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Sources of Risk to the Health of the Population, by Inhalation of PM_{2.5} in the Toluca Valley, Mexico

Fuentes de riesgo a la salud de la población, por inhalación de PM_{2.5} en el Valle de Toluca, México

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Abstract:

Introduction: PM_{2.5} air pollution causes death and morbidity in populations, 4.2 million premature deaths have been reported worldwide per year and can cause cardiovascular, respiratory, cancer, among other diseases. As a result, it is important to know the sources that produce them. **Objective:** Determine the possible Sources of Risk (SR) to health, by inhalation of Elemental Chemical Composition (EQC) obtained from PM_{2.5} samples in the Toluca Valley (TV). **Method:** Sampling was carried out (26/11/16-14/03/18) in San Mateo Atenco, Ceberuco, Nueva Oxtotitlán, San Lorenzo Tepaltitlán, Zinacantepec and San Cristóbal Huichochitlán, using medium volume equipment every six days for 24 hours. It was calculated: gravimetry, analysis by atomic technique PIXE (Proton Induced X-Ray Emission) to obtain the EQC. The emission sources were determined with multivariate analysis, the elemental risk for three sensitive classes of the population and their possible sources of risk. **Results:** The SRs determined: Dust-Soil, Industry, Hydrocarbons, Vehicle, Burn-Fuels, Fine Gravimetric Mass, Coal burning, Metallurgy and Sulphates. **Discussion:** The SRs with the highest values, for sensitive populations, were Industry and Dust-Soil, this as a consequence of the large number of existing industries that produce EQC. **Conclusion:** The risks of inhalation of EQC present in PM_{2.5} for sampling sites were high, because of this there is a high probability of contracting some diseases that can be caused by EQC. The risk determined for sources in the ZMTV, to date, does not exist in similar research in the literature.

Keywords: PIXE; Multivariate analysis, Source; Emission; Risk; Mexico; ZMVT

Introduction

In recent years, environmental problems such as air pollution have been growing steadily and the population has become aware of the current risks. It is estimated that environmental air pollution, both in cities and rural areas, was the cause of 4.2 million premature deaths worldwide per year; this mortality has been associated with exposure to PM_{2.5} particles (particles with aerodynamic diameter less than or equal to 2.5 µm), which are related to the development of cardiovascular diseases,

respiratory diseases and cancer (WHO 2018).

In our country, the General Law of Ecological Balance and Environmental Protection, in its latest reform published DOF 18-01-2021, defines pollution as the presence in the environment of one or more pollutants or any combination of them that causes ecological imbalance and environmental contingency as a risk situation, derived from human activities or natural phenomena, which may endanger the integrity of one or more ecosystems (DOF 2021).

The NOM (Norma Oficial Mexicana) NOM-025-SSA1-2014, referring to environmental health, assigns permissible limit values for the Fine Gravimetric Mass (MGF) of PM_{2.5} in ambient air, for purposes of protecting the health of the most vulnerable population and establishes reference values of 45 µg/m³, as a 24-hour average and 12 µg/m³, as an annual average (SEGOB 2014). The National Environmental and Natural Resources Information System (SNIARN 2018) reported that the most severe case of air pollution with these particles occurred in the ZMVT, in 2016, where the annual concentration recorded was 43 µg/m³, that is, more than three times the allowed annual value.

The volume and characteristics of pollutants emitted into the atmosphere, both locally and regionally, determine the air quality in a particular area. However, climatic and geographic characteristics also influence the concentrations and permanence of pollutants in the air, to which populations are exposed (SNIARN 2018).

In the search to control emissions of pollutants in the atmosphere, which is reflected in the impact on population health by affecting chronic diseases due to poor air quality, it is necessary to perform an analysis of emission sources to identify the contribution of pollutants. Emission sources are grouped based on the type of origin (SEMARNAT 2016): stationary sources (industries), mobile sources (gasoline or diesel motor vehicles), area sources (stores, services, homes) and natural sources (soil erosion and biogenic emissions, among others).

The ZMVT is the second most important conurbation in the State of Mexico after the Metropolitan Zone of the Cuautitlán-Texcoco Valley. It is considered one of the most important towns in the central region of Mexico. It is of great industrial, commercial and service importance. Around 2,347,692 inhabitants live in this metropolis (COESPO 2019). Currently this urbe grew from 14 municipalities (2005) to 22 municipalities (2021) and consequently resulted in an increase in the demand for public services, transportation and housing. In most cases, the main source of energy, after electricity, is the combustion of fossil fuels. In addition to combustion, there are other activities that generate emissions into the atmosphere, such as the use of solvents, paint application, street paving and asphaltting, fuel storage and distribution, and even some natural phenomena such as soil erosion and plant metabolism (SMAGEM 2007).

The Management Program to Improve Air Quality in the State of Mexico (ProAire 2018), conducted emissions inventories, including sources that emit PM_{2.5}. Table 1 presents emissions data for different types of sources.

Table 1. Inventory of PM_{2.5} emissions in the ZMVT, from 2016 (ProAire 2018)

PM_{2.5} Emission Sources	
Source Type	Tons / year
Stationary sources	442
Area sources	4,271
Mobile sources	502
Total	5,216

Table 1 shows that there are high levels of emissions, which represent a high risk to the health of the

population. Measuring exposure to air pollution and the numerous environmental factors that influence it is complex because there are no adequate health information and monitoring systems to assess the magnitude and severity of the risks. With the objective of contributing to the evaluation of health risk in this study, the CQE of PM_{2.5} was determined, the health risk due to inhalation of the elements that constitute its composition was calculated in the sensitive age groups of the population, and the health risk caused by each type of source. It should be noted that the CQE is not routinely determined by the country's atmospheric monitoring networks and therefore neither is the health risk estimated for each element, nor the risk caused by each source.

Materials and Methods

Study site selection

For the selection of the monitoring site, the USEPA reference codes were considered (USEPA, 2012). Within which the following criteria were considered to locate the monitoring site:

1. Be representative of the area in which they are located.
2. Provide data comparable with other stations.
3. Be useful for at least the entire time period of the study.
4. Be permanently accessible.
5. Have reliable electrical power.
6. Be conditioned to withstand extreme temperature conditions.
7. Free of trees and buildings (recommended free radius of 10 m. around the sampling site).
8. 20 m. distance from the sampling site to industrial, commercial or mobile emissions sources is recommended.
9. Sampling height of 2 to 15 meters.

Under these criteria, the following study sites were selected: San Mateo Atenco (SM), Ceboruco (CB), Nueva Oxtotitlán (NO), San Lorenzo Tepaltitlán (SL), Zinacantepec (ZN) and San Cristóbal Huichochitlán (SC).

Sampling campaign

The sampling campaign was conducted under the following characteristics: the sample collection period was from November 26, 2016 to March 14, 2018 with a sampling frequency of every six days, for 24 hours each sample. Filters of 47 mm diameter and pore size of 0.4 micrometers (Nucleopore, # WHA111137) were used for PM_{2.5}. The sampling method was active, using low volume equipment model ECHO PM TCR TECORA (flow 16 l/min) and OMNI BGI (flow 7 l/min).

Fine Gravimetric Mass Analysis

A high-precision analytical balance, Mettler Toledo M5 series No. 11441 (Mettler 2008), was required to determine the amount of matter deposited on the filters. Calculations of the PM_{2.5} concentration in ambient air were performed using the following expression:

$$MGF = \frac{mf - mi}{Vt} = \mu g/m^3$$

Where:

MGF: Concentration of PM_{2.5} in air

mf: Final mass in the filter (μg)

mi: Initial mass in the filter (μg)

Vt: Total volume (m^3)

Elemental Chemical Composition Analysis

The Chemical Elemental Composition (CQE) was determined using the atomic technique called PIXE. The experimental characteristics were:

- Calibration of the PIXE system was performed using high purity MicromatterTM brand standards, (Al, S, K, Ca Ti, V, Cr, Mn, Fe, Co, Ni Cu Zn, Br and Pb), using the same experimental conditions with which the samples were irradiated.
- 12 MV Van de Graaff Tandem Accelerator (Figure 1).
- Ion: Proton
- Beam energy (E): 2.5 MeV
- Beam current (I): 10.0 nA
- Charge on filter (Q): 4.0 μC
- Ge-Li detector with a resolution of 180 eV
- Software for X-Ray Characteristic Spectra analysis: GUPIXWIN

Figure 1. Experimental set-up at the ININ Van de Graaff Tandem Accelerator

From the characteristic X-Ray spectrum generated and the adjustments made with the GUPIXWIN software, the X-Ray yield (N_x) was calculated for each of the elements present in the sample.

The elemental chemical concentration $c(Z)$ present in the sample is proportional to the number of detected X-rays (N_x) and inversely proportional to the charge supplied to the sample, i.e:

$$c(Z) = [N_x / (Y_R Q)] \dots (1)$$

Where:

Q = Is the load supplied to the sample during irradiation.

Y_R= is the response factor involving physical fundamentals of the experimental setup.

With:

$$Y_R = (\Omega/4\pi) \sigma_x \xi T (1/q) \dots (2)$$

Where:

Ω= Solid Angle of the detector.

σ_x= Shock cross section for X-Ray production.

ξ= Efficiency of the detector.

T=Transmittance

q= Charge due to the incident particle.

This response factor (Y_R) is obtained for each element, with the calibration of the system (Folkmann 1975), so using equations 1 and 2 the expression 3 is obtained, with which it is possible to calculate the concentration of the elemental chemical composition of the sample in µg/m³.

$$C(Z) = c(Z) [S / V] \dots (3)$$

C(Z)= Elemental chemical concentration of the sample (µg/m³)

c(Z)= Areal concentration of the sample on the filter (µg/cm²).

S= Filter area (cm²).

V= Sampled volume (m³).

Determination of emission sources

For the identification of possible emission sources in this research, statistical tools such as multivariate techniques were used.

The sequence followed for the identification was carried out according to Jhonson and Wichern (1992) and consisted of the following steps:

1. Calculate the correlation matrix between variables. The correlation matrix was calculated using SPSS version 22 software.
2. Apply extraction method. With the same software, the extraction of factors was performed using the rectangular components method. This analysis considers n quantitative variables and mixes them by means of linear combinations reducing to p < n variables that summarize the information facilitating its interpretation.
3. Apply transformation method. The method used to transform, to rotate the matrix, was VARIMAX established by Kaiser 1958, based on the criterion of maximizing the variance of the loadings of each component. To do this, it takes the total variance associated with the retained and unrotated components and redistributes it through the new rotated VARIMAX components. The same software was also used for this rotation.
4. Determine the number of significant factors. The most significant components were defined and selected. For this purpose, the components with the highest total variance explained (greater than 70%) were considered.

The data handled through this sequence were subjected to statistical criteria such as the Kaiser-Meyer-Olkin (KMO) and Bartlett's test, which showed that the statistical significance of the data structure is appropriate.

Elemental Chemical Composition Risk

For risk calculation, it is essential to have the Exposure Dose (ED), Exposure Factors (EF) and Reference Dose (RD).

Exposure Dose

For the calculation of Exposure Dose, according to the sources Peña et al. (2001), CEPIS and PAHO (1997), ATSDR (2018) and USEPA (2016), the elemental concentrations obtained for the elements, whose reference dose was found in the literature were used: S, Cl, Ti, V, Cr, Mn, Ni, Cu, Zn, and Pb, obtained through the PIXE technique, as well as the exposure factors shown in Table 2, taken from USEPA (1997).

Table 2. Parameters for exposure dose analysis

Parameter	Children 2-6 years	Children 6-12 years	Adults 70 Years
Average body weight (kg)	16	29	70
Inhaled Air Rate (m ³ /day)	6.0	11.04	19.92
Retention Rate for inhaled air	1	1	1
Inhaled Air Absorption Rate	1	1	1
Frequency of Exposure (days)	365	365	365
Duration of the Exhibition (years)	4	6	30
Average Time (days)	1460	2190	25550

The exposure dose is calculated using the expression:

$$\text{Exposure dose (mg/kg/día)} = \frac{C \times TI \times TR \times FE \times DE}{TP \times PC}$$

Where:

C= Concentration of the pollutant in the medium (mg/m³)

TI= Inhaled Air Rate (m³/day)

TR= Retention Rate for inhaled air

TA= Absorption Rate of inhaled air

FE= Frequency of Exposure (days)

DE= Duration of Exposure (years)

TP= Averaging Time (days)

PC= Average Body Weight (kg)

The data obtained for the Exposure Dose for the three age groups are presented in the results section.

Elemental Chemical Composition Risk Calculation

Con la Dosis de Exposición calculada como se indica en la sección anterior y la Dosis de Referencia (DR) y/o Mínimo Nivel de Riesgo (MNR) obtenida de las referencias ATSDR (2018), EPA (2017), se calculó el riesgo elemental de las PM_{2.5} utilizando la siguiente expresión:

$$\text{Risk} = \frac{\text{Exposure Dose (mg / kg / día)}}{\text{Reference Dose (mg / kg / día)}}$$

or the concentration of the contaminant of the contaminant and the MNR in the expression:

$$\text{Risk} = \frac{\text{Pollutant concentration (mg/m}^3\text{)}}{\text{Minimum Risk Level (mg/m}^3\text{)}}$$

With the two previous formulas it is concluded that values greater than or equal to 1 indicate the presence

or existence of risk and values less than 1 indicate the non-existence of risk.

Identification of risk sources

In order to determine the sources of risk to health by inhalation of PM_{2.5}, the emission sources obtained in accordance with the previous section, determination of emission sources, were considered, assigning the elemental risk to each of the elements present in the source. These results are presented in the corresponding section.

Results and discussions

Monitoring

The monitoring was carried out in the ZMVT, which is made up of 22 municipalities, covering an area of 2,669 km², which corresponds to 11.9% of the state territory. The average altitude of the municipalities is 2,610 meters above sea level, with a range from 2,560 to 2,740 meters above sea level. It has 2 million 347 thousand 692 inhabitants, as of 2019 (COESPO 2019). The selected sites are SM, CB, NO, SL, ZN and SC, as shown in Figure 2.

Figure 2. Selected monitoring sites in the ZMVT

Table 3 shows the coordinates of the sampling sites.

Table 3. Coordinates of the sampling sites in the ZMVT (RAMA 2021)

Site	Latitude North	Longitude West
SM ^a	19° 16' 49.5''	99° 32' 30.0''
CB ^b	19° 15' 37.1''	99° 38' 44.6''
NO ^c	19° 17' 0.40''	99° 41' 0.56''
SL ^d	19° 19' 2.0''	99° 37' 18.0''
ZN ^e	19° 17' 07.5''	99° 44' 07.1''
SC ^f	19° 19' 38.0''	99° 38' 3.44''

^aSM (San Mateo Atenco), ^bCB (Ceboruco), ^c(Nueva Oxtotitlán), ^dSC (San Cristóbal Huichochitlán), ^eSL (San Lorenzo Tepaltitlán), ^f ZN (Zinacantepec)

Sampling campaign

The sampling campaign was carried out under the characteristics described in the methodology.

Fine Gravimetric Mass Analysis

Table 4 shows the results of FGM obtained from the samples collected in the selected sites of the ZMVT; the maximum, average and standard deviation values are presented in units of $\mu\text{g}/\text{m}^3$.

Table 4. Estadísticos descriptivos de la MGF, para las muestras de la ZMVT

Sampling Site	N	Maximum $\mu\text{g}/\text{m}^3$	Average $\mu\text{g}/\text{m}^3$	Standard Deviation
SM	79	69	34	15
CB	79	178	47	22
NO	79	425	39	66
SL	79	583	71	106
ZN	79	109	39	19
SC	79	1070	75	149

The maximum values, as shown in Table 4, in CB, NO, SC and SL, correspond to values obtained on December 25 and January 1, 2016-2017, repeating high values for 2017-2018, corresponding to Christmas and New Year. Days that usually have bonfires, burning tires and wood (December 25) and in addition to these, fireworks (January 1). The six study sites exceeded the maximum permissible limits which is $12 \mu\text{g}/\text{m}^3$ (DOF, 2014) as an annual average. The minimum value for SM exceeded it 2.8 times and the maximum value for SC exceeded it 6.2 times. These values indicate the degree of risk in the ZMVT, without considering the CQE.

Elemental Chemical Composition Analysis

This section shows the results obtained, by PIXE, for the CQE of $\text{PM}_{2.5}$ in the ZMVT, Table 5 presents their descriptive statistics.

Table 5. Elemental Chemical Composition obtained by particle-induced X-ray emission

Z	N	SM		CB		NO		SC		SL		ZN	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
		ng/m³											
Phosphorus (P)	79	790	3020	4394	35413	3172	17444	11468	52194	11811	67932	1150	7302
Sulfur (S)	79	1310	1619	1164	1003	1278	1708	2412	8096	2086	3270	1210	1547
Chlorine (Cl)	79	939	4105	199	223	1133	5251	3385	13591	2331	10186	222	280
Potassium (K)	79	1079	4634	521	681	1340	5239	3817	15407	2298	8278	468	630
Calcium (Ca)	79	265	541	885	1644	356	1534	514	2231	1349	4019	791	1799
Titanium (Ti)	79	45	163	62	188	187	1135	193	1274	409	2563	65	147
Vanadium (V)	79	8	21	5	14	6	11	7	20	9	28	6	18
Chromium (Cr)	79	16	62	12	27	64	327	37	275	243	1536	26	78
Manganese (Mn)	79	35	95	10	20	133	600	76	368	78	359	50	267
Iron (Fe)	79	302	615	542	506	293	999	445	1622	796	2049	488	552
Cobalt (Co)	79	16	63	5	33	26	222	33	235	94	833	106	795
Nickel (Ni)	79	89	305	109	578	169	957	148	1006	261	1566	184	1366
Copper (Cu)	79	30	110	283	1991	12	63	46	224	22	56	215	1381
Zinc (Zn)	79	190	314	182	971	149	1158	71	241	533	2745	277	1175
Yttrium (Y)	79	39	240	137	627	53	248	57	290	365	1240	309	1127
Lead (Pb)	79	79	182	24	121	804	6950	362	2263	2300	19736	4	28

Risk Determination

Elemental Chemical Composition Risk

Table 6 presents the estimated risks for inhalation of PM_{2.5} composition. It is observed that there is an increased health risk from exposure of PM_{2.5} content of contracting any disease related to the elements: Cl, Ti, Cr, Mn and Pb for the inhalation exposure route and for the sensitive classes of the population considered. These elements present a health risk by this route of entry and most of them are very high risk, for example: Chlorine for SC (children 6-12 years old), Titanium for NO (adults and children), Chromium for SL (children 6-12 years old), Manganese for NO (children 6-12 years old) and Lead for SC (adults and children). From these results it is observed that the most affected sensitive classes of the population are for adults and children 6-12 years old and the highest risk sites are SC and SL. Individually, there is no possibility of contracting any disease as a consequence of exposure to the elements S, V, Ni, Cu, Zn and MGF, which are the elements that are presented with the lowest risk value (<1), however, exposure to these elements is as a whole, therefore, we do not rule out that the individual effects may interact in synergy.

Table 6. Relationship of health risk values for CQE inhalation, present in PM_{2.5} in the six sites of the ZMVT

Elements	NO			SC			CB		
	Children 2-6 years	Children 6-12 years	Adults 70 años	Children 2-6 years	Children 6-12 years	Adults 70 años	Children 2-6 years	Children 6-12 years	Adults 70 years
	R= DE/DR			R= DE/DR			R= DE/DR		
S	0.394	0.4	0.128	0.663	0.673	0.216	0.167	0.17	0.054
Cl	137.004	139.083	44.557	363.109	368.618	118.092	6.11	6.203	1.987
Ti	31.706	31.706	31.706	15.644	15.644	15.644	3.654	3.654	3.654
V	0.002	0.002	0.001	0.004	0.004	0.001	0.003	0.003	0.001
Cr	14.092	14.306	4.583	1.213	1.231	0.394	0.621	0.63	0.202
Mn	73.598	74.715	23.936	25.914	26.307	8.428	1.857	1.885	0.604
Ni	0.059	0.06	0.019	0.023	0.023	0.007	0.037	0.037	0.012
Cu	0.002	0.002	0.002	0.005	0.005	0.005	0.027	0.027	0.027
Zn	0.0003	0.0003	0.0001	0.001	0.001	0.0003	0.002	0.002	0.001
Pb	20.316	20.316	20.316	106.64	106.64	106.64	15.181	15.181	15.181
MGF	0.014	0.014	0.014	0.018	0.018	0.018	0.002	0.002	0.002
Riesgo Total	277.188	280.604	125.263	513.233	519.164	249.445	27.66	27.794	21.724

Elements	ZN			SL			SM		
	Children 2-6 years	Children 6-12 years	Adults 70 años	Children 2-6 years	Children 6-12 years	Adults 70 años	Children 2-6 years	Children 6-12 years	Adults 70 años
	R= DE/DR			R= DE/DR			R= DE/DR		
S	0.253	0.257	0.082	0.733	0.744	0.238	0.313	0.318	0.102
Cl	4.746	4.818	1.544	255.297	259.171	83.029	88.945	90.295	28.927
Ti	6.731	6.731	6.731	29.686	29.686	29.686	3.906	3.906	3.906
V	0.002	0.002	0.001	0.005	0.005	0.002	0.005	0.005	0.002
Cr	3.684	3.74	1.198	32.554	33.048	10.587	1.223	1.242	0.398
Mn	16.853	17.109	5.481	27.455	27.871	8.929	8.797	8.93	2.861
Ni	0.019	0.019	0.006	0.072	0.073	0.023	0.025	0.025	0.008
Cu	0.029	0.029	0.029	0.002	0.002	0.002	0.007	0.007	0.007
Zn	0.005	0.006	0.002	0.008	0.008	0.003	0.002	0.002	0.001
Pb	1.292	1.292	1.292	61.119	61.119	61.119	17.191	17.191	17.191
MGF	0.002	0.002	0.002	0.012	0.012	0.012	0.001	0.001	0.001
Riesgo Total	33.617	34.005	16.368	406.944	411.74	193.631	120.415	121.922	53.403

As a result of the calculations for the inhalation risk of CQE present in PM_{2.5} in the ZMVT, for the vulnerable populations, Table 7 presents the summary of the total risks of the same.

Table 7. Summary of CQE inhalation hazards in the ZMVT

(Totals) Site	Children 2-6 years	Children 6-12 years	Adults 70 years
SM	120.41	121.92	53.40
CB	27.66	27.79	21.71
NO	277.17	280.59	125.25
SL	406.93	411.73	193.62
ZN	33.62	34.00	16.37
SC	513.21	519.15	249.43

Determination of Emission Sources

Statistical tools such as multivariate techniques were used to identify possible emission sources in this investigation. Tables 8 to 13 show the results obtained.

Table 8 shows that the rotated matrix of the data (VARIMAX) results in three significant components, which were associated with soil dust, hydrocarbons and sulfates. The principal component analysis shows that these three components explain 97.4 % of the variability of the data.

The association of the elements Ca, Ti, Cu, Mn, Cr, K, Ni, Cl and Fe, to determine the source of Soil Dust are in agreement with those found by Almeida et al. (2020) in Europe and Central Asia, Alvarez and Suarez (2020) in Peru and Rojas et al. (1990) in Santiago de Chile. The source of Hydrocarbons, FGM, V and Zn, agreed with Banerjee et al. (2015) in India and Rojas et al. (1990). The sulfate factor composed of Pb and S, agreed with Rojas et al. (1990).

Table 8. Emission sources obtained for PM_{2.5} from SM site

Element	Soil dust	Hydrocarbons	Sulfates	Community	% Variance	% Cumulative
Ca	0.990			0.990	64.907	64.907
Ti	0.986			0.988		
Cu	0.982			0.955		
Mn	0.980			0.980		
Cr	0.978			0.999		
K	0.977			1.000		
Ni	0.975			0.908		
Cl	0.906			0.999		
Fe	0.903			1.000		
MGF		0.976		1.000	18.076	82.983
V		-0.922		1.000		
Zn		-0.739		0.998		
Pb			0.954	0.902	14.431	97.414
S			0.768	0.920		

Table 9, corresponding to BC, shows the possible emission sources obtained, where it is observed that the rotated matrix of the data (VARIMAX) results in three significant components, which were associated with Soil Dust, Metallurgy and Fuel Burning. The principal component analysis shows that these three components explain 83.04% of the variability of the data.

The elements Ca, Fe, Ti, Zn and Cr, are associated with the source Soil dust and agree with what was reported by Almeida et al. (2020) and Owoade et al. (2015). The K, Cl and MGF corresponding to the Metallurgy source agree with that reported by Owoade et al. (2015) in Nigeria. The S and Mn elements associated with the Fuel Burning source agree with Banerjee et al. (2015).

Table 9. Emission sources obtained for PM_{2.5} from the BC site

Element	Soil dust	Metallurgy	Fuel burning	Community	% Variance	% Cumulative
Ca	0.966			0.939	38.350	38.350
Fe	0.932			0.888		
Ti	0.905			0.906		
Zn	0.697			0.830		
Cr	0.668			0.934		
K		0.933		0.823	22.795	61.145
Cl		0.884		0.798		
MGF		0.592		0.684		
S			0.916	0.911	21.897	83.042
Mn			0.719	0.592		

At the NO site, the possible emission sources were obtained, Table 10 shows that the rotated matrix of the data (VARIMAX) results in three significant components, which were associated with Industry, Coal Burning and Soil Dust. In the principal component analysis these three explain 100 % of the variability of the data.

The Ni, V, Zn, Cr and Mn elements corresponding to the Industry source agree with those reported by Banerjee et al. (2015). The coal burning source (Cl, FGM, S, Fe) agrees with that reported by Owoade et al. (2015). K and Ca were assigned to the Soil Dust source and agrees with that reported by Alvarez and Suarez (2020).

Table 10. Emission sources obtained for PM_{2.5} from the NO

Element	Industry	Coal burning	Soil dust	Community	% Variance	% Cumulative
Ni	0.984			1.000	43.460	43.460
V	0.971			1.000		
Zn	0.899			1.000		
Cr	0.853			1.000		
Mn	0.823			1.000		
Cl		0.999		1.000	32.069	75.529
MGF		-0.985		1.000		
S		-0.763		1.000		
Fe		0.700		1.000		
K			0.989	1.000	24.471	100.000
Ca			0.846	1.000		

In SL, Table 11 shows the possible emission sources and it is observed that the rotated matrix of the data (VARIMAX) results in three significant components, which were associated with Industry, Soil Dust and Vehicular. The principal component analysis shows that these three components explain 100% of the variability of the data.

The source associated with Soil Dust with the elements Fe, V, Ca, S, Cr and Ti, coincides with that related by Almeida et al. (2020) and Owoade et al. (2015). The elements Cl, Mn, K and Zn being associated with

the Metallurgy source, agrees with Owoade et al. (2015). Cu and MGF were associated with the Vehicular source and is in agreement with Banerjee et al. (2015).

Table 11. Emission sources obtained for PM_{2.5} from the SL site.

Element	Soil dust	Metallurgy	Vehicular	Community	% Variance	% Cumulative
Fe	0.952			1.000	41.600	41.600
V	0.888			1.000		
Ca	0.852			1.000		
S	0.850			1.000		
Cr	0.839			1.000		
Ti	0.819			1.000		
Cl		0.994		1.000	37.765	79.365
Mn		0.993		1.000		
K		0.977		1.000		
Zn		0.792		1.000		
Cu			0.889	1.000	20.635	100.000
MGF			0.876	1.000		

In ZN, Table 12, results in three significant components, which were associated with Soil Dust, Vehicular and FGM. The principal component analysis shows that these three components explain 100% of the variability of the data.

The Soil Dust source was associated with the elements Fe, Zn, Ti, Cl and Ca, which are in agreement with Almeida et al. (2020) and SDA (2009). THE source assigned as Vehicular (Cr, Mn, K, S) agrees with Owoade et al. (2015). FGM indicates another source.

Table 12. Emission sources obtained for PM_{2.5} from the ZN site

Element	Soil dust	Vehicular	MGF	Community	% Variance	% Cumulative
Fe	0.997			1.000	50.408	50.408
Zn	0.993			1.000		
Ti	0.941			1.000		
Cl	-0.930			1.000		
Ca	0.850			1.000		
Cr		0.671		1.000	34.834	85.242
Mn		0.973		1.000		
K		0.961		1.000		
S		0.950		1.000		
MGF			0.975	1.000	14.758	100.000

Table 13 shows the possible emission sources obtained at the SC site, where it is observed that the rotated matrix of the data (VARIMAX) results in three significant components, which were associated with Soil Dust, Hydrocarbons and Industry. The principal component analysis shows that these three components explain 92.8% of the variability of the data.

The source corresponding to Soil Dust which presents the elements Zn, K, Cl, Ti, Mn, Fe, MGF and Ca is in agreement with Owoade et al. (2015). Cu, S and V were assigned for the factor Hydrocarbons which agrees with Almeida et al. (2020) and Núñez (2019). The Cr element was assigned the Industry source which is in agreement with the data presented by Almeida et al. (2020).

Table 13. Emission sources obtained for PM_{2.5} from the SC site.

Element	Soil dust	Hydrocarbons	Industry	Community	% Variance	% Cumulative
Zn	0.996			0.893	47.796	47.796
K	0.970			0.936		
Cl	0.943			0.950		
Ti	0.790			0.962		
Mn	0.790			0.826		
Fe	0.786			0.886		
MGF	0.709			0.944		
Ca	0.609			0.941		
Cu		0.898		0.968	27.923	75.718
S		0.896		0.996		
V		0.889		0.838		
Cr			-0.961	0.997	17.087	92.805

According to the emissions inventory conducted by ProAire (2018), the ZMVT ranks fourth among the most polluted in the country. Mobile sources, represented by motor vehicles, are responsible for the greatest load of air pollutants in the entity. In the State of Mexico, 16% of the industry is located in the Toluca Valley. Extractive activities, the operation of furnaces for the manufacture of red brick, as well as soil erosion and forest fires also contribute to this problem, which explains the variability in the determination of the sources. Table 14 shows a summary of the emission sources.

Table 14. Summary of possible sources of PM_{2.5} emissions at the study sites.

Site	Possible Emission Sources		
SM	Soil dust	Sulfates	Hydrocarbons
SC	Soil dust	Industry	Hydrocarbons
NO	Soil dust	Industry	Coal burning
CB	Soil dust	Metallurgy	Fuel burning
SL	Soil dust	Metallurgy	Vehicular
ZN	Soil dust	MGF	Vehicular

The results obtained in this study for the possible sources of PM_{2.5} emissions are in accordance with research conducted in other cities around the world by different researchers, as shown in Table 15.

Table 15. Possible emission sources obtained in this work and their comparison with other results at the international level

Reference	Site	Emission Source	Pollutant
<i>This research</i>	<i>Toluca Valley Metropolitan Area, Mexico</i>	Soil dust	Ca, Ti, Cu, Mn, Cr, K, Ni, Cl, Fe, Zn, V, S, MGF
		Sulfates	Pb, S
		Hydrocarbons	MGF, V, Zn, Cu, S
		Metallurgy	K, Cl, MGF, Mn, Zn, Cr, S
		Industry	Ni, V, Zn, Cr, Mn
		Coal burning	Cl, MGF, S, Fe
		Fuel burning	S, Mn
		Vehicular	Cu, MGF, Fe, Zn, Ti, Cl, Ca,
		MGF	MGF
(Almeida et al. 2020)	Urban areas in Europe and Central Asia	Secondary sulfate	Sulfate, Br, Pb, C
		Biomass burning	K, Pb, Cu, BC, Cl, Zn, Br, S
		Gasoline combustion	V, Ni, S, SO ₃
		Coal combustion	SO ₂
		Industrial emissions	Mn, Fe, Pb, Zn, Cu y Cr, Ca, Al
		Traffic	OC ^a , EC ^b y BC ^c . Ba, Cu, Mn, Pb, Zn, Al, Ca, Fe, Mn, Si y Ti
		Land (soil/crust)	Al, Ca, Fe, Mn, Si y Ti, Cr, V y Ni
		Salt	Sea salt
(Álvarez y Suárez 2020)	Urban sites in the Mantaro Valley, Peru	Soil dust	Al, Ca, Fe, Si, Ti, K
		Smelting	As, Zn, Pb, S, K, Ti, Si
		Biomass burning	K
		Vehicles	As
(Núñez 2019)	Barranquilla, Colombia	Fuel oil burning	Ni, V y Cu
		Fertilizer production	Ca, P, K ⁺ y SO ₄ ²⁻
		Marine Aerosol	Mg, Cl, Na ⁺ , K ⁺ , Mg ²⁺ y Cl ⁻
		Secondary sources and civil works	Ca ²⁺ , NO ₃ ⁻ y SO ₄ ²⁻ .
		Resuspended soil	BC, Mn, Zn, Cu y Pb
		Suelo resuspendido	Al, Si, K, Ti, Mn y Ca
(Owoade et al. 2015)	Road Ife-Ibadan, Nigeria	Coking coal	Na, S, Cl, K, Fe, Zn, As, Br, Pb, BC
		Soil	Na, Mg, Al, Si, S, k, Ca, Ti, Mn, Fe, Zn
		Electronic waste	Na, Mg, Si, K, Cu, Zn, Ga, Cd, Sn
		Metallurgy	Mg, Al, S, Cl, K, Ca, Mn, Fe, Zn, As, Cd, Pb, BC
(Banerjee et al., 2015)	India	Crustal resuspensions and road dust	Al, Ca, Fe, Na y Mg
		Vehicle emissions	Fe, Cu, Pb, Cr, Ni, Mn, Ba y Zn
		Industrial emissions	Co, Cr, Zn, V, Ni, Mn, Cd
		Gasoline combustion	K, NH ₄ ⁺ , SO ₄ ⁻ , As, Te, S, Mn
		Marine aerosols	Na, Mg, K
		Biomass / waste burning	Cd, V, K, Cr, As, TC, Na, K, NH ₄ ⁺ , NO ₃ ⁻ , OC ^a
(SDA 2009)	Bogotá, Colombia High vehicular traffic area	Resuspended dust / Natural soil	Mg, Na, B, Ca y Al
		Vehicles + Fe	SO ₄ ⁼ , NO ₃ ⁻ , NH ₄ ⁺ , Cl ⁻ , Fe, Pb
		Industry	Cr, Ni, Pb
		Diesel vehicles	Cu, Cl ⁻
		PO ₄ ⁻³ , Fe	PO ₄ ⁻³ + Fe
(Rojas et al. 1990)	Santiago de Chile	Soil dust / Industrial	Al, Si, P, Mn, Fe, Cu, Zn, Pb
		Sulfate	P, S, Zn, Pb, Mass

	Automotive emissions	S, V, Mn, Fe, Zn, Br, Pb
	Wood burning	K, V, Mass

^a Organic carbon, ^b Elemental Carbon, ^c Black carbon.

Identification of risk sources

In order to determine the sources of risk to the health of the three sensitive classes of the population, due to PM_{2.5} inhalation, the emission sources obtained were considered and their elemental risk was assigned to each element.

Figure 3 shows the sources of risk to the health of the population in SM, which are Soil Dust, Hydrocarbons and Sulfates, where Soil Dust is the highest risk source and Hydrocarbons the lowest. The population that obtained the highest risk by inhalation of soil dust is children from 6 to 12 years old, so they are the most prone to suffer some of the diseases caused by the elements that make up the source.

Figure 3. Health risk due to PM_{2.5} inhalation caused by SM emission sources.

The CB site has three sources of risk, which are soil dust, metallurgy and fuel burning, as shown in Figure 4. The population that is most sensitive to the components of the Metallurgy source are children from 6 to 12 years of age; this population group is more exposed to getting sick due to the effect of the chemical elements that constitute it.

Figure 4. Health risk due to PM_{2.5} inhalation caused by CB emission sources

At the NO site, the sources of risk were determined for Industry and Coal Burning, which are presented in Figure 5. At this site, only the two sources mentioned are considered because the Reference Doses for the elements K and Ca were not available, which determined the third source considered as Soil Dust according to Alvarez and Suarez (2020) and Owoade et al. (2015). The source with the highest risk is Coal burning and the population with the highest sensitivity is children from 6 to 12 years old, for the same source.

Figure 5. Health risk due to PM_{2.5} inhalation caused by NO emission sources.

Figure 6 shows the sources of health risks for the SL area, which are Metallurgy, Soil Dust and Vehicular. Metallurgy is the highest risk source and Fuel Burning is the lowest. The population that obtained the highest risk due to inhalation of the elements that form the Metallurgy source are children from 6 to 12 years old, therefore they are the most prone to suffer some of the diseases caused by the elements that make up the source

Figure 6. Health risk due to PM_{2.5} inhalation caused by SL emission sources

Figure 7 shows the sources of health risk for the sensitive ZN classes, which are Vehicular, FGM and Metallurgy. The Metallurgy source is the highest risk and FGM the lowest. The population that obtained the highest risk by inhalation of the elements that compose the Metallurgy source are children from 6 to 12 years old, so they are the most prone to suffer some of the diseases caused by these elements.

Figure 7. Health risk due to $PM_{2.5}$ inhalation caused by ZN emission sources

Figure 8 presents the results of the health risk sources for inhalation of Soil Dust, Industry and Hydrocarbons in the SC area. The highest inhalation risk is for the Soil Dust Source and the lowest for Hydrocarbons. Children from 6 to 12 years old are the sensitive population with the highest risk of contracting diseases due to the inhalation of the elements that compose the Soil Dust source.

Figure 8. Health risk due to PM_{2.5} inhalation caused by SC emission sources

Table 16 presents the CQE of the sources of risk obtained and the possible diseases that can be contracted by sensitive groups of the population.

Table 16. Pathologies associated with the elemental chemical composition of PM_{2.5} (Lenntech 2021; ATSRD 2018; USEPA 2016 and Montero 2010)

Elements	Diseases
S, Ni	Asthma, Respiratory arrest
S	Alterations of hormonal metabolism, Bronchopneumonia, Fever, Damage to liver functions
S, Cl, Ni	Cardiac damage
S, Pb	Damage to kidney functions
S, Cl, Mn, Cu	Headache
S, Cl	Chest pain and obstruction
S, V, Mn, Cl, Ni	Bronchitis
S, V, Cr	Nose irritation
S, Cl, V	Throat irritation
S, Cl, Cr, Pb	Death
Cl	Itching or burning sensation in nose and throat
Zn, Ti	Interstitial fibrosis
Zn	Metal fume fever, Anemia and pancreatic damage

Conclusions

1. The gravimetric concentration of $PM_{2.5}$, was exceeded during the entire one-year study period, in accordance with the NOM-025-SSA1-2014 Standard.
2. CQE was determined for P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Cu and Pb, through the PIXE atomic technique.
3. Nine possible emission sources were identified for CQE, namely soil dust, sulfates, industry, metallurgy, hydrocarbons, coal burning, fuel burning, vehicles and FGM.
4. The inhalation risks of CQE present in $PM_{2.5}$ particles for the six sampling sites were high, which implies that there is a high probability of developing some of the diseases that can be caused by these elements.
5. The population with the highest health risk from inhalation of the elemental chemical composition present in $PM_{2.5}$ was children aged 6 to 12 years at all sites. It is worth noting that both child populations are vulnerable to the risk of inhalation of $PM_{2.5}$.
6. With the risks obtained and the possible emission sources, the sources of risk can be determined. This indicates which source may be the most harmful to the health of the population.
7. In ZMVT the elements Cl, S, Cr, Ti, Mn and Pb require monitoring, based on the risk analysis, because they have an impact on the health of the population.
8. The risk obtained for this work is considered only for CQE; the risk for other environmental pollutants such as bacteria, fungi, polycyclic aromatic hydrocarbons, among others, which are present in $PM_{2.5}$, is not considered.
9. Based on the knowledge of the pollutants that present a risk to the health of the population that inhales them, it is now necessary to establish mitigation or remediation strategies.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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