operation verified, leaving the equipment ready to collect air samples. The sampling device sucked ambient air at a controlled flow of 7.2 L min^{-1} that passed through a particle size separator and then through a Whatman brand 47 mm quartz fiber filter during a 24 h sampling period. The particle size separation is achieved by impaction.

Figure 6.1 PM10 Sampling using the Minivol sampling device

Source: Own elaboration from photographs taken at the study site.

6.3.3 Mass concentration of PM10: gravimetric analysis

Before sampling, all the filters were conditioned at constant temperature and humidity values, to be gravimetrically calibrated. After the samples were collected, they were conditioned again in the laboratory at constant temperature and humidity. Filters with any visual irregularities were completely discarded. The procedure for weighing the filters is based on the document "Reference Method for the Determination of Suspended Matter in the Atmosphere" 40 CFR 50, appendix B, which indicates that the filters must be conditioned at least 24 hours at a controlled temperature between 15 ° C and 30 ° C with less than ± 3 ° C variation during the conditioning period (25 ° C for this study), while for humidity it must be less than 50% of constant relative humidity with a variation of the ± 5%. Filters were handled with vinyl gloves (no powder) and the use of metal tweezers was avoided so as not to interfere with the metal determination analysis. Filters were carefully stored in plastic Petri dishes, labeled for 24 hours of conditioning. Each filter was weighed in triplicate with a previously calibrated Sartorious LA 130 SF Analytical Microbalance (with 1 mg resolution) and the results were recorded.

The calculation of the gravimetric concentration is given by the following equation:

$$CPM_{10} = \frac{W_f - W_i}{Vol.} \times 10^6 \qquad (1)$$

Where:

CPM_{10} = Gravimetric concentration

W_f = final weight

W_i = starting weight

Vol = standard sample volume

6.3.4 Determination of heavy metals in PM10 by Atomic Absorption Spectrometry

Acid digestion of metals: Filters were placed in 150 ml glass beakers, and 10 mL of aqua regia (25 mL of HNO_3 + 75 mL of HCl) and 1.065 mL of $HClO_4$ were added, leaving them in contact for 18 hours. The contents of each glass were heated at 60 ° C for approximately 70 minutes, until almost dry. Then 20 mL of hot water were added to facilitate the filtration that was carried out when the content of each glass was cooled. Finally, the content of each glass was placed in flasks that were graduated to 50 mL using deionized water, after which the samples were stored in polypropylene containers for later analysis (Machado et al., 2007).

Calibration curves preparation: The standard solutions of Cd, Co, Fe, Zn and Cu were prepared by successive dilution from standard solutions of 1000 ppm HYCEL brand for atomic absorption. The stock solutions of each metal were prepared with a concentration of 10 mg / L of the standard solutions, graduated in 100 mL flasks, with a 2% HNO_3 solution. For each metal, 5 dilutions were prepared from each stock solution, which were measured at 100 mL each and used for the calibration curve of each metal.

Samples Analysis: For the analysis of the samples, an atomic absorption spectrophotometer was used. Thermo Scientific iCE 3000 Series AAS (Figure 2). Measurements were carried out according to the standard conditions recommended by the spectrophotometer manual, that is, specific wavelengths for each metal (Table 6.1). In all measurements, a deuterium lamp was used as a background corrector (Mahecha et al., 2015). Table 6.1 shows the wavelengths used to determine each of the metals considered in the study.

Table 6.1 Wavelength used for the analysis of each metal

Wavelenght (nm)				
Cd	Co	Cu	Fe	Zn
2288	**240.7**	**324.8**	**248.3**	**213.9**

Source: Own elaboration

Figure 6.2 Atomic Absorption Spectrophotometer, Thermo Scientific Brand, model iCE 3000 Series AAS used in this work

Source: Own elaboration from pictures taken in the laboratory

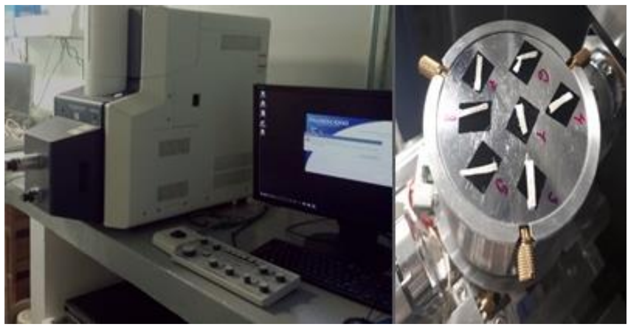
The basic instrumentation for atomic absorption equipment is constituted by a monochromatic radiation source (specific for each element), or polychromatic, an atomizer to produce the excited atoms of the substance to be analyzed: a mono-chromator to select the desired wavelength; a detector sensitive to the emitted radiation and a processor of the signal and the output reading. In general terms, it goes through the atomization system that contains the sample in atomic gas state, it reaches the mono-chromator that eliminates the radiation that is not of interest for the study, passing to the developer or absorbed radiation detector, which is then processed and amplified, giving as result in a read-out. The type of flame used to determine the metals analyzed in PM10 samples was a mixture of air (oxidant) - acetylene (fuel) – at a temperature between 2.100 to 2.400 ° C, being optimal for bring atoms to their fundamental state (Gallegos et al., 2012).

6.3.5 Scanning electronic microscopy- energy dispersive spectroscopy analysis (sem/eds) of selected particles

The analysis was made according to the guide for the monitoring of particles published in 1998 by the EPA (method of analysis of individual particles by SEM). This analysis uses electrons instead of light to form an image, the equipment has a device (filament) that generates an electron beam to illuminate the sample and with different detectors, the electrons generated from the interaction with the surface are then collected to create an image that reflects the surface characteristics of the same, being able to provide information on the shapes, textures and chemical composition of its constituents.

The morphology of the particles and their elemental composition with respect to metal content was evaluated using a Hitachi FLEXSEM-SU1000 (Scanning Electron Microscope) scanning electron microscope equipped with an Energy Dispersive (EDS) X-ray detection system TM 40000 Quantax 75/80 of Bunker that works at 20kV. The low vacuum scanning electron microscope was calibrated with a copper (Cu) grating, a filament current of 300 mA, and a working distance of 5 cm. A 1 mm x 0.5 mm rectangle was cut for analysis and the filters were analyzed as received after sampling, that is, no pre-treatment was necessary for this analysis. Figure 6.3 shows an image of the SEM /EDS equipment used, as well as the way in which the filter sections were mounted for analysis.

Figure 6.3 Electronic Microscope used for the elemental and morphological analysis of PM10 particles and view of the filters mounted on the equipment



Source: Own elaboration from pictures taken in the laboratory

6.3.6 Measurement of Air criteria pollutants and meteorological parameters

The criteria air pollutants and meteorological parameters data were monthly provided by the SEICA of the state of Guanajuato. Pollutants and meteorological parameters measurements were averaged to determine the average concentrations for each period. The measured meteorological parameters were the following: Temperature (° C), relative humidity (%), wind speed (m/s), wind direction (degrees azimuth), atmospheric pressure (mm Hg) and solar radiation (W/m^2). The criteria air pollutants were measured by automatic analyzers: CO (Teledyne Model 3000E Equipment, Filter Correlation Method), NO_2 (Teledyne Model 200E Equipment, Chemiluminescence Method), O_3 (Teledyne Model 400E Equipment, UV Absorption Method), and PM10 (Met One Instruments Equipment model BAM 1020, Beta-ray attenuation method).

6.3.7 Statistical Analysis

Pearson's correlation were calculated in order to identify bivariate relationships between heavy metals in PM10, criteria air pollutants, and meteorological variables. Similarly, a principal component analysis (PCA) was performed to explain the variation and discover the structure of the data set. The results of the ACP analysis generally is represented in bi-plots or factor loading tables, which reveal correlations between the observations. The information disclosed by ACP is useful to identify whether a pollutant is primary or secondary, or to identify the specific source of the pollutants.

6.3.8 Meteorological analysis

The wind direction data was ordered and reviewed, with which it was possible to perform a wind analysis to determine the origin of the pollutants with respect to the wind direction on each of the sampling days.

Wind Rose Analysis: Wind rose diagrams show the distribution of wind direction and speed at a specific location. This analysis was made with the WRPLOT software (Wind Rose Plots for Meteorological data) that simulates the direction and speed of the prevailing winds in the study site, available at: www.weblakes.com/products/wrplot/index.html

Air mass 24-h backward trajectories calculation: Air mass 24-h backward trajectories were calculated for the sampling period. This type of model is useful to determine the origin and to infer probable sources of the measured air pollutants. This analysis was made using the HYSPLIT tool (Hybrid Lagrangian Integrated Trajectory Model) available in: https//ready.arl.noaa.gov/HYSPLIT_traj.php.

6.3.9 Health Risk Assessment

Carcinogenic and Non-carcinogenic Health Risk Assessment of metals in PM10: The exposure to heavy metals in PM10 was expressed in terms of the daily dose per lifetime or LADD, which allows calculating the corresponding level of risk of each metal, considering two groups of population: adults and children. The LADD helps determine the amount in which a pollutant has negative effects on health when it is absorbed by the human body in a given period of time and is calculated with the following equations (Di Vaio et al., 2018).

$$LADD = E \times C \quad (2)$$

$$E = \frac{IR}{BW} \times \frac{ET \times EF \times ED}{AT \times 365} \quad (3)$$

Where for equation (2), C is the concentration of the metal of interest in PM10, which is assumed to be the same at the point of exposure, while E in equation (2) is obtained from equation (3), where IR (m^3 h^{-1}) is the rate of air inhalation, ET (24 h day^{-1}) is the exposure time, EF (350 day $year^{-1}$) is the exposure frequency, ED (years) is the duration of the exposure, BW (Kg) is the body weight and finally AT (days) is the average time, using ATc for carcinogenic risk and ATn for non-carcinogenic risk (U.S. EPA, 2009). Table 6.2 provides the parameters used to calculate the exposure.

Table 6.2 Parameters used to calculate exposure. *25550 days corresponding to the age according to the typical life expectancy (70 years x 365 days/year); **ED (24 years) multiplied by 365 days/year x 24 days; *** ED (6 years) multiplied by 365 days/year x 24 h/day

Parameter	Symbol	Units	Adults	Children
			Numeric Value	
Inhalation rate	IR	m^3/h	0.9	0.7
Body weight	BW	Kg	40	15
Exposure time	ET	h/day	24	24
Exposure frequency	EF	Days/year	350	350
Exposure duration	ED	Year	24	6
Average time	ATc	Days	25550*	25550*
Average time	ATn	Days	210240**	52560***

Source: DiVaio, 2018

CR represents the increased likelihood of disease caused by tumors above average due to the impact of compounds that produce carcinogenic effects. Values below 10^{-6} are considered negligible. For carcinogenic substances the CR is determined with the following equation:

$$CR = LADD \times CSF \quad (4)$$

Where, CR = probability of cancer occurrence during a life time of 70 years, LADD = daily dose per lifetime expressed in mg $Kg^{-1}day^{-1}$. Carcinogenic risk is defined as the increased likelihood of a person experiencing cancer during a lifetime as a result of exposure to a specific carcinogenic potential (U.S. EPA 2009). The SF is calculated with the following equation:

$$SF = IUR \times \frac{BW}{(IR \times ET)} \times 1000 \quad (5)$$

Where, IUR=Reference value reported in data base by EPA. The following table (Table 6.3) presents the values for IUR and RfC. With regard to inhalation risk units (IUR) and reference concentrations (RfC), only values for Cd, Co and Mn are reported, of which we are interested in the first two.

Table 6.3 Inhalation Unit Risk (IUR) Reference Concentration (RfC) from EPA expressed in mg m^{-3}

Metal	CAS	IUR	RfC
Cd	7440-43-9	1.8 x 10^{-3}	1.00 x 10^{-5}
Co	7440-48-4	9.00 x 10^{-3}	6.00 x 10^{-6}

Source: Environmental Protection Agency (EPA 2009)

The information on the human health assessment on metals is based on EPA guidelines that take into account the IRIS toxicity database (https://www.epa.gov/iris), Sections I (Assessments of health hazards due to non-carcinogenic effects) and II (Lifetime Exposure Carcinogenicity Assessment). The methods used to derive the values given in IRIS were taken from the guidance documents located on the IRIS website. The carcinogenic assessment of metals considers the judgment of the weight of evidence of the probability that the substance is a carcinogen to humans and quantitative estimates of the risk of exposure by inhalation. Quantitative estimates of inhalation risk are presented in three ways. The slope factor is the result of applying a low-dose extrapolation procedure and is presented as the risk per (mg / kg) / day. The unit risk is the quantitative estimate in terms of risk per μg m^{-3} of air breathed. The third way in which the risk is presented is to inhale a certain concentration of air containing the substance in question (heavy metal) that can cause cancer risks of 1 in 10,000, 1 in 100,000 or 1 in 1,000,000. The methods used to develop carcinogenicity information in IRIS are described in The Risk Assessment Guidelines 1986 (EPA / 600 / 8-87 / 045) and in the IRIS background document. Of the metals studied in this work, only Cadmium and Cobalt are considered by the EPA: Cadmium is assessed by the IRIS Program and Cobalt is assessed by the Superfund Health Risk Technical Support Center. According to IRIS-EPA, Cadmium is classified as B1 (probable human carcinogen) (https://iris.epa.gov/ChemicalLanding/&substance_nmbr=141), although, the human carcinogenity data is limited. Cadmium has been associated to lung, trachea, bronchus cancer deaths (in test animals and humans (Thun et al, 1985). The Supperfund Health Risk Technical Support Center has published provisional peer reviewed toxicity values for cobalt. IARC (IARC, 1991) has classified Cobalt sulfate and other soluble cobalt II salts as possibly carcinogenic to humans. ACGIH (2004) has classified Cobalt in category A3 (confirmed animal carcinogenic with unknown relevance to humans). The Integrated Risk Information System (IRIS) does not report a Reference Dose (RfD) for cobalt (U.S. EPA, 2007). We used the values of IUR (Inhalation unit risk) reported by HEA (Health Effects Assessment) (US EPA, 1987) derived form a sub chronic inhalation (9x10^{-3} mg/m^3) and a chronic inhalation (RfC of 9x10^{-6} mg/m^3). Adverse health effects of Cobalt inhalation has been reported in humans, resulting in an increase in cancer mortality (Moulin et al. 1998). There is substantial evidence from some studies that Cobalt is associated to respiratory tumors (Morgan et al 1983; Tuchsen et al. 1996). Carcinogenic risk for zinc, iron and cupper was not determined in this study, since these metals are classified as D (Not classifiable as to human carcinogenicity) and the Quantitative Estimate of Carcinogenic Risk from Inhalation Exposure is not assessed under the IRIS Program.

With respect to the non carcinogenic risk, the THQ (risk coefficient) is calculated as follows:

$$THQ = \frac{ADI}{RfDi} \tag{6}$$

Considering that for THQ there is an exposure level (RfDi) below which it is unlikely for any type of population to experience adverse health effects. When the exposure level (ADI) exceeds the stated value of 1, there may be concern about possible non-carcinogenic health risks; THQ values greater than 1 could suggest further concern. The RfDi represents the inhaled dose at which there are considered no negative effects (EPA, 2009) and is defined as:

$$RfDi = RfC \times \frac{20m^3}{day} \times \frac{1}{70kg} \quad (for\ adults) \tag{7}$$

$$RfDi = RfC \times \frac{7.6m^3}{day} \times \frac{1}{15kg} \quad (for\ children) \tag{8}$$

Where ADI, is the estimated dose that the recipient receives from exposure to polluted air (Di Vaio et al,, 2018), and is calculated with the same variables for cancer risk.

$$ADI = E \times C \tag{9}$$

6.3.10 Enrichment Factor Analysis

The enrichment factor (EF) was used to calculate the contribution of anthropogenic emissions to the levels of metals in the atmosphere, it evaluates the degree of enrichment of an element compared to its relative abundance in the earth's crust. One of the metals with the greatest presence in the earth's crust is iron, for this reason, it was used as a tracer of natural origins. Wedepohl, 1995 indicates the chemical composition of the earth (Table 4). EF then, was calculated using the following equation:

$$EF = \frac{\left(\frac{X}{Ref}\right)air}{\left(\frac{X}{Ref}\right)crustal} \tag{10}$$

Where: X= Concentration of metal to be analyzed and Ref= concentration of the reference metal. Fe was used as the reference metal in this study. The following table (Table 6.4) shows the composition of the metals of interest that has their origin in the earth's crust. Elements with an EF close to 1 have a natural source, while those with high values mostly come from anthropogenic sources (Marcazzan, 2001). The following table (Table 6.5) determines the enrichment indication according to Lawson and Winchester in 1979.

Table 6.4 Metals concentration in the earth's crust

Cd	Co	Cu	Fe	Zn
ppm	ppm	ppm	ppm	ppm
0.102	11.6	14.3	30,890	52

Source: Wedepohl, 1995

Table 6.5 Levels of the enrichment factor

EF Value	Origin Interpretation
<10	Suggests that the metal has its origin in the crustal
100-1000	The element concentration is affected by one or several anthropogenic sources (moderate enrichment)
>1000	It is considered that the element is highly enriched by anthropogenic sources

Source: Lawson D.R, 1979.

6.4 Results and discussion

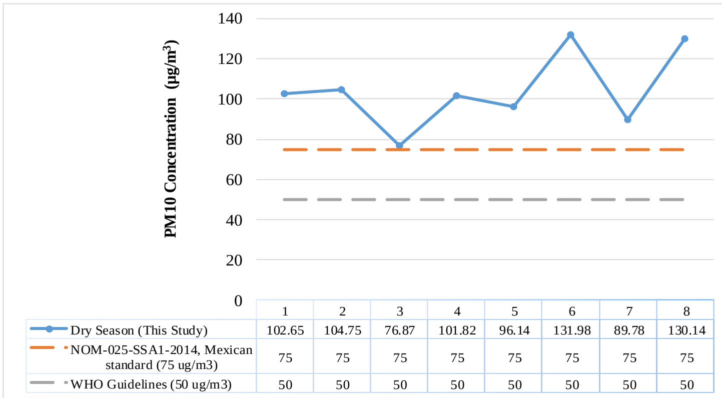
6.4.1 Mass concentration of PM10

Concentrations of PM10 are shown in Graphic 6.1, where the daily average values observed in this study were within the range of 76.8 (µg m^{-3}) to 130.1 (µgm^{-3}), with an average of 104.2 (µg m^{-3}) for the winter season. NOM-025-SSAI-2014 indicates that the maximum permissible exposure limit in 24 h is 75 (µg m^{-3}), however, the 2005 WHO guide indicates that the health of the exposed population is at risk when the limit of 50 (µg m^{-3}) is exceeded. All days of the sampling period showed exceedances to these limits. The high reported concentrations in this period may be due to the fact that in winter it is common to develop thermal inversions that limit the dispersion of pollutants, causing that their concentrations to remain high during the early hours of the morning and until noon-afternoon, when the inversion is broken. This fraction of particulate material is related to primary particles that are mechanically generated in the atmosphere, such as the re-suspension of dust and particles that can come from unpaved highways and roads. The high incidence of vehicular traffic during the early mornings coincides with the peak hours due to the beginning of the school and work activities. Table 6.6 shows the data of the meteorological parameters recorded during the sampling period.

6.4.2 Trace metals concentrations in *PM10*

Five metals were detected: Cd, Cu, Co, Fe and Zn. The results can be seen in Graphic 6.2, where the average per metal is shown. Fe and Zn were the metals with the highest concentrations during the study period; 1.5 (µg m^{-3}) and 0.6 (µg m^{-3}) respectively, which is not surprising because Fe is one of the most abundant elements in the earth's crust (Acevedo et al., 2004), this agree with that found in other similar studies (Table 6.7), where these metals also had a high value of concentration.

Graphic 6.1 PM10 Mass concentrations in the study site



Source: Own elaboration from gravimetric concentrations data

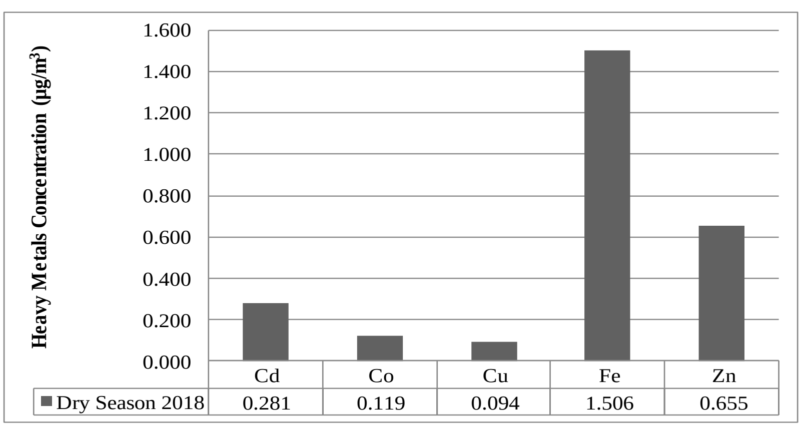
Table 6.6 Meteorological parameters

Wind Speed Km/h	Wind Direction °Azimut	Temperature °C	Relative Humidity %	Barometric Pressure mmHg
1.062	258.085	17.368	43.261	617.959
0.896	218.647	16.644	39.053	618.268
0.930	193.053	16.333	37.545	617.221
1.236	181.070	17.081	35.789	616.723
1.079	211.865	15.851	30.795	617.071
1.224	210.306	16.395	26.584	615.689
1.296	249.074	17.895	35.293	615.581
1.110	184.750	16.335	22.165	617.010

Source: Own elaboration from meteorological parameters measurements.

Followed in abundance were Cd with 0.281 (µg m^{-3}), Co with 0.119 (µg m^{-3}) and Cu with 0.094 (µg m^{-3}). Cadmium is observed to exceed the limit established by the WHO (0.015 µg m^{-3}) although it is significantly lower than in previous and subsequent studies as shown in Table 6.7. The anthropogenic contribution of Cd is due to the iron and steel foundry industry (Oldiges & Glaser, 1986) and since this region is an important production area for the foundry industry, the high concentrations found at the site are not surprising.

Graphic 6.2 Heavy metals concentrations in PM10 in the study site



Source: Own elaboration from heavy metals concentrations data.

The average gravimetric concentration of PM10 found in the city of Leon is lower than the studies carried out in Havana (Cruz & Valdivia, 2018), southwestern Italy (Contini et al., 2014), Ecuador (Zalakeviciute et al., 2019) (Zegarra et al., 2020) and lower than in Phitsanulok, Thailand (Srithawirat et al., 2016). In addition, the maximum permissible limits of NOM-025-SSA1-2014 and WHO are exceeded. Co compared to that reported in other studies resulted in intermediate concentrations (Table 6.7). Although the concentration of Cu in this study is higher than that reported for the cities of Tampico and Puebla, as well as in Southwest Italy, it was exceptionally less than that reported for Mexico City (Morton et al., 2021) with a value of 123.6 (μg m^{-3}). Higher concentrations of this metal were found in Havana (Cruz & Valdivia, 2018) and in Quito, Ecuador (Zalakeviciute et al., 2019) where concentrations of 100.31 (μg $m^{-3)}$ and 97.7 (μg m^{-3}) respectively were reported.

Table 6.7 Comparison of results of studies carried out in other sites

	PM_{10} (μg/m^3)	Cd	Co	Cu	Fe	Zn
This study	104.2	0.28	0.094	0.119	1.506	0.655
Cruz et a.l. 2018, Cuba	39.85	7.74	N/M	100.3	N/A	54.82
Contini et al. 2014, Italy	34.4	<0.6	N/M	0.012	0.229	0.023
Zalakeviciute et al. 2019, Quito	24.9	2.9	N/M	97.7	0.44	121.2
Zegarra et al. 2020, Cuenca	50.0	3.14	N/M	1.06	N/A	1.99
Srithawirat et al. 2016, Phitsanulok	123.5	0.5	N/M	0.6	5.8	0.9
Martínez. 2019, Sonora	32	N/M	N/M	0.208	0.627	N/M
Morton-Bermea et al. 2021, CDMX	40.7	1.5	0.5	123.6	N/M	N/M
Flores-Rangel et al. 2015, Tampico	23.44	N/M	N/M	0.033	0.236	0.04
Morales-Garcia et al. 2014, Pueblala	55.9	0.005	0.002	0.09	1.203	N/A
N/M: Not measured						

Source: Own elaboration from cited references showed in the Table

6.4.3 Morphology and elemental content of particles

SEM-EDS Analysis: The particulate material has a wide range of morphological, chemical, physical and thermodynamic properties (EPA, 2004). These pollutants are emitted into the atmosphere as a result of different activities, both natural and anthropogenic (Artiñano, 2003). The particles analyzed in this work showed differences in morphology, which include amorphous and spherical irregularities and groups of small particles that form larger particles. For this study, several particles were analyzed, for practical purposes only the 5 most representative ones are shown for the analysis of their elemental content (Table 6.8) and 3 micrographs of the three most representative types of particles (Figures 6.4-6.6). As it can be observed in Table 6.8, particle marked as 991 is rich in C, Ca, P and Zn. Particle identified as 999 showed a high content of Cl, P, Zn, Pb and Ca, whereas, particle labelled as 1005 showed high mass percentages of Ca, Mg, P and Zn. Particles marked as 1013 and 1034 showed high content of Ca, Cr, P, S and Zn; and Ca, O, P, Si and Zn, respectively. The presence of zinc, phosphorus, calcium and magnesium in the analyzed particles shows the influence of agricultural activities in the area on PM10 particles, since these metals could come from the application of fertilizers on crops. The Bajío area is characterized not only by being an important industrial zone but also by the rise of agriculture at the national level. The particle marked 999 shown in Figure 4 denotes a typical formation of Calcium Carbonates (Calcite). Various studies attribute this mineral to the brick, ceramic and cement industries. The presence of these particles is closely related to processes that involve the firing of bricks and ceramics, where Silica is also present to obtain the products, although little is known about the transformations undergone by the silicate and carbonate phases at the interfaces of reaction (Cultrone et al., 2001). The EDS analysis presents higher mass content for Ca, Si and O, which confirms the presence of Calcite and Silicate, while the elements C, F, Na, Mg, Al, P, S, Cl and Fe are in percentages very small.

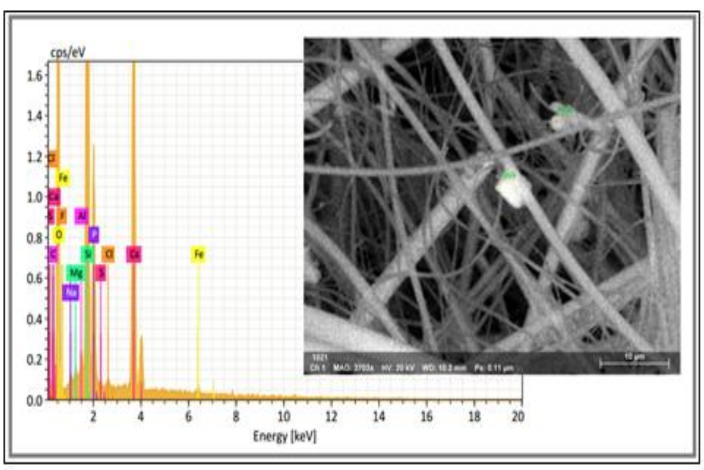
Table 6.8 Elemental Content (% mass) of analyzed selected particles

Elemental Content	Identification Code of selected particles				
Al	**991**	**999**	**1005**	**1013**	**1034**
Ba	0.35	0.51	0.39	0.21	0.35
C	12.33		0.39		
Ca	4.59	4.5	7.78	4.47	2.37
Cl	0.49	12.85	0.62		0.23
Cr		0.16		2.08	
Cu					
Fe					
Mg	0.23	0.36	25.29		
Mn	0.31	0.24	0.27		0.40
Na			0.32		
O	0.96	0.34	0.71	0.45	16.36
P	45.88	53.74	42.92	27.09	51.38
Pb		5.5			
S				54.07	
Si	2.48		0.53		9.28
Zn	32.39	21.31	20.78	10.76	18.52
Summation (%)	**100**	**100**	**100**	**100**	**100**

Source: Own elaboration from the SEM-EDS results

The spherical shape of particle 1005 shown in the lower center of Figure 6.5 is a typical indicator of iron oxides (ferrites). The formation of these spherical particles is an indicator of material melting under oxidizing conditions. The origin of these particles is closely related to processes that involve the condensation of vapors in the atmosphere once they have been emitted by industries such as iron foundry, in this way, an important contribution in the generation of spherical ferrite particles, are steel companies or steel mills (Aragón, 2011). The EDS analysis shows a higher content of O, Fe and Si, which confirms the presence of ferrites, while the elements C, Na, Mg, Al, S, Ca, Mn and Ba have very low percentages. An analysis of particle 1043 is shown in Figure 6.6 and concentrations of Pb, O and Si were found. Although Pb was not analyzed in atomic absorption (because this analysis requires that the atomic absorption spectrometer be equipped with a graphite furnace) several lead particles were still found contained in the filters. In the Metropolitan Area of the Valley of Mexico, the presence of lead in PM10 has been related to vehicular emissions (Labrada, 2007), since in areas such as the central and south of Mexico City, there are no industrial establishments; However, they are considered by the Ministry of Transportation and Roads as areas in which the largest number of trips are made by means of transportation in the Valley of Mexico (PITV, 2002). Generally, these lead oxide particles are presented as spheres that form conglomerates, although the size of the conglomerates can range between 1 and 5 µm, each of the constituent particles is of the order of 400 nm on average. Human exposure to lead for prolonged periods, greater than or equal to one year, has an impact on people's health, and can cause chronic effects, therefore in Mexico the air quality standard NOM-026-SAA1-1993 indicates that it does not the exposure limit of 1.5 μgm^{-3} must be exceeded within an arithmetic period of 3 months.

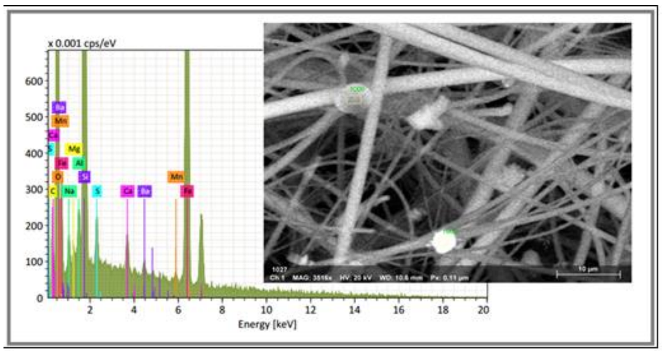
Figure 6.4 SEM-EDS analysis of the selected 999 particle showing Ca and Si content



Source: Own elaboration from SEM / EDS analysis

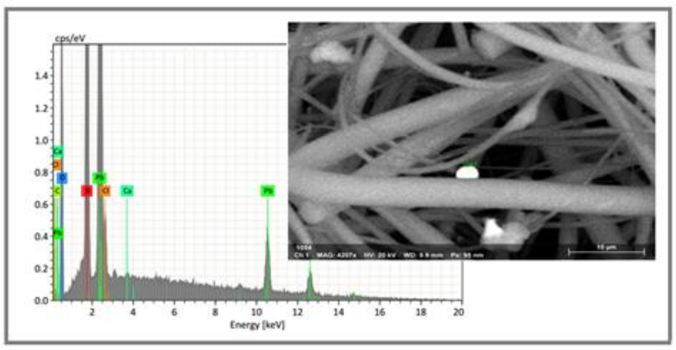
According to the results shown, an evident relationship is observed among the presence of certain anthropogenic particles, their morphology and elemental content, and the activities carried out around the study area. The above due Leon city is an important industrial zone with at least 9 industrial parks distributed in this area, with a constant growth and development, therefore, it is not surprising the found composition of the particles suspended in the air. It should be noted that geography, meteorological conditions such as temperature, rainfall and weather season are also an important part of the development and composition of the particles.

Figure 6.5 SEM-EDS analysis to the selected 1005 particle showing Fe content



Source: Own elaboration from SEM / EDS analysis

Figure 6.6 SEM-EDS analysis of selected 1043 particle showing high Pb content



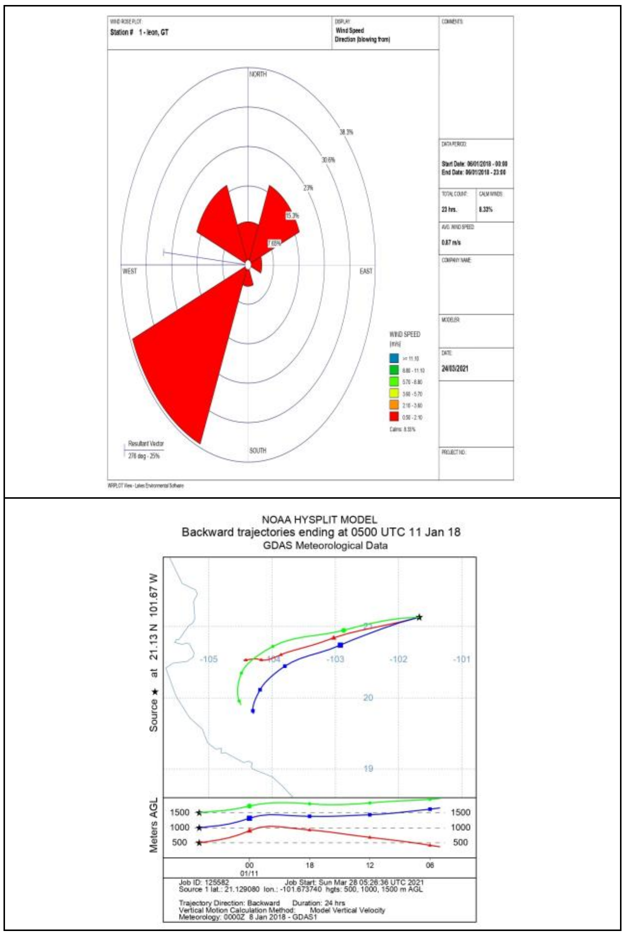
Source: Own elaboration from SEM / EDS analysis

6.4.4 Wind analysis

To determine the possible origin of the pollutants of interest, daily wind analysis were carried out, taking into account the speed and direction parameters of the sampling period. In Figure 7 it can be observed a representative wind rose for the sampling period (cold dry). The rose petals indicate the different wind directions, being the largest petal the predominant wind, the percentage values indicate the frequencies of occurrence and the colors indicate the wind speed in m/s. For this season the winds came from different directions, being more representative the vectors resulting from NE and SW. Based on the results, possible emission sources were identified in the study area with the help of the Google Earth software. At least 7 industrial parks were found, distributed in the in the study area, being San Cristin, Bicentennial Industrial Cluster, and Colinas de Leon, the closest industrial parks (at 5.2 km, 9 km, and 10 km, respectively), located at SW, NE, and SW, respectively. The main economic activity in this area is related to the automotive industry (assembly, manufacture or assembly of auto parts). Other important economic which can be an important source of metallic particles is mining. The municipality of Leon is part of the mining region No. 1 also made up of Guanajuato, Sierra, San Antonio de las minas and La Sauceda where Ag, Au, Pb, Zn and Hg are extracted (SGM, 2018). Fine particles are suspended in the air and these interact depending on their size and morphology, making it possible to transport them over long distances (Balán, 2013). In Figure 6.7 you can see one of the trajectories of air masses during sampling, generally used to determine the impact of meteorology on the measured pollutants, seem to reinforce the idea of mining, being one of the main anthropological activities that contribute to the increase of the concentrations of these metals, having a greater influence on the SW direction where the mines are located.

It is evident that not only these activities, but also the meteorological conditions of the region influence the level of pollution in the air, by allowing pollutants to travel long distances, generating a negative impact.

Figure 6.7 Representative wind rose and trajectory of air masses for the studied period



Source: Own elaboration from the result of WRPLOT tool and HYSPLIT software.

6.4.5 Statistical analysis

More detailed information about the behavior of the pollutants studied was revealed through bi-varied (Pearson) and multi-varied (ACP) analysis. Table 6.9 shows Pearson's correlation analysis, where a strong correlation was observed between Zn with Cd and Zn with Cu (0.84 and 0.66 respectively). These metals are associated with industrial emissions. Cd had a moderate correlation with Cu (0.57), these elements are mainly produced by incineration waste, electricity generation plants and industrial sources (Barratt, 1988).

In multivariate analysis or principal component analysis (PCA) the relationship between multiple variables is detailed. In Figure 6.8 the results for PCA are shown, as it can be seen in the bi-plot, two factors (F1 and F2) were needed to explain 60.61% of the variability of the data. 3 groups and variables could be identified where F1 represents the metals (Cd, Cu and Zn) associated with industrial sources, especially Zn that is generated by mobile sources, in road sediments and soil in an area of high vehicular density (Machado et al., 2008). The second group of variables F2, included the meteorological parameters, while the third group F3 included only cobalt, indicating that this metal could have its origin in a different source.

Table 6.9 Elemental Content (% mass) of analyzed selected particles

	Zn	Cd	Fe	Cu	Co	WS	WD	T	RH
Zn	**1**								
Cd	**0.84**	**1**							
Fe	0.50	0.19	**1**						
Cu	0.66	**0.57**	0.08	**1**					
Co	-0.39	-0.01	-0.50	0.008	**1**				
WS	0.31	0.26	0.15	0.23	0.32	**1**			
WD	-0.003	-0.04	0.007	0.27	0.37	0.60	**1**		
T	0.130	-0.21	0.13	0.05	-0.45	0.48	0.34	**1**	
RH	-0.66	**-0.90**	0.04	-0.44	-0.12	-0.02	0.26	0.50	**1**
Values in bold are different at a significant level of alfa=0.05; WS: Wind speed; WD: Wind direction; T: Temperature; RH: Relative humidity									

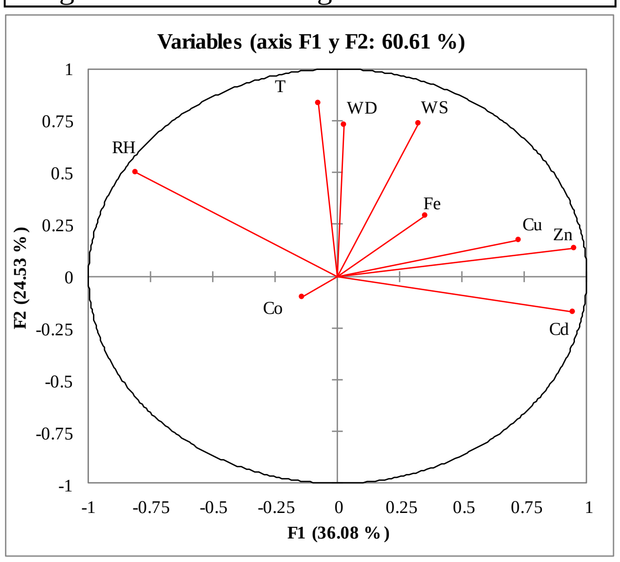
Source: Own elaboration from data using XLSTAT software

6.4.6 Enrichment factor analysis

The enrichment factor (EF) is used to evaluate the degree of enrichment of a single element compared to the relative abundance of that element in a cortical material. Iron (Fe) was used as the reference metal in this study due to its abundance in the terrestrial crust. Table 6.10 shows the results of the EF calculation for each of the metals analyzed. A separation of two groups can be made, the first, made up of Co (166.212), Cu (170.688) and Zn (258.36) presenting values between 100-1,000. These metals are considered highly enriched by anthropogenic sources (see Table 6.10), agreeing with the previous discussion where it is pointed out that these metals can have industrial origins and come from burning of fossil fuels. The second group is made up of Cd with the highest EF value of 56,566.915, indicating that this metal had its origin in anthropogenic processes without any influence from the earth's crust.

Figure 6.8 Analysis of principal components for winter (factor table and biplot)

Square cosines of the variables			
Variables	F1	F2	F3
Zn	**0.908**	0.018	0.062
Cd	**0.893**	0.029	0.014
Fe	0.125	0.087	0.351
Cu	**0.533**	0.030	0.032
Co	0.020	0.010	**0.905**
WS	0.104	**0.543**	0.159
WD	0.001	**0.538**	0.261
T	0.006	**0.700**	0.103
RH	**0.658**	0.252	0.046
Values in bold correspond to those who were significant at a level of significance of alfa=0.05			



Source: Own elaboration from data using XLSTAT software

Table 6.10 Enrichment factor results for metals

Enrichment Factor (EF)		
Cold dry climatic season	Cd	**56566.915**
	Co	**166.212**
	Cu	**170.688**
	Fe	**1**
	Zn	**258.363**

Source: Own elaboration from metals concentrations.

6.4.7 Health risk assessment

The risk coefficients (CR) of suffering cancer in the life time for Cadmium and Cobalt were estimated, presenting values lower than those established by the WHO (1×10^{-6}) (See Table 6.11), however, they are only one order of magnitude below the acceptable limit, so if emissions of particles containing these metals are not reduced, in the future carcinogenic effects related to the inhalation of these metals in PM10. Cancer risk coefficient values were higher for the adult population compared to the child population. These differences may be due to the greater mobility of the adult population due to their work and occupations, spending more time than the child population exposed to the open air. Breathing air even at low cadmium concentrations for a long time (for years) causes cadmium accumulation in the kidneys; if it reaches high enough levels it can cause kidney disease. In the case of chronic inhalation cobalt can lead to chronic lung problems. Inhalation for long periods can lead to breathing problems that are similar to asthma or pulmonary fibrosis, such as shortness of breath and a reduction in resistance to exercise. Table 6.12 shows the results for the non-carcinogenic risk (THQ) for cadmium and cobalt. These values must be <1 in order not to present a health risk, as is evident, although the Cd value in infants is higher than in adults, neither of the two metals exceeded this parameter. The above suggests that the child population is at greater risk of suffering some negative effect related to the respiratory tract, however, the risk is low, taking into account that it does not exceed the value established by the WHO of 1.0.

Table 6.11 Average values of carcinogenic risk coefficients of metals

Risk Cancer Coefficient (CR)	Metal	Adult population	Child Population
	Cadmium	4.56×10^{-7}	1.14 x 10-7
	Cobalt	9.65×10^{-7}	2.41×10^{-7}

Source: Own elaboration from calculated data.

Table 6.12 Average values of non-carcinogenic risk coefficients of metals

Non-cancer Risk Coefficient (Hazard Quotient: HQ)	Metal	Adult population	Child Population
	Cadmium	0.0439	0.205
	Cobalt	0.0310	0.144

Source: Own elaboration from calculated data

6.5 Conclusions

The gravimetric concentrations of PM10 in the study site exceeded the maximum permissible limits established by the Mexican Regulations (NOM-025-SAA1-2014: 75 µg m^{-3}) and by the World Health Organization (50 µg m^{-3}), indicating that exposure to PM10 at the study site may represent a potential risk to the health of the population established in the center of the city of Leon. The results of the analysis of the content of heavy metals (Cd, Co, Cu, Fe and Zn) in the collected PM10 particles showed that the dominant metal was Fe, followed in order of importance by Zn during the study period. This finding was to be expected since because these metals are abundant in the earth's crust, which is consistent with what has been reported around the world by other authors. Cu and Co were found in lower proportions, the latter being the one that presented the lowest concentrations of all the metals measured. Cd presented lower values than those reported in most international studies but exceeded the values reported in Mexican studies.

The meteorological analysis showed that sources located to the southwest and northwest of the study site (industrial complexes and metal and mineral extraction activities) could contribute to the levels of PM10 and its content of heavy metals. The enrichment factor (EF) analysis showed that all the analyzed metals were highly influenced by anthropological activity (industrial sources, biomass burning and vehicular traffic). Cd was the metal that showed the highest EF values, probably due to a poor efficiency of the internal combustion engines of the vehicles in the area, without any contribution from the earth's crust. This is in agreement with what has been reported in other studies. The bi-variate analysis (Pearson's correlation matrix) and the multivariate analysis (Principal Component Analysis) confirmed the anthropogenic origin of Cd, Cu and Zn and their common source (burning of fossil fuels). Co was probably originated from production of batteries, industrial processes of metal refining and the expulsion of smoke and gases from these processes. The results of the health risk assessment showed that the cancer risk coefficients values (CR) did not exceed the threshold value established by the EPA of 10^{-6} for Cd and Co during the sampling season. Despite this, CR values in adults are higher than in infants, which is to be expected due to mobility related to their work activities and occupations. The non-cancer risk coefficients (HQ) were higher for the child population in both Cadmium and Cobalt, although neither of the two metals exceeded the maximum allowable limit established by the WHO and the EPA. The SEM-EDS analysis of selected particles allowed to study the morphology and content of the main metals in the PM10 samples. From the morphological analysis of the studied particles it was possible to deduce their possible origin. It was confirmed that Fe was the dominant metal in the collected particles with spherical and irregular shapes, so this metal could have its origin beyond natural sources (the earth's crust) and it could be influenced by re-suspension processes, mining, smelting and welding activities. It is recommended for future work to carry out more intensive sampling campaigns that cover more climatic seasons throughout the year at the study site (cold dry, warm dry and rainy), as well as include the determination of a greater number of trace metals contained in PM10 particles.

6.6 References

Acevedo, O., Ortiz, E., Cruz, M., & Cruz, E. (2004). El papel de óxidos de hierro en suelos. Terra Latinoamericana, 22(4), 485-497. https://www.redalyc.org/articulo.oa?id=57311096013

ACGIH (American Conference of Governmental Industrial Hygienists). 2004. TLVs® and BEIs®: Threshold Limit Values for Chemical Substances and Physical Agents, Biological Exposure Indices. Cincinnati, OH.

Aragón, A. (2011). ¿Cómo son las particulas atmosfericas antropogenicas y cuál es su relación con los diversos tipos de fuentes contaminantes? San Luis Potosi, S.L.P, México: Editorial Groppe Libros (1ra edición).

Artiñano, B. S. (2003). Anthropogenic and natural influence on the PM10 and PM2.5 aerosol in Madrid (Spain). Analysis of high concentration episodes. Environmental Pollution, 125, , 453-465.

Báez, A., García, R., & Belmont, R. (2001). Trace heavy elements in rain water collected in México city. Universidad Nacional Autónoma de México, México.

Balán, R. A. (2013). Estudio del contenido de hidrocarburos policíclicos aromáticos y metales en partículas atmosféricas de diferentes diámetros aerodinámicos de La Comarca Lagunera, México [Tesis de doctorado, CIMAV] http://cimav.repositorioinstitucional.mx/jspui/handle/1004/898 .

Barratt, R. S. (1988). Cadmium in urban atmospheres. Science of the total environment, 72, 211-215.

Concon, J. (2009). Heavy metals in food. Food Toxicology. New York Dekker (pp. 1043-1045).

Cruz , L., & Valdivia, J. A. (2017). Cuantificación de la concentración de Zn, Cu, Pb y Cd en partículas menores de 10µm procedentes del aerosol atmosférico. Clasificación de las fuentes contaminantes en la zona de estudio. Killkana Técnica, 1(3), 17-24. https://doi.org/10.26871/killkana_tecnica.v1i3.82

Contini, D., Cesari, D., Donateo, A., Chirizzi, D., & Belosi, F. (2014). Characterization of PM10 and PM2. 5 and their metals content in different typologies of sites in South-Eastern Italy. Atmosphere, 5(2), 435-453.

Cultrone, G., Rodriguez, C., Sebastian, E., Cazalla, O., & De La Torre, M. J. (2001). Carbonate and silicate phase reactions during ceramic firing. European Journal of Mineralogy, 13(3), 621-634.

Di Vaio, P., Magli, E., Caliendo, G., Corvino, A., Fiorino, F., Frecentese, F., ... & Perissutti, E. (2018). Heavy metals size distribution in PM10 and environmental-sanitary risk analysis in Acerra (Italy). Atmosphere, 9(2), 58.

Gallegos, W., Vega, M., & Noriega, P. (2012). Espectroscopía de absorción atómica con llama y su aplicación para la determinación de plomo y control de productos cosméticos. Revista de ciencias de la vida, 15, 19-26.

Guanajuato. (2016). Inventario de Emisiones del Estado de Guanajuato. Leon de los Aldama: Instituto de Ecologia del Estado de Guanajuato.

Henry, J. G., & Heinke, G. W. (1999). Ingeniería ambiental. Pearson Educación.

IARC (International Agency for Research on Cancer). 1991. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 52: Chlorinated Drinking-Water; Chlorination By-Products; Some Other Halogenated Compounds; Cobalt and Cobalt Compounds. p. 363-472.

INSAG. (2019). Instituto para la Salud Geoambiental. Consultado el 9 de marzo de 2019, de https://www.saludgeoambiental.org/

IPCS. (2002). Environmental Health Criteria: Copper. Geneva: World health Organization, 234-252.

Lawson, D. R., & Winchester, J. W. (1979). A standard crustal aerosol as a reference for elemental enrichment factors. Atmospheric Environment (1967), 13(7), 925-930.

López Ayala, O. (2021). Evaluación de la distribución de hidrocarburos aromáticos policíclicos en material particulado suspendido en sitios críticos del área metropolitana de Monterrey y su relación con la exposición de población infantil Tesis para obtener el grado de Doctor con orientación en química analítica ambiental, Universidad Autónoma de Nuevo León, Marzo 2021. http://eprints.uanl.mx/id/eprint/21003

Machado, A., García, N., García, C., Acosta, L., Córdova, A., Linares, M., Giraldoth, D., & Velásquez, H. (2008). Contaminación por metales (Pb, Zn, Ni y Cr) en aire, sedimentos viales y suelo en una zona de alto tráfico vehicular. Revista internacional de contaminación ambiental, 24(4), 171-182.

Machado, A., Velázquez, H., García, N., García, C., Acosta, L., Córdova, A., & Linares, M. (2007). Metales en PM10 y su dispersión en una zona de alto tráfico vehicular. Interciencia, 32(5), 312-317.

Mahecha, J. D., Trujullo, J. M., & Torres, M. A. (2015). Contenido de metales pesados en suelos agrícolas de la región del Ariari, Departamento del Meta. Orinoquia, 19(1), 118-122.

Mar, V. (2003). Niveles, composición y origen del material particulado atmosférico en los sectores Norte y Este de la Península Ibérica y Canarias. Universidad de Barcelona.

Marcazzan, G. M., Vaccaro, S., Valli, G., & Vecchi, R. (2001). Characterisation of PM10 and PM2. 5 particulate matter in the ambient air of Milan (Italy). Atmospheric Environment, 35(27), 4639-4650.

Martínez, T. (2019). Estudio de PM10 y metales (Cu, Fe, Mn, Pb) en aire ambiente, en la región de Cananea, Sonora, México. Sonora, México: universidad de Sonora.

Molina L. T. and Molina M. J. (2004). Diseño, evaluación y preparación de mecanismos de ejecución para las estrategias de mejoramiento de la calidad de aira en la ZMVM 2001-2010. Informe Final. Elaborated for CAM. MIT.

Molina, Y.H., Monrroy, V., and Rosa, X. (2021). Biomonitoreo de elementos traza en área urbana e industrial de Lurigancho-Chosica utilizando especies Tillandsia latifolia y T. purpurea como biomonitores. Tesis para obtener el Título Profesional de Ingeniero Ambiental. Universidad Peruana Unión. Lima, Perú, Mayo de 2021. http://hdl.handle.net/20.500.12840/4477.

Morales, S. S., Rodriguez, P. F., Jonathan, M. P., Navarrete, M., Herrera, M. A., & Munoz-Sevilla, N. P. (2014). Characterization of As and trace metals embedded in PM 10 particles in Puebla City, Mexico. Environmental monitoring and assessment, 186(1), 55-67.

Morgan, L. G. (1983). A study into the health and mortality of men exposed to cobalt and oxides. Occupational Medicine, 33(4), 181-186. https://doi.org/10.1093/occmed/33.4.181

Morton, O., Hernández, E., Almorín, M. A., Ordoñez, S., Bermendi, L., & Retama, A. (2021). Historical trends of metals concentration in PM 10 collected in the Mexico City metropolitan area between 2004 and 2014. Environmental Geochemistry and Health, 1-18. https://doi.org/10.1007/s10653-021-00838-w.

Moulin, J. J., Wild, P., Romazini, S., Lasfargues, G., Peltier, A., Bozec, C., ... & Perdrix, A. (1998). Lung cancer risk in hard-metal workers. American journal of epidemiology, 148(3), 241-248. https://doi.org/10.1093/oxfordjournals.aje.a009631

NOM-025-SAA1-2014. (2014). Salud Ambiental. Valores límite permisibles para la concentración de particulas suspendidas PM10 y PM2.5 en el aire ambiente y criterios para su evaluación.

Oldiges, H., & Glaser, U. (1986). The inhalative toxicity of different cadmium compounds in rats. Trace elements in medicine, 3(2), 72-75.

OMS. (s.f.). Recuperado el 6 de septiembre de 2018, de Calidad del Aire y Salud: https://www.who.int/es/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health

OMS. (2006). Guias de calidad dela ire de la OMS relativas al materal particulado, el ozono, el dioxido de nitrogeno y el dioxido de azufre. Actualizacion mundial 2005.

OSHA. (n.d.). United State Department of Labor. Consultado el 15 de marzo de 2019, de Occupational Safety and Health Administration: www.osha.gov

PITV. (2002). Programa Integral de Transporte y Vialidad 2001-2006. Consultado en: http://www.setravi.df.gob.mx/programas/pitv.pd

Pritchard, J. (2019). No mandatory Cadmium Limits. Consultado el 15 de noviembre de 2019. Associated press: http://tinyurl.com/27ywhzc.

Flores, R. M., Rodríguez, P. F., de Oca, J. M., Mugica, V., Ortiz, M. E., Navarrete, M., ... & Morales, S. S. (2015). Temporal variation of PM 10 and metal concentrations in Tampico, Mexico. Air Quality, Atmosphere & Health, 8(4), 367-378. https://doi.org/10.1007/s11869-014-0291-6.

SEICA. (2019). Sistema Estatal de Información de Calidad del Aire (SEICA) del Estado de Guanajuato. Consultado el 9 de marzo de 2019, de https://smaot.guanajuato.gob.mx/sitio/seica/

SEMARNAT. (2012). Informe de la Situacion del Medio Ambiente. Compendio de Estadisticas Ambientales. Indicadores Clave, de Desemeño Ambiental y de Crecimineto Verde. México: Semarnat.

SGM. (2018). Panorama minero del Estado de Guanajuato. Secretaria de minería .

Srithawirat, T., Latif, M. T., & Sulaiman, F. R. (2016). Indoor PM10 and its heavy metal composition at a roadside residential environment, Phitsanulok, Thailand. Atmósfera, 29(4), 311-322.

Tüchsen, F., Jensen, M. V., Villadsen, E., & Lynge, E. (1996). Incidence of lung cancer among cobalt-exposed women. Scandinavian journal of work, environment & health, 444-450.

Thun, M.J., T.M. Schnorr, A.B. Smith and W.E. Halperin. (1985). Mortality among a cohort of U.S. cadmium production workers: An update. J. Natl. Cancer Inst. 74(2): 325-333.

U.S. EPA. (1996). Air Quality Criteria for Particulate Matter. U.S. Environmental Protection Agency, EPA 600/P-95/001.

U.S. EPA. (2007). ATSDR. Recuperado el 15 de Marzo de 2021, de Resúmenes de Salud Pública - Bario (Barium): https://www.atsdr.cdc.gov/es/phs/es_phs24.pdf.

U.S. EPA. Risk Assessment Guidance for Superfund—Vol. I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment); US EPA: Washington, DC, USA, 2009.

U.S. EPA. 1987. Health Effects Assessment for Cobalt. Prepared by the Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Cincinnati, OH for the Office of Solid Waste and Emergency Response, Washington, DC. ECAO-CIN-H120.

Warneck, P. (1999). chemistry of the natural atmosphere. Academic Press, Ink London.

Wedepohl, K. H. (1995). The composition of the continental crust. Geochimica et cosmochimica Acta, 59(7), 1217-1232. https://doi.org/10.1016/0016-7037(95)00038-2.

Wichman, E. and Peters A. (2000). Epidemmiological Evidence on the Effects of Ultrafine Particle Exposure. in L. M. Brown, N. Collins, R. M. Harrison, A. D. Maynard and R. L. Maynard. (Ed.), Ultrafine Particles in the atmosphere. (pp. 243-267). Imperial College Press.

Zalakeviciute, R., Rybarczyk, Y., Granda-Albuja, M. G., Suarez, M. V. D., & Alexandrino, K. (2020). Chemical characterization of urban PM10 in the Tropical Andes. Atmospheric Pollution Research, 11(2), 343-356.

Zegarra, R., Andrade, S., Parra, M., Mejía, D., & Roda, C. (2020). Análisis espacial de PM10 en el aire y su composición de metales con relación a factores ambientales alrededor de centros de educación preescolar en Cuenca. Maskana, 11(1), 57-68.