Article

Trace Metal Content and Health Risk Assessment of PM₁₀ in an Urban Environment of León, Mexico

Julia Griselda Cerón Bretón ^{1,*}, Rosa María Cerón Bretón ¹, Alberto Antonio Espinosa Guzman ², Claudio Guarnaccia ³ , Stephanie Martínez Morales ¹, Reyna del Carmen Lara Severino ¹, Marcela Rangel Marrón ¹, Guadalupe Hernández López ¹, Simón Eduardo Carranco Lozada ⁴, Jonathan D.W. Kahl ⁵, Ildefonso Esteban Pech Pech ⁶, Evangelina Ramírez Lara ⁷ and Maria de la Luz Espinosa Fuentes ⁸

¹ Universidad Autónoma del Carmen, Calle 56 Num. 4 Esq. Ave. Concordia, Col. Benito Juárez, C.P. 24180 Ciudad del Carmen, Campeche, Mexico; rosabreton1970@gmail.com (R.M.C.B.); stephanie.mm@msn.com (S.M.M.); reyna.lara.sev@gmail.com (R.d.C.L.S.); mrangel@pampano.unacar.mx (M.R.M.); lupitha.k-1796@hotmail.com (G.H.L.)

² Conacyt-Universidad Autónoma de Campeche, Av. Héroe de Nacozari No. 480, Campus 6 de Investigaciones, C.P. 24070 San Francisco de Campeche, Campeche, Mexico; aaespino@uacam.mx

³ Civil Engineering Department, University of Salerno, Via Giovanni Paolo II, 132 84084 Fisciano (SA), Italy; cguarnaccia@unisa.it

⁴ Instituto Politécnico Nacional, CECyT 17 Leon. Boulevard Caliope Num. 1055, Col. Las Joyas, León, 7738 Guanajuato, Mexico; scarrancol@ipn.mx

⁵ Department of Mathematical Sciences, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201, USA; kahl@uwm.edu

⁶ Centro de Investigación en Corrosión de la Universidad Autónoma de Campeche, Av. Héroe de Nacozari No. 480, Campus 6 de Investigaciones, C.P. 24070 San Francisco de Campeche, Campeche, Mexico; ildepech@uacam.mx

⁷ Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Ave Universidad S/N Cd. Universitaria, C.P. 66455 San Nicolás de los Garza, Nuevo León, Mexico; evangelina.ramirezl@uanl.mx

⁸ Universidad Nacional Autónoma de México, Centro de Ciencias de la Atmósfera, Investigación Científica s/n, 04510 Ciudad de México, CDMX, México; marilu@atmosfera.unam.mx

* Correspondence: jceronbreton@gmail.com; Tel.: +52-272-120-3456

Received: 26 August 2019; Accepted: 17 September 2019; Published: 23 September 2019

Abstract: Trace metal concentrations in PM₁₀ were measured in an urban–industrial site in León, Mexico in three different seasons. PM₁₀ were collected in quartz fiber filters of 47 mm diameter using low volume equipment operating with a controlled flow of 5 L min^{−1} over 24 h. Mass concentrations were gravimetrically determined and it was found that PM₁₀ samples showed values in excess of the Mexican standard and the established values by WHO during cold dry and warm dry seasons. Morphology of selected particles was studied by SEM-EDS analysis, and the elemental composition was determined. Collected samples were analyzed by atomic absorption spectrometry in order to quantify ambient air concentrations of some trace metals (Cu, Co, Zn, Cd, Fe, Mg, and Mn). Median concentrations of trace metals showed the maximum value for iron (3.079 µg m^{−3}) and the minimum value for Cd (0.050 µg m^{−3}) over the entire period. From the meteorological analysis, it was found that sources located SW and ESE of the sampling site contributed to the levels of trace metals in PM₁₀ in the studied site. The health risk assessment found that the population of León is at increased lifetime risk of experiencing cancer because of exposure to these concentrations of PM₁₀ and their trace metal content.

Keywords: PM₁₀; heavy metals; risk analysis; SEM-EDS; enrichment factor

1. Introduction

The metropolitan area of León (MAL) located in Guanajuato, Mexico, is one of the most important urban areas in the center of the country due to its commercial, industrial, and economic development, with a population of 1,578,626 inhabitants within an area of about 1220 km² [1]. Various industrial complexes have been established in the study area, including tanneries, footwear production, food, textile, brick, car assembly, and chemical industries, as well as plastic containers, metal cutlery, automotive oils, and steel wire products. The extensive industrial activities have caused a marked increase in urban development and in traffic density. This situation has resulted in a growing need for transport, both public and private, with associated increases in fuel consumption and thus a greater generation of atmospheric pollutants. The vehicular fleet registered for León in 2016 included 353,199 automobiles, 6915 passenger buses, and 57,012 motorcycles. In 2016, the population density in León was 1292.3 inhabitants km⁻². All these factors have significantly contributed to the degradation of air quality in this area. It is common to find air pollutant concentrations greater than the maximum permissible limits established by Mexican standards, representing a health risk for the city's inhabitants. According to the emissions inventory for Guanajuato State [2], for León municipality the total emissions of the air pollutants CO, NO_x, VOC's, TOC, and PM₁₀ are 615,866 tons y⁻¹, 31,930 tons y⁻¹, 65,944 tons y⁻¹, 68,827 tons y⁻¹, and 7126 tons y⁻¹, respectively. The main sources of CO and NO_x emissions are motor vehicles, while VOC's and TOC are mainly emitted from area sources related to the usage and consumption of solvents and manufacture of products derived from oil and coal, respectively. PM₁₀ emissions are mainly due to the transit of vehicles over unpaved roads and farming activities including the burning of agricultural waste.

PM₁₀ is the pollutant that has caused the most concern in León city due to its effects on the population's health, even though it only represents 0.89% of the total annual emissions. PM₁₀ constitutes an important health risk factor because its diverse and complex mixture of chemical compounds with varying degrees of toxicity [3,4]. Trace metals, in particular, represent a substantial aspect of PM₁₀ toxicity. Despite its importance, there have not been enough studies about the content of trace metals in PM₁₀ in the ambient air of León, Guanajuato, nor about the degree of exposure of the population to these air toxins. The aims of the present study, including hypotheses (H) to be tested, were the following:

- To determine if there are seasonal variations in gravimetric concentrations of particulates (PM₁₀) and their trace metal content (Cu, Co, Zn, Cd, Fe, Mg, and Mn) in an urban-industrial site located in the city of León, Guanajuato, Mexico. (H1: There are seasonal variations in concentrations of PM₁₀ or its trace metal content.)
- To investigate by statistical analysis whether there are associations among the different measured trace metals present in PM₁₀. (H2: There are associations among the trace metals present in PM₁₀.)
- To analyze whether there is an influence of meteorological parameters on the heavy metal concentrations associated with PM₁₀. (H3: Meteorological parameters have influence on heavy metals concentrations.)
- To determine whether the concentrations of trace metals found in PM₁₀ constitute a threat to the health of the population of León. (H4: Trace metal concentrations pose no threat to León's population health.)

2. Materials and Methods

2.1. Monitoring Site, Sampling Methodology, and Gravimetric Determination of Mass in PM₁₀ Samples

The city of León is located at an altitude of 1798 meters above sea level, bounded to the north by San Felipe town; to the east by Guanajuato and Silao cities; to the south by Silao, Romita, and San Francisco del Rincon cities; and to the west by Purisima Del Rincon and the State of Jalisco. León is a regional center with important health care institutions, universities, and research centers, and business,

industrial, and tourism activities. It is a city with a reputation for business activities, with national leadership in the production of leather goods and footwear as well as significant developments in the automotive industry, features which have turned the city into an urban–industrial center.

The sampling site had an urban–industrial land use type and was located on the Boulevard Adolfo Lopez Mateos, one of the main roads in the city that connects with the León–Silao–Guanajuato highway, specifically at the fire station, within the facilities of the air quality monitoring station known as the CICEG Station at 21°06′6.26 " N and 101°38′4.66 " W (Figure 1). This air quality monitoring station belongs to the SINAICA (National System of Air Quality) [<https://sinaica.inecc.gob.mx/>], and therefore meets all established criteria by SINAICA considering design and location according to the physical description of the environment, spatial scale, and representativeness.

Three climatic seasons have been identified in the study region: cold dry, warm dry, and rainy. Based on this, the following representative sampling periods of these three seasons were selected: from 5 January to 12 January 2018, from 16 May to 23 May 2018, and from 6 August to 13 August 2018 for the cold dry, warm dry, and rainy seasons, respectively. Manual sampling and automatic monitoring of PM₁₀ particles was carried out during these periods. The automatic monitoring was carried out with a BAM-1020 analyzer (Met One Instruments) that operated under the principle of beta-ray attenuation, continuously recording hourly concentrations. The 24 h PM₁₀ samples were collected manually on quartz fiber filters (Whatman 1851–047) of 47 mm diameter using a Mini-Vol air sampler, model TAS-5.0 (Tactical Air Sampler of Airmetrics) at a controlled flow rate of 5 L min^{−1}, positioned at 2 m height. A total of 24 ambient air samples of PM₁₀ particles were collected. Prior to sampling, filters were conditioned at a controlled temperature (25 °C + 3 °C) and humidity (50% + 5%), with their weight subsequently recorded. The filter weighing was carried out using a Sartorius micro analytical balance LA130S-F with an accuracy of 0.1 µg. After sampling, filters were stored in Petri boxes within sealed plastic bags and were refrigerated during transportation back to the laboratory, where they were conditioned and weighed again. The gravimetric concentration was determined by weight difference (before and after sampling) for each of the samples, considering both the flow and sampling time and the filter area according to the US EPA Method IO2.1 [5].

Quality assurance was provided by simultaneous measurements of three control filters, which were kept together with the samples at the established controlled temperature and humidity in a desiccator.

Figure 1. Location of the sampling site (CICEG).

2.2. Chemical Analysis for Trace Metals Determination

Samples were extracted by acid extraction procedure according to US EPA Method IO-3.1 [6]. The filters were placed in 150 mL glass beakers, and were then subjected to acid digestion for 18 h by adding 10 mL of regal water (25 mL HNO₃ + 75 mL HCl), and 1.065 mL of HClO₄. The content of each glass was then heated to 60 °C for 70 minutes, and 20 mL of hot water was added to facilitate the filtration using 0.45 mm Acrodisc syringe filters to remove any insoluble material. Finally, the contents of each glass were placed in flasks that were calibrated to 50 mL using deionized water, after which the samples were stored in polypropylene containers for further analysis [7].

2.2.1. Preparation of Standard Solutions for Trace Metal Determination

Heavy metal concentrations in each sample were determined by atomic absorption spectrometry. Working standard solutions for Mg, Mn, Fe, Co, Cu, Zn, and Cd were prepared by successive dilution from concentrated stock solutions of each metal (1000 ppm of concentration) in order to calibrate the instrument. The stock solutions of each metal were prepared with a concentration of 10 mg L⁻¹ of certified standard solutions, calibrated in 100 mL flasks, with a 2% HNO₃ solution [8]. The calibration range adopted was 5–500 µg L⁻¹ (seven point calibration) for each metal; the correlation coefficients (R²) for the calibration curves were all greater than 0.998.

2.2.2. Trace Metal Determination by Atomic Absorption Spectrophotometry

Trace metals in PM₁₀ were determined using an atomic absorption spectrophotometer, Thermo Scientific™ iCE 3000 Series AAS, according to standard analytical US EPA Methods IO.3.1 [6] and I.O.3.2 [9]. The measurements were made at the following wavelengths: 217 nm for Mg, 279.5 nm for Mn, 248.3 nm for Fe, 240.7 nm for Co, 324.8 nm for Cu, 213.9 nm for Zn, and 228.8 nm for Cd. In all measurements, a deuterium lamp was used as a background corrector [8]. Limits of detection (LODs) of trace metals were in the range of 0.003–0.06 µg L⁻¹ (Table 1). Recovery percentages of trace metals from the spike method (n = 3) ranged from 97.4% to 104.56%, and expanded uncertainties ranged from 0.01262 to 0.05234 (Table 1). In order to verify reproducibility and low background metal concentrations of reagents and filters, 5% of the total number of samples were taken as blanks and analyzed for the presence of trace metals.

Table 1. Detection limits (LOD), recovery percentage, and uncertainties of the considered trace metals.

Trace Metals	LOD (µg L ⁻¹)	Recovery % + SD	u _{rep}	u _{sol}	u _x	U _C	U _E
Mg	0.003	100.53	0.00259	0.00772	0.00791	0.01135	0.02270
Mn	0.020	97.9	0.00248	0.00769	0.00984	0.01273	0.02547
Fe	0.050	98.56	0.00080	0.00800	0.01955	0.02114	0.04228
Co	0.060	97.61	0.01100	0.01348	0.01955	0.02617	0.05234
Cu	0.033	97.40	0.00275	0.00365	0.00434	0.00631	0.01262
Zn	0.010	104.56	0.00136	0.00800	0.00416	0.00912	0.01824
Cd	0.013	99.30	0.00234	0.00225	0.00561	0.00648	0.01296

rep: uncertainty derived from repeatability; u_{sol}: uncertainty derived from solution preparation; u_x: uncertainty derived from stock solutions of calibration standards; U_C: combined uncertainty; U_E: expanded uncertainty.

2.3. Meteorological Conditions

Figure 2 shows the dominant wind conditions for the three seasons studied (cold dry, warm dry, and rainy). Dominant winds blew from southwest during the cold dry and warm dry seasons. Nine industrial parks are located to the southwest and southeast of the sampling site. These industrial complexes are related to the automotive industry and include auto parts assembly and automotive suppliers. During the rainy season, dominant winds arrived from the southeast. Guanajuato municipality is located to the southeast of León City (59.2 km away), where mining activity for the

extraction of metals has been of great importance for many years. Currently, deposits of As, Cr, Cu, Pb, Cd, and Hg, among others, continue to be exploited [10]. These sources may have contributed to the levels of heavy metals in the PM₁₀ particles collected at the study site. In Table 2, the mean values of the meteorological parameters (relative humidity, temperature, and barometric pressure) are shown. The warm dry season showed higher wind speed, temperature, and solar radiation compared to the values registered during the cold dry and rainy seasons.

2.4. Statistical Analysis

Descriptive statistics, non-parametric tests (Friedman test), and Spearman's rank correlation coefficients were employed to make comparisons among climatic periods and to assess the associations between pairs of the measured metals. All data analyses were performed using XLSTAT 2016 software.

Figure 2. Wind during the studied period; (a) cold dry season, (b) warm dry season, (c) rainy season.

Table 2. Mean values of the meteorological parameters for the considered climatic seasons.

Season	Wind Speed m s ⁻¹	Wind Direction Azimut	Temperature °C	Relative Humidity %	Barometric Pressure mm Hg	Solar Radiation W m ⁻²
Cold Dry	1.1	SW	13.9	40.8	632.6	356.8
Warm Dry	6.1	SSW	21.8	35.2	603.8	443.2
Rainy	1.9	SE	16.8	66.8	617.5	295.5

2.5. Morphological Analysis Using SEM-EDS

The morphology of the particles and their elemental composition were evaluated using a Hitachi brand scanning electron microscope (SEM) FLEXSEM-SU1000 equipped with a Bruker TM 40000 Quantax 75/80 energy dispersive X-ray detection system (EDS) that worked at 20 kV. The low vacuum scanning electron microscope was calibrated with a copper grid (Cu), a filament current of 300 mA, and at a working distance of 5 cm. All collected samples were analyzed by SEM-EDS. Single portions (5 mm × 2 mm) of the quartz filters were cut from the central part of the membranes and mounted on SEM aluminum stubs using double sided carbon tape. Ten particles from each sample were randomly selected and images were taken at magnifications of 500×, 1500×, 2500×, 5000×, 8000×, 10,000×, and 25,000×. Spectra for individual particles were obtained by EDS, with a measurement time of 100 s for each particle.

2.6. Health Risk Assessment

Exposure, expressed in terms of the lifetime average daily dose (LADD), allowed determination of the corresponding level of cancer risk (CR) for each metal. LADD serves to determine the amount of intake per kg of body weight per day of a pollutant suspected of having adverse effects on health when it is absorbed into the body over a long period, and is calculated with the following equations [11]:

$$LADD = E \times C \quad (1)$$

$$E = \frac{IR}{BW} \times \frac{ET \times EF \times ED}{AT} \quad (2)$$

where C (mg m⁻³) is the concentration of the metal of interest in PM₁₀, which is assumed to be the same as the exposure point, E (m³ Kg⁻¹ day⁻¹) is obtained from Equation (2) where IR (m³ h⁻¹) is the air inhalation rate, ET (24 h day⁻¹) is the exposure time, EF (350 days year⁻¹) is the exposure frequency, ED (years) is the exposure duration, BW (Kg) is the body weight, and finally AT (days) is the average time, with AT_c denoting carcinogenic risk and as AT_n denoting non-carcinogenic risk [12,13]. The analysis was done separately for adults and children. The parameters used in Equation 2 are shown in Table 3.

Cancer risk (CR) represents the increased probability of occurrence of diseases caused by tumors above the general average due to the impact of compounds that produce carcinogenic effects. The CR for carcinogenic substances is considered 1 × 10⁻⁶ (the risk of developing cancer during human life is 1 in 1,000,000). Values below 1.00 × 10⁻⁶ for individuals are considered negligible. For carcinogenic substances, the CR value is determined with the following equation:

$$CR = LADD \times CSF \quad (3)$$

where CR is the probability of occurrence of cancer in the exposed population during a lifetime of 70 years, which is determined by multiplying the LADD (mg Kg⁻¹ day⁻¹) and CSF (cancer slope factor) (mg Kg⁻¹ day⁻¹). The carcinogenic risk is defined as the increased probability of a person experiencing cancer during a lifetime as result of the exposure to a substance with specific carcinogenic potential [12]. The CSF is calculated with the following equation:

$$CSF = IUR \times \frac{BW}{(IR \times ET)} \times 1000 \quad (4)$$

where IUR (inhalation risk unit) is a reference value reported in the database of the US Environmental Protection Agency [12]. The values for IUR and RfC (reference concentration values) are presented in the Table 4. Regarding IUR and RfC, only values for Cd, Co, and Mn are reported.

Table 3. List of parameters used in the exposure calculation.

Parameter	Acronym	Unit of Measurement	Adult	Child
Numeric Value				
Inhalation rate	IR	m ³ h ⁻¹	0.9	0.7
Body weight	BW	Kg	70	15
Exposure time	ET	h day ⁻¹	24	24
Exposure frequency	EF	day year ⁻¹	350	350
Exposure duration	ED	year	24	6
Average Lifetime	ATc	day	25,550 *	25,550 *
Average Lifetime	ATn	day	210,240 **	52,560 ***

* 25,550 days corresponds to the typical life expectancy (70 years × 365 days/year); ** ED (24 years old) multiplied by 365 days/year × 24 h/day; *** ED (6 years) multiplied by 365 days/year × 24 h/day.

Table 4. Inhalation unit risk (IUR) and reference concentration (RfC) data from USEPA database.

Metal	CAS	IUR (µg m ⁻³) ⁻¹	RfC (mg m ⁻³)
Cd	7440-43-9	1.80 × 10 ⁻³	1.00 × 10 ⁻⁵
Co	7440-48-4	9.00 × 10 ⁻³	6.00 × 10 ⁻⁶
Mn	7439-96-5	-	5.00 × 10 ⁻⁵

Regarding non-carcinogenic risk, the THQ (target hazard quotient) can be calculated according to the following equation:

$$THQ = \frac{ADI}{RfDi} \quad (5)$$

For THQ, it was considered that there is a level of exposure (RfDi) below which it is unlikely for even a sensitive population to experience adverse effects on health. When the exposure level (ADI) exceeds the value indicated as 1.00, there may be concern about possible non-carcinogenic health effects; THQ values higher than 1.0 suggest higher levels of concern. RfDi (mg Kg⁻¹ day⁻¹) represents an inhalation dose considered to have no effects on health [13], and is defined by the equation:

$$RfDi = \begin{cases} RfC \times \frac{20 \text{ m}^3}{\text{day}} \times \frac{1}{70 \text{ Kg}} & (\text{adult}) \\ RfC \times \frac{7.6 \text{ m}^3}{\text{day}} \times \frac{1}{15 \text{ Kg}} & (\text{child}) \end{cases} \quad (6)$$

ADI (mg Kg⁻¹ day⁻¹) is the estimated dose that the receptor receives from exposure to polluted air [12] and is calculated with the same variables used for cancer risk:

$$ADI = E \times C \quad (7)$$

3. Results

3.1. PM₁₀ Levels

It is widely known that PM₁₀ exposure may cause adverse effects to public health. The maximum permissible level established by the Mexican Air Quality Standard is 75 µg m⁻³ [14]. In order to protect population health, this value may not be exceeded more than once a year. Figure 3 and Table 5 show the descriptive statistics for PM₁₀ gravimetric concentrations for the three climatic seasons. PM₁₀ concentrations exceeded the Mexican Standard during the cold dry season in six cases. The value established by the WHO (50 µg m⁻³) [15] was also exceeded during the cold dry and warm dry seasons. Median concentrations of PM₁₀ ranged from 27.992 µg m⁻³ to 9.385 µg m⁻³, being higher during the cold dry season. According to the non-parametric Friedman test, there were significant differences among seasonal values (at a significance level α = 0.05).

Figure 3. PM₁₀ gravimetric concentrations for the sampling site during the three climatic periods. The central horizontal bars are the medians. The lower and upper limits of the box are the first and third quartiles. + is the mean value; • represents maximum and minimum values.

Table 5. Descriptive Statistics for the sampling site during the three climatic periods.

Parameter	PM ₁₀ (µg m ⁻³) Cold Dry Season	PM ₁₀ (µg m ⁻³) Warm Dry Season	PM ₁₀ (µg m ⁻³) Rainy Season
Minimum	67.784	45.779	17.480
Maximum	132.620	64.124	45.325
1st Quartile	77.099	53.231	19.516
Median	91.386	55.602	24.585
3rd Quartile	109.915	61.960	36.134
Mean	95.969	56.419	27.992

The lower concentrations for PM₁₀ during the rainy season could be explained by wet deposition or precipitation scavenging. These are natural processes in which the interaction between hydrometeors and particles results in particle deposition to the Earth's surface [16]. On the other hand, higher PM₁₀ concentrations during cold dry season could be related to a higher atmospheric stability, lower wind speed values, and higher incidence of thermal inversions. PM₁₀ concentrations registered during the warm dry season may have been related to a higher incidence of wildfires and uncontrolled agricultural burnings.

3.2. Metal Concentrations

Descriptive statistics for metal concentrations during the three seasons are shown in Figure 4a–c and Tables 6–8, for Cd–Co–Cu, Fe–Zn, and Mg–Mn, respectively. Considering median concentrations, Fe was the dominant trace metal in the study site (2.553 µg m⁻³, 3.079 µg m⁻³, and 2.070 µg m⁻³ for the cold dry, warm dry, and rainy seasons, respectively). According to the Friedman test, Cd, Cu, and Mg showed significant differences among seasonal periods ($p < 0.05$), whereas, Co, Fe, Zn, and Mn did not exhibit significant seasonal variation. Cd, Cu, and Mg showed a clear seasonal pattern: Cu and Mg showed higher concentrations during the warm dry season, decreasing during the rainy season and registering lower values during the cold dry season (Figure 4). Cd showed higher values during the rainy season, decreasing during the warm dry season and showing lower values during the cold dry season, with median values ranging from 0.050 to 0.098 µg m⁻³. Median concentrations for Co, Zn, and Mn were found in the following ranges: from 0.068 to 0.124 µg m⁻³, from 0.365 to 1.61 µg m⁻³, and from 0.052 to 0.271 µg m⁻³, respectively. Cd is classified within group I by the International Agency for Research on Cancer [17] as carcinogenic in humans. In this work, median values for this metal exceeded by 10 to 20 times the maximum limit values established by European Union regulation

(5 ng m^{-3}) [15]. Mn median values during the cold dry season exceeded by two times the limit value established in the World Health Organization standards (150 ng m^{-3}) [15].

Figure 4. Descriptive statistics for metal concentrations during the three considered climatic periods for: (a) Cd–Co–Cu, (b) Fe–Zn, and (c) Mg–Mg. The central horizontal bars are the medians. The lower and upper limits of the box are the first and third quartiles. + is the mean value; • represents maximum and minimum values.

Table 6. Descriptive Statistics for Cd, Co, and Cu concentrations during the three climatic periods.

	Cd			Co			Cu		
	CD	WD	R	CD	WD	R	CD	WD	R
$\mu\text{g m}^{-3}$									
Min	0.006	0.044	0.003	0.008	0.045	0.037	0.030	0.254	0.153
Max	0.089	0.162	0.152	0.248	0.266	0.205	0.434	0.324	0.291
1° quartile	0.031	0.075	0.089	0.018	0.074	0.073	0.083	0.265	0.221
Median	0.050	0.093	0.098	0.068	0.124	0.104	0.115	0.276	0.254
3° quartile	0.084	0.128	0.129	0.127	0.182	0.181	0.141	0.313	0.274
Mean	0.053	0.100	0.099	0.087	0.136	0.120	0.145	0.286	0.241

Note: CD.-Cold dry season; WD.- Warm dry season; R.-Rainy season; Min.- Minimum; Max.- Maximum.

Table 7. Descriptive Statistics for Fe and Zn concentrations during the three climatic periods.

	Fe			Zn		
	CD	WD	R	CD	WD	R
	$\mu\text{g m}^{-3}$					
Min	0.728	1.554	0.896	0.067	0.390	0.374
Max	12.532	4.538	4.117	1.112	1.888	3.552
1° quartile	1.670	1.987	1.544	0.195	0.507	0.984
Median	2.553	3.079	2.070	0.365	0.580	1.161
3° quartile	4.847	3.434	3.092	0.736	1.360	1.668
Mean	3.871	2.885	2.337	0.470	0.921	1.433

Note: CD.- Warm dry season; WD.- Warm dry season; R.- Rainy season; Min.- Minimum; Max.- Maximum.

Table 8. Descriptive Statistics for Mg and Mn concentrations during the three climatic periods.

	Mg			Mn		
	CD	WD	R	CD	WD	R
	$\mu\text{g m}^{-3}$					
Min	0.004	1.142	0.164	0.010	0.002	0.055
Max	3.036	7.300	7.608	1.929	0.370	0.344
1st quartile	0.272	3.668	2.195	0.036	0.007	0.071
Median	0.426	4.180	3.561	0.271	0.052	0.109
3rd quartile	0.586	4.903	4.038	0.653	0.125	0.143
Mean	0.685	4.290	3.398	0.498	0.096	0.136

Note: CD—Cold dry season; WD—Warm dry season; R—Rainy season; Min—Minimum; Max—Maximum.

3.3. Statistical Analysis (Bi-Variate and Factor Analysis)

Table 9 shows the Spearman's rank correlation coefficients between the trace metal concentrations in PM_{10} found in this study. Spearman's rank correlation coefficients were significant at $\alpha = 0.05$ for Cd–Cu (0.366), Cu–Mg (0.577), Cu–Zn (0.450), Cd–Mg (0.457), and Zn–Mg (0.457), indicating that these metals could have originated from common sources (probably fossil fuel combustion). Concentrations of Fe, Co, and Mn did not show correlations with the rest of metals, indicating that sources of these elements are different and more diverse. Analyzed trace metals data were subjected to a factor analysis in order to investigate the interrelationships between trace metals [18]. We used XLSTAT statistical software to determine factors and their principal loadings. Table 10 shows the results of the factor analysis; two factors were obtained, which together contributed to the maximum variability of data with 49.597% of the total variability. Factor 1 showed 24.974% variability and had higher principal loadings for Fe and Mn. The second factor (F2) showed 24.623% variability and higher loadings for Cd, Co, Cu, Zn, and Mg.

Table 9. Spearman's rank correlation coefficients between the trace metal concentrations in PM_{10} .

Trace Metals	Cd	Co	Cu	Fe	Zn	Mg	Mn
Cd	1	−0.080	0.536	−0.104	0.074	0.457	−0.195
Co	−0.080	1	−0.010	−0.058	0.040	0.337	−0.020
Cu	0.536	−0.010	1	−0.100	0.450	0.577	0.096
Fe	−0.104	−0.058	−0.100	1	0.334	0.310	0.190
Zn	0.074	0.040	0.450	0.334	1	0.457	0.241
Mg	0.457	0.337	0.577	0.310	0.457	1	0.023
Mn	−0.195	−0.020	0.096	0.190	0.241	0.023	1

Values in bold are significant at $\alpha = 0.05$.

Table 10. Factor analysis of trace metals in PM₁₀.

Trace Metals	F1	F2
Cd	−0.359	0.448
Co	0.014	0.202
Cu	−0.226	0.709
Fe	0.930	−0.001
Zn	0.116	0.444
Mg	−0.008	0.872
Mn	0.831	−0.145
Variability (%)	24.974	24.623
Cumulative (%)	24.974	49.597

Bold values shows the significant values at $\alpha = 0.05$.

3.4. Health Risk Assessment

The lifetime average daily dose (LADD) and the probability of occurrence of cancer in the exposed population (CR) were calculated for each studied heavy metal. Calculations were made separately for two representative population groups, children and adults, assuming an adult lifetime of 70 years. The International Agency for Research on Cancer (IARC) [17] classifies substances based on the carcinogenic potential they may have for humans. According to this classification, cobalt (Co) and cadmium (Cd) belong to group 2B (possibly carcinogenic to humans) and group 1 (carcinogenic to humans), respectively. For this reason, CR values were calculated only for these metals. CR and LADD values are shown in Table 11 for each heavy metal considered in this study. Target hazard quotients were calculated for Cd, Co, and Mn and these values and their confidence limits are shown in Table 12.

Table 11. Cancer risk level (5% lower confidence and 95% upper confidence limits) and lifetime average daily dose for cadmium (Cd) and cobalt (Co) during the three climatic periods.

Cold Dry Season					
Chemical	Type of Result	Median	5% Lower Confidence Limit	95% Upper Confidence Limit	Age Group/LADD Lifetime Average Daily Dose
Cd	Cancer Risk	8.67×10^{-8}	9.628×10^{-8}	6.333×10^{-7}	Adults: 1.48×10^{-8}
		2.17×10^{-8}	2.888×10^{-8}	1.392×10^{-7}	Children: 1.35×10^{-8}
Co	Cancer Risk	7.07×10^{-7}	7.093×10^{-8}	2.081×10^{-6}	Adults: 2.42×10^{-8}
		1.77×10^{-7}	4.549×10^{-9}	3.066×10^{-7}	Children: 2.20×10^{-8}
Warm Dry Season					
Cd	Cancer Risk	3.62×10^{-7}	6.577×10^{-8}	3.114×10^{-7}	Adults: 2.78×10^{-8}
		4.05×10^{-8}	4.769×10^{-8}	2.312×10^{-7}	Children: 2.53×10^{-8}
Co	Cancer Risk	2.10×10^{-6}	3.519×10^{-7}	1.442×10^{-6}	Adults: 3.76×10^{-8}
		4.75×10^{-7}	1.845×10^{-8}	4.403×10^{-7}	Children: 3.42×10^{-8}
Rainy Season					
Cd	Cancer Risk	2.60×10^{-7}	4.844×10^{-9}	2.494×10^{-7}	Adults: 2.74×10^{-8}
		4.00×10^{-8}	2.992×10^{-9}	1.718×10^{-7}	Children: 2.49×10^{-8}
Co	Cancer Risk	9.76×10^{-7}	2.558×10^{-7}	2.075×10^{-6}	Adults: 3.34×10^{-8}
		2.44×10^{-7}	1.486×10^{-8}	3.451×10^{-7}	Children: 3.03×10^{-8}

Table 12. Target hazard quotient (THQ) for cadmium (Cd), cobalt (Co), and manganese (Mn) during the three climatic periods, and 5% lower confidence and 95% upper confidence limits.

Cold Dry Season					
Chemical	Type of Result	Median	5% Lower Confidence Limit	95% Upper Confidence Limit	Age Group
Cd	Non-carcinogenic THQ	0.220	0.169	0.394	Adults
		0.450	0.130	0.515	Children
Co	Non-carcinogenic THQ	0.628	0.421	1.199	Adults
		1.285	0.880	1.591	Children
Mn	Non-carcinogenic THQ	0.082	0.017	0.308	Adults
		0.169	0.1005	0.365	Children
Warm Dry Season					
Cd	Non-carcinogenic THQ	0.432	0.187	1.303	Adults
		0.883	0.189	1.344	Children
Co	Non-carcinogenic THQ	0.975	0.422	1.489	Adults
		1.995	1.231	2.204	Children
Mn	Non-carcinogenic THQ	0.326	0.197	0.581	Adults
		0.667	0.205	0.834	Children

There are other methods, such as the respiratory tract model (from International Commission of Radiological Protection, ICRP) and multiple-path particle dosimetry model (MPPD), that consider detailed data on particle properties, individual factors such as breathing patterns (nasal or oronasal), ventilation rates, and lung morphology, among other factors [19–21]. Both models require physiological and quantitative respiratory tract morphometry data. The lack of this information in León City, as well as the lack of a mass size distribution in different fractions for the collected samples made it impossible to apply this kind of model in order to estimate cancer risk (CR) and the hazard quotient (non-cancer risk) in the present study.

3.5. Morphological Analysis Results (SEM-EDS)

The morphology and composition of collected PM₁₀ samples were analyzed by SEM-EDS. Figures 5–7 show images of selected particles collected during the cold dry, warm dry, and rainy seasons, respectively. Figure 5 shows a particle labeled as 950 (collected during the cold dry season) with a semi-circular shape that showed the presence of some heavy metals and the following elemental content: O (40.73%), Si (25.12%), Fe (18.07%), Cu (1.50%), and Zn (0.49%). Figure 6 shows a particle collected during the warm dry season, labeled as 1111, with an irregular shape and bright appearance, containing an elemental composition as follows: O (52.71%), Si (34.08%), Ba (12.81%), Fe (10.89%), C (5.19%), Cu (2.80%), S (1.98%), Zn (1.43%), and Mg (0.53%). Figure 7 shows particle 1820 (collected during rainy season), with a spherical shape (typical of iron oxides generated from the condensations of vapors [22]) and a high proportion of Fe (16.04%), O (49.87%), and Si (32.55%), and a lesser proportion of Na (0.94%), Ca (0.32%), and Al (0.28%).

Figure 5. Micrograph and EDS spectra showing morphology and composition for a selected particle collected during the cold dry season.

Figure 6. Micrograph and EDS spectra showing morphology and composition for a selected particle collected during the warm dry season.

Figure 7. Micrograph and EDS spectra showing morphology and composition for a selected particle collected during the rainy season.

4. Discussion

A comparison among the median values of PM_{10} concentrations and trace metals content from this study with those found in other studies around the world can be observed in Table 13. The range

of the median values of PM₁₀ gravimetric concentrations in the present study were similar to those found in Tampico, Mexico [23], but lower than found concentrations in Puebla, Mexico [24], Algiers, Algeria [25] and Ahvaz, Iran [26]. The range of the median values of Cd concentrations were similar to those reported in Silesia, Poland [27] but higher than those found in Acerra, Italy [11], Athens, Greece [23] and Tijuana, Mexico [27]. The range of the median values of Co were lower than reported for Ahvaz, Iran [26] but higher than those reported for Acerra, Italy [11], Riohacha, Colombia [28], Tijuana, Mexico [29] and Puebla, Mexico [24]. Range of the concentration median values of Cu in this study were higher than those reported in Acerra, Italy [11], Tampico, Mexico [23] and Athens, Greece [30], but lower than those reported for Silesia, Poland [27] and Algiers, Algeria [25]. Fe median concentrations in the study site were higher than the reported value for Rio de Janeiro, Brazil [31], Riohacha, Colombia [28], Tampico, Mexico [23] and Acerra, Italy [11], but lower than registered value in Algiers, Algeria [25] and Silesia, Poland [27]. Range of the concentration median values of Mg found in this study was higher than reported values for Rio de Janeiro, Brazil [31], Tijuana, Mexico [29], Colima, Mexico [32] and Riohacha, Colombia [28]. Range of the median Mn concentrations were higher than reported concentrations for Rio de Janeiro, Brazil [31], Acerra, Italy [11], Tijuana, Mexico [29], Colima, Mexico [32], but lower than those reported for Algiers, Algeria [25] and Silesia, Poland [27]. Zn median levels were similar to those found in Riohacha, Colombia [28], but higher than those reported in Rio de Janeiro, Brazil [31], Acerra, Italy [11], Tijuana, Mexico [29] and Tampico, Mexico [23], and lower than reported levels Ahvaz, Iran [26].

Table 13. Comparison of PM₁₀ concentrations and their trace metals content in this study with the reported results in other sites around the world.

Site	PM ₁₀	Cd	Co	Cu	Fe	Mg	Mn	Zn
Median Range of Trace Metals Concentrations (µg m ⁻³)								
León, Guanajuato (This Study)	27.9–91.4	0.050–0.098	0.068–0.12	0.12–0.27	2.55–3.08	0.426–4.180	0.052–0.27	0.36–1.16
Rio de Janeiro, Brazil [31]	13.1–47.0	-	-	0.13–0.253	2.479–6.490	0.744–1.933	0.03–0.09	0.073–0.182
Acerra, Italy [11]	11.10–123.0	0.003–0.006	0.001–0.006	0.008–0.036	0.717–2.362	-	0.012–0.042	0.032–0.195
Riohacha, Colombia [28]	3.75–81.2	-	0.003–0.030	0.524–1.569	0.256–0.467	0.333–0.427	0.004–0.006	0.323–1.949
Athens, Greece [30]	24.0–217.0	0.0001–0.009	-	0.012–0.191	-	-	0.0002–0.113	-
Algiers, Algeria [25]	15.46–111.30	-	-	1.007–6.601	11.41–17.00	-	2.313–7.221	-
Tampico, Mexico [23]	21.0–92.0	0.002–0.21	-	0.013–0.09	0.180–1.635	-	0.001–0.363	0.134–0.431
Tijuana, Mexico [29]	14.0–32.0	0.0003–0.013	0.00012–0.00017	-	0.30–0.40	0.20–0.30	0.0058–0.0081	0.003–0.018
Puebla, Mexico [24]	55.9–199.2	0.002–0.0193	0.0002–0.0061	0.019–0.461	0.326–5.850	-	0.0002–0.089	-
Colima, Mexico [32]	14.9–78.5	0.0001–0.0009	-	0.04–0.398	0.20–1.6	0.10–0.73	0.0037–0.373	0.0045–0.106
Upper Silesia, Poland [27]	8.0–157.0	0.036–0.192	-	0.223–1.550	20.707–48.718	-	0.242–0.642	-
Ahvaz City, Iran [26]	410.0–741.0	0.190–0.876	0.298–1.582	-	-	-	-	2.810–8.231

From the Factor Analysis (Section 3.3), it was corroborated that the Fe–Mn pair probably originated from common sources at the study site. We were able to infer that the Cd, Co, Cu, Zn, and Mg probably had sources in common (fossil fuel combustion, steel and non-ferrous metal production industrial emissions, and waste combustion) [33–38].

All CR values were below the acceptable level (1.00×10^{-6}) except for cobalt (Co) in adults during the warm dry season. CR values for single species were higher for adults for all periods, being the highest during the warm dry season. Exposure frequency (EF) may have different values depending on age groups and occupations. Other authors [11,38,39] also have reported that adult risks are higher than those for children, due to the exposure time related to working activities. The integrated cancer risk (Section 3.4) for Co and Cd were below the acceptable level (1.00×10^{-6}), showing the following values for adults: 7.94×10^{-7} for the cold dry season, 1.26×10^{-6} for the warm dry season, and 1.14×10^{-6} for the rainy season. The integrated CR values for children were 1.99×10^{-7} , 3.15×10^{-7} , and 2.84×10^{-7} for cold dry, warm dry, and rainy periods, respectively. All THQ values were higher in children for the three seasons, showing the highest values during the warm dry season. THQ values for Co were higher than 1.0 for children, suggesting a non-carcinogenic potential risk for children's health in the study site, including adverse health effects like allergic dermatitis, rhinitis, and asthma [39]. Our results should be regarded as preliminary, and further research should be undertaken considering specific biometric factors, particle mass distribution, and different size fractions in order to apply other models such as

the respiratory tract model and MPPD, which could provide additional information regarding the potential health effects of PM₁₀ and its heavy metal content on the population of León City.

The results from SEM-EDS showed that the analyzed samples of PM₁₀ were rich in elements such as Fe, Cu, Mg, Mn, O, C, Na, Zn, Al, Ca, S, Ba, and Si. The analysis showed particles with different sizes, morphologies (irregular, spherical, and clusters), and compositions, indicating that the chemical composition of the PM₁₀ in the study site was influenced by both anthropogenic and natural sources. Some authors [40–42] have related spherical particles to anthropogenic sources (high temperature combustion processes), whereas other studies have reported an association between natural sources and particles with irregular morphologies [40,43,44]. The analyzed samples showed the dominant presence of Iron both in spherical particles and in irregularly shaped particles, which indicates that this element had its origin in both natural and anthropogenic sources. Manganese is frequently emitted during the combustion of hydrocarbons [45] or from metallurgical industry [46,47]. Rounded zinc oxide particles has been associated with high temperature combustion processes [47] and metallurgical industrial emissions [22]. It is important to mention that the sampling site was located on one of the most important roads in the city (Adolfo Lopez Mateos Boulevard), with frequent vehicular traffic; this could explain the presence of Cu, Fe, and Zn. In urban areas, these metals are released as a consequence of tire wear and brake abrasion when vehicles are continuously accelerating and decelerating [43]. In the presence of Zn–S, Ba can also be associated with the paint industry, and in the presence of C and O, it can be associated with the mining industry. On the other hand, some analyzed particles showed irregular shapes which have been associated with mineral origin [41–47].

5. Conclusions

The results lead to the acceptance of all four hypotheses:

- H1: seasonal variations in particulates and their trace metals were found.
- H2: associations were found among the trace metals present in PM₁₀.
- H3: meteorological parameters influenced the concentrations of heavy metals.
- H4: the heavy metal concentrations found pose a threat to the population of León.

PM₁₀ mass concentrations in collected samples exceeded the maximum permissible level established by the World Health Organization and the Mexican standard during the cold dry season. Gravimetric PM₁₀ concentrations found in this study were similar to those found in Tampico and higher than those reported in Rio de Janeiro, Riohacha, and Colima, but lower than those reported for Algiers and Ahvaz. Meteorological analysis showed that sources (several industrial complexes and mining activities) located southeast and southwest of the sampling site could have contributed to the PM₁₀ levels and to their heavy metal content. Iron was the dominant trace metal in this study, with homogeneously distributed concentrations during the three climatic seasons. Cd, Cu, and Mg showed significant differences among seasonal periods ($p < 0.05$). Spearman's rank correlation coefficients and factor analysis showed that Zn, Cu, Mg, and Cd had common sources and a probable anthropogenic origin (vehicular and industrial sources), and Fe, Mn, and Co did not correlate with any other metals, indicating that these metals had their origins in different and diverse sources. The SEM-EDS results confirmed that iron was the dominant heavy metal in the sampled particles during this study. This metal showed a great variety of shapes, such as spherical, conglomerate, and irregular, suggesting sources such as mineral and crustal origin, re-suspension and fusion processes, and iron smelting and welding. Cd and Mn exceeded the maximum limit established by WHO (10 to 20 times and 3 times, respectively), indicating that PM₁₀ containing these heavy metals could be a health threat for León's population. The carcinogenic and non-carcinogenic risk was increased during the warm dry season, since the individual CR value for Co (in adults) and hazard quotients (in children) exceeded the permissible maximum limit during this period. The results provided by this study highlight PM₁₀ mass concentration, Mn, Cd, and Co as causes of concern and potential threats to the public health within the study area. Currently, the air quality-monitoring network in León City provides continuous

measurements of PM₁₀ mass concentration, but chemical characterization of the metal content is not routinely made. It is necessary to establish an environmental policy that includes a sampling and analysis program for the determination of the heavy metal contents in PM₁₀. Such a policy would provide information on the spatial and temporal variation of PM₁₀, as well as information on chemical and morphological characteristics that would allow the establishment of control measures of these pollutants in the study area.

Author Contributions: J.G.C.B. and R.M.C.B. were the responsible to design the study, wrote and revise the paper. A.A.E.G. performed gravimetric determination and coordinated all the sampling activities. C.G. carried out the statistical analysis. I.E.P.P. was the responsible to carry out the SEM/EDS analysis of collected samples. S.E.C.L. and R.d.C.L.S. contributed to the determination of metals by A.A., M.R.M., E.R.L. and M.d.I.L.E.F. directed the analytical determination and the quality control. J.D.W.K. was the responsible of the meteorological analysis. S.M.M. and G.H.L. carried out the sampling activities, analysis of data and lab work.

Funding: This research received no external funding.

Acknowledgments: The authors appreciate the support provided by the Department of Research on Environment and Materials Degradation of the Corrosion Research Center (CICORR) of the Autonomous University of Campeche (UAC).

Conflicts of Interest: Authors declare no conflict of interest.

References

1. National Institute of Geography and Informatics Statistics (INEGI). Intercensal Survey 2015. Available online: <https://www.inegi.org.mx/programas/intercensal/2015/default.html#Documentacion> (accessed on 11 January 2019).
2. Guanajuato's State Ecology Institute. Emissions Inventory for Guanajuato State 2008. Available online: <https://smaot.guanajuato.gob.mx/sitio/calidad-del-aire/4/Inventario-de-Emisiones-de-Contaminantes-Criterio> (accessed on 24 February 2019).
3. Pope, C.; Dockery, D.; Kanner, R.; Villegas, G.; Schwartz, J. Oxygen Saturation, Pulse Rate, and Particulate Air Pollution. *Am. J. Respir. Crit. Care Med.* **1999**, *159*, 365–372. [CrossRef] [PubMed]
4. Schwela, D. Air Pollution and Health in Urban Areas. *Rev. Environ. Health* **2000**, *15*, 13–42. [CrossRef] [PubMed]
5. United States Environmental Protection Agency (US EPA). Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air—Compendium Method IO-2.1. In *Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM₁₀ Using High Volume (HV) Sampler*; US EPA: Cincinnati, OH, USA, 1999.
6. United States Environmental Protection Agency (US EPA). Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air—Compendium Method IO-3.1. In *Selection, Preparation and Extraction of Filter Material*; US EPA: Cincinnati, OH, USA, 1999.
7. Machado, A.; Velazquez, H.; Garcia, N.; Garcia, C.; Acosta, L.; Cordova, A.; Linares, M. Dispersion and Metals in PM₁₀ in a high vehicular traffic impact zone. *Interciencia* **2007**, *32*, 312–317.
8. Leili, M.; Naddafi, K.; Nabidzadeh, R.; Yunesian, M.; Mesdaghinia, A. The study of TSP and PM₁₀ concentration and their heavy metal content in central area of Tehran, Iran. *Air Qual. Atmos. Health* **2008**, *1*, 159–166. [CrossRef]
9. United States Environmental Protection Agency (US EPA). Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air—Compendium Method IO-3.2. In *Determination of Metals in Ambient Particulate Matter Using Atomic Absorption (aa) Spectroscopy*; US EPA: Cincinnati, OH, USA, 1999.
10. Ramos-Arroyo, Y.R.; Siebe, C.D. Estrategia para identificar jales con potencial de riesgo ambiental en un distrito minero: Estudio de caso en el Distrito minero de Guanajuato, México. *Rev. Mex. Cienc. Geológicas* **2006**, *23*, 54–74.
11. Di Vaio, P.; Magli, E.; Caliendo, G.; Corvino, A.; Fiorino, F.; Frecentese, F.; Saccone, I.; Santagada, V.; Severino, B.; Onorati, G.; et al. Heavy Metals Size Distribution in PM₁₀ and Environmental-Sanitary Risk Analysis in Acerra (Italy). *Atmosphere* **2018**, *9*, 58. [CrossRef]

12. United States Environmental Protection Agency. Part F, Supplemental Guidance for Inhalation Risk Assessment. In *Risk Assessment Guidance for Superfund—Volume I: Human Health Evaluation Manual*; US EPA: Washington, DC, USA, 2009.
13. United States Environmental Protection Agency. Part A, Supplemental Guidance for Inhalation Risk Assessment. In *Risk Assessment Guidance for Superfund—Volume I: Human Health Evaluation Manual*; US EPA: Washington, DC, USA, 1989.
14. Diario Oficial de la Federación. Norma Oficial Mexicana NOM-025-SSA1-2014. In *Valores Límites Permisibles Para la Concentración de Partículas Suspensas PM10 y PM2.5 en el Aire Ambiente y Criterios Para su Evaluación*; Secretaría de Salud: Ciudad de México, México, 2014.
15. World Health Organization (WHO). *Air Quality Guidelines for Europe*, 2nd ed.; Regional Publication, European Series, No. 91; WHO Regional Office for Europe, World Health Organization: Copenhagen, Denmark, 2000.
16. Feng, X.; Wang, S. Influence of different weather events on concentrations of particulate matter with different sizes in Lanzhou, China. *J. Environ. Sci.* **2012**, *24*, 665–674. [[CrossRef](#)]
17. International Agency for Research on Cancer (IARC). A review of human carcinogens: Arsenic, metals, fibres, and dusts. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, 100C; World Health Organization: Lyon, France, 2012; pp. 121–141.
18. Berg, T.; Røyset, O.; Steinnes, E.; Vadset, M. Atmospheric trace element deposition: Principal Component Analysis of ICP-MS data from moss samples. *Environ. Pollut.* **1995**, *88*, 67–77. [[CrossRef](#)]
19. Debanada, R.; Seo, Y.C.; Kim, S.; Oh, J. Human health risks assessment for airborne PM10-bound metals in Seoul, Korea. *Environ. Sci. Pollut. Res.* **2019**, *26*, 24247–24261.
20. Widziewicz, K.; Rogula, K.W.; Loska, K.; Kociszewska, K.; Majewski, G. Health Risk Impacts of Exposure to Airborne Metals and Benzo(a)Pyrene during Episodes of High PM10 Concentrations in Poland. *Biomed. Environ. Sci.* **2018**, *31*, 23–36.
21. Cheng, S.C.; Liao, C.M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* **2006**, *366*, 112–123. [[CrossRef](#)] [[PubMed](#)]
22. Aragón Piña, A. ¿Cómo son las partículas atmosféricas antropogénicas y cuál es su relación con los diversos tipos de fuentes de contaminantes? In *Universidad Autónoma de San Luis Potosí, Instituto de Metalurgia*; Facultad de Ingeniería: San Luis Potosí S.L.P., México, 2011; pp. 1–177.
23. Rodríguez, P.; Flores, R.; Mugica, V.; Morales, S. Sources of trace metals in PM10 from a petrochemical industrial complex in Northern Mexico. *Air Qual. Atmos. Health* **2017**, *10*, 69–84. [[CrossRef](#)]
24. Morales, S.; Rodríguez, P.; Jonathan, M.; Navarrete, M.; Herrera, M.; Muñoz, N. Characterization of As and trace metals embedded in PM10 particles in Puebla City, México. *Environ. Monit. Assess.* **2014**, *186*, 55–67. [[CrossRef](#)] [[PubMed](#)]
25. Talbi, A.; Kerchich, Y.; Kerbach, R.; Boughedaoui, M. Assessment of annual air pollution levels with PM1, PM2.5, PM10 and associated heavy metals in Algiers, Algeria. *Environ. Pollut.* **2018**, *232*, 252–263. [[CrossRef](#)] [[PubMed](#)]
26. Heidari, M.; Shirmardi, M.; Gourdazi, G.; Alavi, N.; Ahmadi, K.; Zallaghi, E.; Naelmabadl, A.; Hashemzadeh, B. The evaluation of heavy metals concentration related to PM10 in ambient air of Ahvaz city, Iran. *J. Adv. Environ. Health Res.* **2013**, *1*, 120–128.
27. Pastuszka, J.; Rogula, W.; Zajusz, E. Characterization of PM10 and PM2.5 and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. *Environ. Monit. Assess.* **2010**, *168*, 613–627. [[CrossRef](#)] [[PubMed](#)]
28. Rojano, R.; Arregoces, H.; Restrepo, G. Composición Elemental y Fuentes de Origen de Partículas Respirables (PM10) y Partículas Suspensas Totales (PST) en el Área Urbana de la Ciudad de Riohacha, Colombia. *Inf. Tecnol.* **2014**, *25*, 3–12. [[CrossRef](#)]
29. Cruz, M.; Alberto, A.; Cárdenas, B.; Blanco, S.; Molina, L.; Querol, X. Mass concentration, composition and sources of fine and coarse particulate matter in Tijuana, Mexico, during Cal-Mex campaign. *Atmos. Environ.* **2014**, *88*, 320–329.
30. Manalis, M.; Grivas, G.; Protonatarios, V.; Moutsatsou, A.; Samara, C.; Chaloulakou, A. Toxic metal content of particulate matter (PM10) within the Greater Area of Athens. *Chemosphere* **2005**, *60*, 557–566. [[CrossRef](#)]
31. Loyola, J.; Arbilla, G.; Quiterio, S.; Escaleira, V.; Minhod, S. Trace Metals in the Urban Aerosols of Rio de Janeiro City. *J. Braz. Chem. Soc.* **2012**, *23*, 628–638. [[CrossRef](#)]

32. Campos, A.; Aragon, A.; Alastuey, A.; Galindo, I.; Querol, X. Levels, composition and source apportionment of rural background PM10 in western Mexico (state of Colima). *Atmos. Pollut. Res.* **2011**, *2*, 409–417. [\[CrossRef\]](#)
33. Bernhard, D.; Rossmann, A.; Wick, G. Metals in cigarette smoke. *IUBMB Life* **2005**, *57*, 805–809. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Cook, M.E.; Morrow, H. *Anthropogenic Sources of Cadmium Transport into Plants*; Canadian Network of Toxicology Centres: Ottawa, ON, Canada, 20–21 June 1995.
35. Chandler, A.J. Characterizing Cadmium in Municipal Solid Waste, Sources of Cadmium in the Environment. In *Inter-Organization Programme for the Sound Management of Chemicals (IOMC)*; Organization for Economic Co-operation and Development (OECD): Paris, France, 1996.
36. Pandey, P.; Soni, D.K. Enrichment of heavy metal in ambient air of Lucknow City and its potential health hazards. *Int. J. Adv. Res.* **2017**, *5*, 299–309. [\[CrossRef\]](#)
37. Lee, C.S.L.; Li, D.X.; Zhang, G.; Li, J.; Dding, J.A.; Wang, T. Heavy metals and Pb Isotopic composition of Aerosols in Urban and Suburban Areas of Hong Kong and Guangzhou, South China Evidence of the Long-Range Transport of Air Contaminants. *Atmos. Environ.* **2006**, *41*, 432–447. [\[CrossRef\]](#)
38. Romanazzi, V.; Casazza, M.; Malandrino, M.; Maurino, V.; Piano, A.; Schiliro, T.; Gilli, G. PM10 size distribution of metals and Environmental-sanitary risk analysis in the City of Torino. *Chemosphere* **2014**, *112*, 210–216. [\[CrossRef\]](#)
39. Lauwerys, R.; Lison, D. Health risks associated with Cobalt exposure—An overview. *Sci. Total Environ.* **1994**, *150*, 1–6. [\[CrossRef\]](#)
40. González, L.T.; Longoria-Rodriguez, F.E.; Sánchez-Domínguez, M.; Leyva-Porras, C.; Acuña-Askar, K.; Kharissov, B.I.; Arizpe-Zapata, A.; Alfaro-Barbosa, J.M. Seasonal variation and chemical composition of particle matter—A study by XPS, ICP-AES and sequential microanalysis using Raman with SEM/EDS. *J. Environ. Sci.* **2018**, *74*, 32–49. [\[CrossRef\]](#)
41. Breed, C.A.; Arocena, J.M.; Sutherland, D. Possible sources of PM10 in Prince George (Canada) as revealed by morphology and in situ chemical composition of particulate. *Atmos. Environ.* **2002**, *36*, 1721–1731. [\[CrossRef\]](#)
42. Li, W.; Shao, L.Y. Transmission electron microscopy study of aerosol particles from the brown hazes in Northern China. *J. Geophys. Res.* **2009**, *114*, 1–10. [\[CrossRef\]](#)
43. Aragón-Piña, A.; Campos-Ramos, A.A.; Leyva-Ramos, R.; Hernández-Orta, M.; Miranda-Ortiz, N.; Luszczewski-Kudra, A. Influencia de las emisiones industriales en el polvo atmosférico de la Ciudad de San Luis Potosí, México. *Rev. Int. Contam. Ambient.* **2006**, *22*, 5–19.
44. Buseck, P.R.; Jacob, D.J.; Posfai, M.; Li, J.; Anderson, J.R. Minerals in the air: An environmental perspective. *Int. Geol. Rev.* **2000**, *7*, 577–594. [\[CrossRef\]](#)
45. Pacyna, J.M.; Semb, A.; Hanssen, J.E. Emission and long-range transport of trace elements in Europe. *Tellus* **1984**, *36*, 163–178. [\[CrossRef\]](#)
46. Querol, X.; Alastuey, A.; Rosa, J.; Sánchez-De-La-Campa, A.; Plana, F.; Ruir, C.R. Source apportionment analysis of atmospheric particles in an industrialized urban site in Southwestern Spain. *Atmos. Environ.* **2002**, *36*, 3113–3125. [\[CrossRef\]](#)
47. Alastuey, A.; Querol, X.; Plana, F.; Viana, M.; Ruiz, C.; Sanchez de la Campa, A.; De la Rosa, J.; Mantilla, E.; Garcia dos Santos, S. Identification and chemical characterization of industrial particulate matter sources in Southwest Spain. *J. Air Waste Manag. Assoc.* **2006**, *56*, 993–1006. [\[CrossRef\]](#) [\[PubMed\]](#)