Trace Metal Content and Health Risk Assessment of PM$_{10}$ in an Urban Environment of León, Mexico

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Abstract: Trace metal concentrations in PM$_{10}$ were measured in an urban–industrial site in León, Mexico in three different seasons. PM$_{10}$ 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 PM$_{10}$ 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 $\mu$g m$^{-3}$) and the minimum value for Cd (0.050 $\mu$g 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 PM$_{10}$ 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 PM$_{10}$ and their trace metal content.

Keywords: PM$_{10}$; 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 km$^2$ [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 PM$_{10}$ 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. PM$_{10}$ emissions are mainly due to the transit of vehicles over unpaved roads and farming activities including the burning of agricultural waste.

PM$_{10}$ 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. PM$_{10}$ 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 PM$_{10}$ toxicity. Despite its importance, there have not been enough studies about the content of trace metals in PM$_{10}$ 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 (PM$_{10}$) 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 PM$_{10}$ or its trace metal content.)
- To investigate by statistical analysis whether there are associations among the different measured trace metals present in PM$_{10}$. (H2: There are associations among the trace metals present in PM$_{10}$.)
- To analyze whether there is an influence of meteorological parameters on the heavy metal concentrations associated with PM$_{10}$. (H3: Meteorological parameters have influence on heavy metals concentrations.)
- To determine whether the concentrations of trace metals found in PM$_{10}$ 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 PM$_{10}$ 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 PM<sub>10</sub> 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 PM<sub>10</sub> 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<sup>-1</sup>, positioned at 2 m height. A total of 24 ambient air samples of PM<sub>10</sub> 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).](image-url)
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 HNO$_3$ + 75 mL HCl), and 1.065 mL of HClO$_4$. 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% HNO$_3$ solution [8]. The calibration range adopted was 5–500 µg L$^{-1}$ (seven point calibration) for each metal; the correlation coefficients ($R^2$) for the calibration curves were all greater than 0.998.

2.2.2. Trace Metal Determination by Atomic Absorption Spectrophotometry

Trace metals in PM$_{10}$ 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 IO.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   | 0.00252   | 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 PM$_{10}$ 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.

![Wind Diagrams](image)

**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]:

\[
\text{LADD} = E \times C \tag{1}
\]

\[
E = \frac{IR \times ET \times EF \times ED}{BW \times AT} \tag{2}
\]

where C (mg m\(^{-3}\)) is the concentration of the metal of interest in PM\(_{10}\), which is assumed to be the same as the exposure point, E (m\(^3\) Kg\(^{-1}\) day\(^{-1}\)) is obtained from Equation (2) where IR (m\(^3\) 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 \times 10^{-6} (the risk of developing cancer during human life is 1 in 1,000,000). Values below 1.00 \times 10^{-6} for individuals are considered negligible. For carcinogenic substances, the CR value is determined with the following equation:

\[
\text{CR} = \text{LADD} \times \text{CSF} \tag{3}
\]

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:

\[
\text{CSF} = \text{IUR} \times \frac{BW}{(IR \times ET)} \times 1000 \tag{4}
\]

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 |
|----------------------------|---------|---------------------|-------|-------|
| Inhilation 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:

$$THQ = \frac{ADI}{RfDi}$$ (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:

$$RfDi = \begin{cases} 
RfC \times \frac{20}{70 \ Kg} \times \frac{1}{70 \ Kg} & \text{(adult)} \\
RfC \times \frac{7.6}{15 \ Kg} \times \frac{1}{15 \ Kg} & \text{(child)} 
\end{cases}$$ (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:

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

3. Results

3.1. PM$_{10}$ Levels

It is widely known that PM$_{10}$ 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 PM$_{10}$ gravimetric concentrations for the three climatic seasons. PM$_{10}$ 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 PM$_{10}$ 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 $\alpha = 0.05$).
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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 5–8, 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.

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       | PM₁₀ (µg m⁻³) Cold Dry Season | PM₁₀ (µg m⁻³) Warm Dry Season | PM₁₀ (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                    |

To be included in the paper:
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\(^{-3}\)) \[15\].

Descriptive statistics for metal concentrations during the three seasons are shown in Figure 4 a, b, c and Tables 6, 7 and 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 \(\mu\)g m\(^{-3}\), 3.079 \(\mu\)g m\(^{-3}\), and 2.070 \(\mu\)g 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 \(\mu\)g m\(^{-3}\). Median concentrations for Co, Zn, and Mn were found in the following ranges: from 0.068 to 0.124 \(\mu\)g m\(^{-3}\), from 0.365 to 1.61 \(\mu\)g m\(^{-3}\), and from 0.052 to 0.271 \(\mu\)g 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](image-url) 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   |
| 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\(^{st}\) 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\(^{rd}\) 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        |
| µg 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    |
| 1st 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    |
| 3rd 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        |
| µg 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 PM₁₀ found in this study. Spearman’s rank correlation coefficients were significant at α = 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 PM₁₀.

| 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 α = 0.05.
Table 10. Factor analysis of trace metals in PM$_{10}$.

| 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.

| 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 $\times$ 10$^{-8}$ | 9.628 $\times$ 10$^{-8}$ | 6.333 $\times$ 10$^{-7}$ | Adults: 1.48 $\times$ 10$^{-8}$ |
|          |                | 2.17 $\times$ 10$^{-8}$ | 2.888 $\times$ 10$^{-8}$ | 1.392 $\times$ 10$^{-7}$ | Children: 1.35 $\times$ 10$^{-8}$ |
| Co       | Cancer Risk    | 7.07 $\times$ 10$^{-7}$ | 7.933 $\times$ 10$^{-7}$ | 2.081 $\times$ 10$^{-6}$ | Adults: 2.42 $\times$ 10$^{-7}$ |
|          |                | 1.77 $\times$ 10$^{-7}$ | 4.549 $\times$ 10$^{-8}$ | 3.066 $\times$ 10$^{-8}$ | Children: 2.20 $\times$ 10$^{-7}$ |
| Cd       | Cancer Risk    | 3.62 $\times$ 10$^{-7}$ | 6.577 $\times$ 10$^{-8}$ | 3.114 $\times$ 10$^{-7}$ | Adults: 2.78 $\times$ 10$^{-8}$ |
|          |                | 4.05 $\times$ 10$^{-8}$ | 4.769 $\times$ 10$^{-8}$ | 2.312 $\times$ 10$^{-7}$ | Children: 2.53 $\times$ 10$^{-8}$ |
| Co       | Cancer Risk    | 2.10 $\times$ 10$^{-6}$ | 3.519 $\times$ 10$^{-7}$ | 1.442 $\times$ 10$^{-6}$ | Adults: 3.76 $\times$ 10$^{-8}$ |
|          |                | 4.75 $\times$ 10$^{-7}$ | 1.845 $\times$ 10$^{-8}$ | 4.403 $\times$ 10$^{-7}$ | Children: 3.42 $\times$ 10$^{-8}$ |
| Cd       | Cancer Risk    | 2.60 $\times$ 10$^{-7}$ | 4.844 $\times$ 10$^{-9}$ | 2.494 $\times$ 10$^{-7}$ | Adults: 2.74 $\times$ 10$^{-8}$ |
|          |                | 4.00 $\times$ 10$^{-8}$ | 2.992 $\times$ 10$^{-9}$ | 1.718 $\times$ 10$^{-7}$ | Children: 2.49 $\times$ 10$^{-8}$ |
| Co       | Cancer Risk    | 9.76 $\times$ 10$^{-7}$ | 2.558 $\times$ 10$^{-7}$ | 2.075 $\times$ 10$^{-6}$ | Adults: 3.34 $\times$ 10$^{-8}$ |
|          |                | 2.44 $\times$ 10$^{-7}$ | 1.486 $\times$ 10$^{-8}$ | 3.451 $\times$ 10$^{-7}$ | Children: 3.03 $\times$ 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.

| Chemical | Type of Result     | Median  | 5% Lower Confidence Limit | 95% Upper Confidence Limit | Age Group |
|----------|--------------------|---------|---------------------------|----------------------------|-----------|
|          | Cold Dry Season    |         |                           |                            |           |
| 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 PM$_{10}$ 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%).
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 PM$_{10}$ 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 Cu were below the acceptable level (1.00 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], Tijuana, Mexico [29] 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 for Algiers, Algeria [25] and Silesia, Poland [27]. 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].

**Table 13.** Comparison of PM$_{10}$ 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   |
|-----------------------|-----------|------|-----|-----|------|------|------|------|
| (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 | 2.479–4.690 | 0.744–1.933 | 0.03–0.09 |
| 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 [29] | 3.75–81.2 | 0.05–0.05 | 0.024–1.569 | 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 | 0.0002–0.21 | - | 0.013–0.09 | 0.180–1.635 | 0.001–0.363 | 0.134–0.431 |
| Tijuana, Mexico [29]  | 14.0–32.0 | 0.0003–0.012 | 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 | 0.0002–0.019 | 0.0002–0.006 | 0.019–0.461 | 0.326–5.850 | - | 0.0002–0.089 |
| Colima, Mexico [32]   | 14.9–78.5 | 0.0001–0.009 | - | 0.04–0.398 | 0.20–1.6 | 0.10–0.73 | 0.0007–0.573 | 0.0045–0.106 |
| Upper Silesia, Poland [27] | 8.0–157.0 | 0.0036–0.192 | - | 0.0223–1.550 | 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 PM$_{10}$ and its heavy metal content on the population of León City.

The results from SEM-EDS showed that the analyzed samples of PM$_{10}$ 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 PM$_{10}$ 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 have 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 PM$_{10}$.
- H3: meteorological parameters influenced the concentrations of heavy metals.
- H4: the heavy metal concentrations found pose a threat to the population of León.

PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM\textsubscript{10} 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 PM\textsubscript{10}. Such a policy would provide information on the spatial and temporal variation of PM\textsubscript{10}, 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 gravimetrical 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.I.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.

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