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Chemical Characterization and Assessment of Public Health Risk Due to Inhalation of $PM_{2.5}$ in the City of Salamanca, Gunaju

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Abstract

In this study, we conducted an analysis of health risks faced by residents of Salamanca, Mexico, who were exposed to fine particulate matter with a diameter of 2.5 µm ($PM_{2.5}$) through inhalation. The characterization and analysis of these particulate matter samples were undertaken. A total of 131 samples were collected from two different sites: 65 from the Red Cross site (RC) and 66 from the Integral Family Development site (DIF). These samples were analyzed for a set of chemical components, including metals and ions. Non-cancerous health risk levels associated with $PM_{2.5}$ exposure through the human respiratory system, as per the WHO benchmark (assigned a value of 1), revealed notable risk values for two elements: Manganese (Mn) with a range of 1.19-2.12 in the adult population and 1.59-2.84 in the child population, and Nickel (Ni) with a uniform risk value of 1.39 for both evaluated population groups. However, concerns arose regarding potential non-cancerous effects as the cumulative risk levels for various assessed elements showed elevated indices. These ranged from 3.81-4.4 in adults and 4.48-5.24 in children. This study provided comprehensive data on composition and its potential impact on human health, offering valuable insights for the implementation of mitigation measures aimed at reducing inhalation-related exposure.

Keywords: characterization; mitigation; cumulative risk; non-cancer health risk

Introduction

Certain human activities associated with industrial processes contribute to increased atmospheric pollution. These activities include construction, mining, disposal of industrial waste, handling and transportation of raw materials involving combustion processes or earthmoving and building renovation (Azarmi & Kumar, 2016; Fan & Wang, 2016; Ramírez et al., 2019; Takaoka et al., 2016). Such activities are prevalent in most urban environments (Motesaddi Zarandi et al., 2019; J. Sun & Zhou, 2017; Y. Sun et al., 2010; Viana et al., 2008). Atmospheric pollution results from a combination of various anthropogenic activities and natural conditions (Lippmann, 2012; M. Tian et al., 2021). Particulate Matter (hereafter referred to as PM), commonly found in the environment, consists of particles to which heavy metals such as chromium, cadmium, lead, zinc, manganese, and some metalloids like arsenic may adhere. These components can be quantified as part of particles (Kumar et al., 2014; Moreno-Ríos et al., 2022; Santibáñez-Andrade et al., 2017; H. Z. Tian et al., 2015). The concentration of these particles varies regionally and can be characterized by their origin or size. $PM_{2.5}$ and PM_{10} refer to particles with an aerodynamic diameter equal to or less than 2.5 and 10 µm, respectively (Perrino, 2010; USEPA, 1996). Significant PM sources include vehicular traffic, which generates precursor gases such as NOx, CO, and volatile organic compounds (Viana et al., 2007; Watson et al., 2001).

Additionally, meteorological factors, such as climate, temperature, wind speed, precipitation, humidity, radiation, geographical location, topography, land cover, and proximity to arid areas, influence the concentration and PM composition (Bayraktar et al., 2010; Minguillón et al., 2014; Schneider et al., 2015; Teixeira et al., 2009). Previous studies have focused on characterizing and determining variations in the behavior of PM2.5 particles in major urban areas worldwide (Amil et al., 2016; Das et al., 2015; Duarte et al., 2022; Kretzschmar, 1994; Pan et al., 2015; Tan et al., 2017). Elevated concentrations of PM in the environment have been linked to premature deaths (Buxton et al., 2020; Hannam et al., 2014; Hansen et al., 2006) and respiratory diseases, including asthma,

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chronic obstructive pulmonary diseases, and earth conditions (Goudarzi et al., 2018; Marabini et al., 2017; Sierra-Vargas et al., 2009; Smith, 2007). In the decade from 2010 to 2020, it has been documented those certain cities in the Mexican Republic exhibit elevated levels of air pollution (IQAir, 2018, 2020), such as the case of Salamanca, Guanajuato. This municipality has been classified as one of the most polluted sites in Mexico, where primary sources of pollution include fixed sources like chemical, petrochemical, and thermoelectric industries (Cortina–Januchs et al., 2015; Linares et al., 2010; Pham et al., 2008). Other contributing sources include fertilizer companies, the textile industry, metal processing, and food production (Herrera Murillo et al., 2012).

In 2003, the Mexican Petroleum Institute (IMP) published a study characterizing $PM_{2.5}$ in the city of Salamanca. The results revealed that particulate matter is composed of 40% organic carbon, 10% elemental carbon, 17% sulfates, 6% nitrates, 5% geological material (silica, oxides, aluminum, calcium, and iron silicates), 2% trace elements (heavy metals), and 20% unspecified compounds. The study describes the sources, indicating that PM_{10} is prevalent in unpaved streets and agricultural lands, while anthropogenic contributions to $PM_{2.5}$ primarily originate from combustion processes (Sosa Iglesias & Ortega López, 2004). Given the environmental challenges in this city, it is essential to conduct studies characterizing the chemical composition of $PM_{2.5}$ and establishing the relationship between potentially toxic chemical elements and the likelihood of adverse health effects through inhalation exposure. This study aims to characterize and assess the public health risk associated with exposure to atmospheric particles smaller than $PM_{2.5}$ in the city of Salamanca, Guanajuato.

Materials and Methods

Study Site and Location of Monitoring Stations

A quantitative study of particulate matter collected in 2014-2015 in the urban area of Salamanca, Mexico, was conducted based on the municipality's industrial activity history. Salamanca is in the central part of the state of Guanajuato, covering an area of 755.6 km^2 with a population of 160,682 people in the municipal seat (National Institute for Statistics and Geography, 2021). Situated at 1720 meters above sea level, the city experiences a semi-warm and slightly humid climate, with predominant rainfall from June to August. The annual average temperature is 19.3 °C, with high temperatures from April to June and low temperatures from December to February (Mexican National Meteorological System, 2010). For the location of monitoring stations, two points were selected: RC with UTM coordinates N 270788.95, E 2277078.44, and the offices of the DIF with UTM coordinates N 270142.61, E 2274808.19 (Figure 1). These were considered strategic and representative due to their proximity to main roads and significant pollutant sources in the urban area.

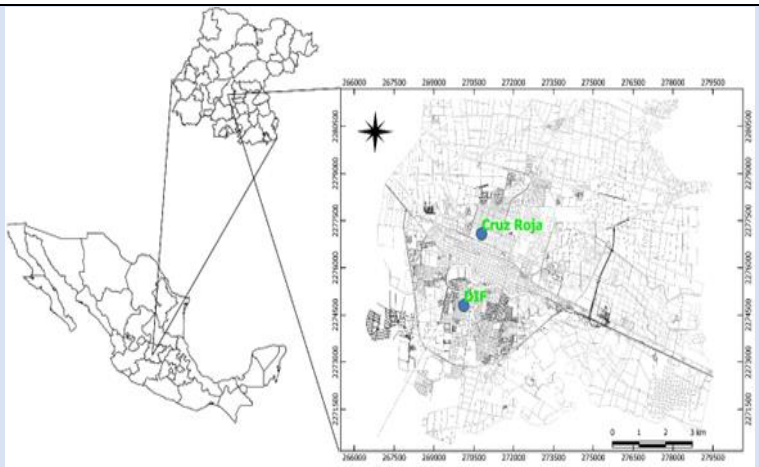

Figure 1: The location of the study area (monitoring stations) was georeferenced in UTM coordinates, map was created using QGIS 3.16.6 (Alkmaar, Netherlands).

Sample Collection

High-volume TISCH ENVIRONMENT samplers with an average flow rate of 68 m^3h^{-1} and a $PM_{2.5}$ head, based on the principle of inertial impaction to classify particles by the desired size, were used for sample collection. Sampling was conducted over 24 hours

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every 6 days, following the schedule of the National Air Quality Information System (SINAICA), with an air capacity of 1.3 m^3min^{-1}. A total of 65 filters were collected at the DIF station, and 66 filters at the station. Filters were stabilized before and after sampling at 22 ± 3°C and 40 ± 5% relative humidity for 24 hours (NOM-035-SEMARNAT-1993, 1993). Particles were collected on 8x10" quartz (SiO_2) filters from Whatman, known for high collection efficiency, inert character, and high purity.

Chemical Analysis of PM

The procedure for chemical characterization, considering the handling of particulate matter on the filter, followed the approach described by Campos and colleagues in their 2010 publication. Approximately 10% of the space impacted by particles on the quartz filter (approximately 150 cm^2) was cut and placed in test tubes. To this, 20 mL of HNO_3-HCl (2.5M-0.5M) was added. Ultrasonic extraction was performed using a Branson Model 5800 ultrasonic bath for 3 hours at a temperature of 60-70°C (Herrera Murillo et al., 2012), followed by centrifugation of the mineralized sample at 6000 revolutions per minute for 10 minutes using a Solbat J40 centrifuge.

Chemical identification was carried out using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies 7500CE). For quality control of the analytical procedure, a small amount (1 mg) of Standard Reference Material® 2706 New Jersey Soil was loaded to obtain recovery percentages. Table 1 shows the recovery data for each analyzed element. External calibration was used for quantification, with six levels of concentration of the multi-elemental standard for environmental samples (V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Ba, Tl, and Pb) in a calibration range of 0-100 mgL^{-1} for all elements.

For the soluble fraction, deionized water (Milli-Q) filtered in 50 mL of water in a tube was used. A 150 cm^2 filter fragment was introduced, and ultrasonic extraction was carried out for one hour. The obtained solution was analyzed by ion chromatography for the determination of Cl^{-1}, SO_4^{-2}, and NO_3^{-1}, and by Flow Injection Analysis (FIA) colorimetry for NH_4^+ on an ICnet METROOHM chromatograph. For quality control in the soluble fraction, blanks and tubes with fragments were used, employing the standard addition method to evaluate the recovery percentage. Table 1 presents the results obtained for the different evaluated anions and cations. External calibration was used for quantification, with concentrations of 0.39, 0.78, 1.56, 3.125, 6.25, 12.5, 25, and 50 μgmL^{-1} for Cl^{-1}, NO_3^{-1}, SO_4-2, Na^{+1}, NH_4^{+1}, and K^{+1}.

Table 1: Recovery percentages and detection limits for different elements, anions, and cations in the chemical characterization of particulate matter.

Analyte	SRM Recovery Percentage 2706	Limit of Detection (µg /m^3)
V	96.48 ± 6.14	0.106
Cr	95.93 ± 4.34	0.133
Mn	95.77 ± 3.69	0.013
Co	80.54 ± 0.11	N. F
Ni	52.02 ± 3.01	0.063
Cu	39.60 ± 2.86	0.084
Zn	105.61 ± 2.62	0.156
As	126.65 ± 1.15	0.096
Se	56.96 ± 0.61	0.126
Mo	91.16 ± 0.51	0.013
Cd	76.65 ± 0.40	0.001
Ba	61.44 ± 3.27	0.006
Tl	103.44 ± 0.01	0.002
Pb	60.82 ± 3.050	0.034
Na^{+1}	112.00 ± 15.71	0.002
NH_4^{+1}	92.98 ± 5.72	0.003
K^{+1}	148.59 ± 2.45	0.001
Ca^{+2}	96.48 ± 5.30	0.002
Cl^{-1}	112.40 ± 9.65	0.0005
$N0_3^{-1}$	87.35 ± 5.677	0.006
SO_4^{-2}	93.00 ± 1.038	0.011

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Exposure Assessment and Inhalation Risk Characterization

Risk analysis is employed to assess issues arising in the environment and human health due to the presence of potentially toxic substances, hazardous activities, and the management of toxic substances. The risk assessment method was conducted based on the procedures described by Peña et al. (2001) and the United States Environmental Protection Agency US EPA (2009). The methodology involves the following steps: risk identification, dose-response assessment, exposure assessment, risk characterization, and the development of regulatory options.

For the calculation of the exposure dose, the following formula was utilized:

$$\text{Exposition dose(mg/Kg/día)} = (C \times I \times r \times A \times F \times D)/(t \times W) \quad (1)$$

Where: C = concentration of the pollutant in the atmosphere (mg m^{-3}), I = rate of inhaled air ($m^3 day^{-1}$), r = retention rate for inhaled air, A = absorption rate of inhaled air, F = exposure frequency (days), D = exposure duration (years), t = average time, W = body weight.

The values used are listed in Table 2.

Regarding the calculation for risk assessment (R), the expression used is:

$$R = DE/RD \quad (2)$$

Where: DE = exposure dose (mg/kg/day), RD = reference dose (mg/kg/day) (Table 3), or the concentration of the pollutant and the Minimal Risk Levels (MRL) in the following expression:

$$R = C/MRL \quad (3)$$

Table 2: Reference Dose (RD) and Minimal Risk Level (MRL) values for risk calculation.

Element	RD (mg/kg/día)	MRL (mg/m^3)
V		1.00E-04
Cr	2.86E-05	3.00E-04
Mn	1.43E-05	3.00E-04
Co	5.00E-06	1.00E-04
Ni	2.00E-02	9.00E-05
Cu	1.00E-01	7.50E-02
Zn	3.00E-01	3.00E-01
As	3.00E-04	
Se	5.00E-03	
Mo	5.00E-03	
Cd		1.00E-05
Ba	2.00E-01	
Pb		5.00E-04

Results and Discussion

Chemical Characterization of Particulate Matter

The number of valid samples by Mexican environmental regulations (NOM-025-SSA1-2014) resulted in 57 filters for the RC monitoring station and 62 filters at the DIF site. In Table 4, concentrations of the analyzed chemical elements are presented, indicating the general behavior of average concentrations (µg m^{-3}) of soluble compounds. For both study sites, the order is the same: SO_4^{-2}>NH_4^{+1}>NO_3^{-1}>Ca^{+1}>K^{+1}>Na^{+1}>Cl^{-1}>NO_2^{-1}>Li^{+1} (µg m^{-3}). The soluble compound with the least occurrence in the sampling sites is NO_2^{-1}, present in 20 samples at the RC monitoring station and 31 samples at the DIF site. The ions with the highest presence and concentration are SO_4^{-2}, NH_4^{+1}, and NO_3^{-1}. Some studies analyzing soluble ions describe SO_4^{-2}, NH_4^{+1}, and NO_3^{-1} as the most representative in concentration (Gao et al., 2015; Liao et al., 2018; Peter et al., 2018).

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Table 3: Elemental Chemical Composition of PM2.5 at DIF and RC Station

	RC				DIF			
Element	N	Maximum (µg/m^3)	Medium (µg/m^3)	SD	N	Maximum (µg/m^3)	Medium (µg/m^3)	SD
Li^{+1}	57	0.007	0.005	0.001	62	0.006	0.005	0.001
Na^{+1}	57	0.563	0.065	0.070	62	0.505	0.080	0.074
NH_4^+	57	3.765	1.826	0.870	62	3.316	1.233	0.637
k^{+1}	57	0.715	0.244	0.153	62	1.229	0.254	0.207
Ca^{+2}	57	0.401	0.112	0.083	62	1.228	0.257	0.211
Cl^{-1}	51	0.511	0.031	0.083	57	0.955	0.048	0.135
NO_2^{-1}	20	0.049	0.011	0.013	31	0.134	0.021	0.028
NO_3^{-1}	57	3.502	0.283	0.507	62	2.918	0.384	0.511
SO_4^{-2}	57	10.287	5.901	2.656	62	9.454	4.181	1.845
V	57	5.480	2.473	0.949	62	8.600	3.959	1.861
Cr	57	3.690	1.368	0.433	62	6.580	1.421	0.732
Mn	57	7.060	1.348	1.093	62	6.880	2.409	1.355
Co	57	0.060	0.031	0.013	62	0.140	0.053	0.028
Ni	57	8.230	2.601	1.641	62	8.030	1.651	1.222
Cu	57	78.840	14.410	16.399	62	39.770	5.900	7.840
Zn	57	88.320	11.025	11.615	62	37.250	12.519	6.627
As	57	1.840	0.442	0.262	62	1.550	0.464	0.235
Se	53	1.030	0.378	0.181	59	0.960	0.383	0.174
Mo	57	2.010	0.774	0.598	62	2.130	0.663	0.493
Cd	56	0.270	0.067	0.055	62	0.250	0.075	0.054
Ba	57	7.410	2.069	1.363	62	7.770	2.710	1.469
Tl	34	0.020	0.011	0.002	39	0.020	0.012	0.004
Pb	57	16.450	1.543	2.224	62	7.280	1.758	1.298

The soluble compound SO_4^{-2} has the highest concentrations in the monitoring sites, with a maximum concentration of 10.287 µgm^{-3}. This value is lower than reported in the city of Xinxiang, where a $PM_{2.5}$ study was conducted in 2014, describing significant atmospheric pollution issues (Feng et al., 2017). The sulfate ion concentration is like the value (10.2 µgm^{-3}) reported by Matawle and colleagues in 2017 in an area with heavy industries, a characteristic shared by the city of Salamanca. The presence of SO_4^{-2} is described to originate from sulfur in fuel, oxidizing into sulfur oxides (Mukta et al., 2020; Wen et al., 2018).

The concentrations of potentially toxic elements for the RC site, in order of concentration levels, are Cu>Zn>Ni>V>Ba>Pb>Mn>Cr>Mo>As>Se>Cd>Co>Tl (µg m^{-3}). The DIF sampling site exhibited the following concentration behavior: Zn>Cu>V>Ba>Mn>Pb>Ni>Cr>Mo>As>Se>Cd>Tl>Co (µg m^{-3}). For the DIF station, the elements V, Mn, Cu, Zn, Ba, and Pb were identified in the 62 analyzed samples, while the RC station had V, Mn, Cu, Zn, and Ba identified in the 57 analyzed samples. The rest of the elements were found in a variable number of samples at both monitoring stations. Lead and vanadium are known to be released into the environment during combustion processes and are considered byproducts of the refining process of certain hydrocarbons (Hassanvand et al., 2015; Hernandez & Rodriguez, 2012; Schauer, 2006). Copper is currently a heavily studied element due to its strong association with anthropogenic activities. Its presence in the urban environment is attributed to high levels of vehicular traffic and the wear of certain automotive parts, contributing to its presence in atmospheric particles (Hulskotte et al., 2007; Izydorczyk et al., 2021; Straffelini et al., 2015).

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Table 4: Average concentration (µg/m3) of potentially toxic elements (PTE) in $PM_{2.5}$ particulate matter from studies conducted in different cities around the world.

Element	Salamanca, Mexico		Shandong China	Tianjin China	Hong Kong China	Chennai India	Jeddah Saudi Arabia	Tehran Iran
	DIF	RC						
V (µg/m^3)	2.47±0.94	3.95±1.86	0.007		0.011	0.001	0.013	0.051
Cr (µg/m^3)	1.37±0.43	1.42±0.73	0.02	0.035	0.002	0.058	0.001	2.19
Mn (µg/m^3)	1.35±1.09	2.40±1.35	0.09	0.065	0.019	0.015	0.01	1.07
Co (µg/m^3)	0.03±0.01	0.05±0.02	0.014	0.006				
Ni (µg/m^3)	2.60±1.64	1.65±1.22	0.009	0.017	0.005	0.132	0.004	1.03
Cu (µg/m^3)	14.41±16.4	5.90±7.84	0.03		0.043	0.005		1.25
Zn (µg/m^3)	11.02±11.62	12.51±6.62	0.07	0.573	0.177	0.219		3.09
As (µg/m^3)	0.44±0.26	0.46±0.23	0.02	0.02	0.004	0.021	0.008	2.31
Se (µg/m^3)	0.38±0.18	0.38±0.17	0.02			0.017		
Mo (µg/m^3)	0.77±0.60	0.66±0.49						
Cd (µg/m^3)	0.07±0.05	0.07±0.05	0.017	0.003	0.001	0.016	0.01	0.76
Ba (µg/m^3)	2.07±1.36	2.71±1.46	0.07		0.019	0.039		
Tl (µg/m^3)	0.01±0.002	0.01±0.004						
Pb (µg/m^3)	1.54±2.22	1.75±1.29	0.31	0.144	0.054	0.008	0.25	1.58
Reference	Present study		(J. Zhang et al., 2018)	(Zhang et al., 2015)	(Liao et al., 2018)	(Peter et al., 2018)	(Harrison et al., 2017)	(Kermani et al., 2018)

Table 5 presents data from studies conducted on $PM_{2.5}$ in different cities worldwide. The concentrations found in this study exceed those reported in various studies. Only the data from the study conducted in Tehran, Iran, show concentrations of Cr, As, Cd, and Pb that are higher than those found in the city of Salamanca, Guanajuato.

Health Risk Analysis for Potentially Toxic Elements (PTEs) in PM2.5 Particulate Matter

The calculated risk, when assessing individual elements in the chemical composition of $PM_{2.5}$ in the city of Salamanca, is presented in Table 6. In the risk levels of exposure to non-carcinogenic heavy metals through the respiratory system, for most of these elements, the risk is less than 1. This value is described in the guidelines by the Agency for Toxic Substances and Disease Registry (ATSDR) (2016), stating that some adverse health effects may occur above this value. There are only two elements in the two monitoring stations that exceed this level, which are Ni and Mn. Ni exceeds the level of 1 in the adult and children population groups at the DIF monitoring station, while in the results from the RC monitoring point, both Mn and Ni had values greater than 1 in both population groups. In a study conducted in central India in areas described with the presence of heavy industries, a characteristic like the city of Salamanca, Ni, and Mn levels are lower ($2.46x10^{-1}$ for Ni and 3.32×10^{-1} for Mn) than those found in the present study. The study from India reports levels exceeding 1 for other elements such as Cd, Co, and Cr (Matawle et al., 2017).

When comparing the results found in Salamanca with risk levels from $PM_{2.5}$ in Xinxiang, a city described as urbanized and located 2 km away from industrial pollution, the Mexican city's risk levels are higher. For example, the risk levels for Cr are $1.58x10^{-1}$ in children and $8.93x10^{-2}$ in adults, and the Mn risk level is $1.92x10^{-1}$ in children and $1.08x10^{-1}$ in adults (Feng et al., 2017). Considering the total risk for each group and at each station, it can be observed that the value is still greater than 1. This indicates that the exposed population is at potential risk of experiencing some effects caused by the evaluated elements, as mentioned by the Agency for Toxic Substances and Disease Registry (ATSDR, 2004), including hepatic, hematological, and neural effects, which are part of the elemental chemical composition of suspended particles with an aerodynamic diameter of 2.5 µm.

Conclusion

Regarding the chemical characterization, 21 soluble and elemental components were identified, highlighting the presence of soluble compounds such as SO_4^{-2} and NH_4^{+1}, with elements such as Cu and Zn also standing out. Since all the analyzed elements are present in the total $PM_{2.5}$ particulate matter, the risk could increase, potentially generating a combination of these elements and, through synergy, increasing the

total risk compared to individual risks. The child population showed a higher risk (5.24 DIF and 4.48 RC), as the total risk values are higher compared to adults (4.40 DIF and 3.81 RC). Therefore, it is concluded that the child population is the most sensitive and vulnerable sector, and efforts should be made to reduce their exposure to PM2.5 particulate matter. The risk has been calculated only for the main inhalation route, and calculating for other routes by summing each corresponding value for the exposure route could reveal an overall increased total risk. It is expected that this study will serve as support for further environmental pollution studies in the city of Salamanca, providing a broader perspective on pollution regulation.

Declarations

Funding

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Conflicts of interest

The authors declare not competing interests

Availability of data and material

The creation of tables and databases was carried out which are available upon request for anyone who requests it.

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