Original Research Article

Spatial Evaluation of Health Risk due to Inhalation of $PM_{2.5}$ Pollutants in the Metropolitan Areas of Toluca Valley and Mexico Valley

ABSTRACT

Aims: In the present work, health risk from inhalation of $PM_{2.5}$ pollutants in both areas was assessed spatially
Place and Duration of Study: The metropolitan areas of the Toluca (MATV) and Mexico Valleys (MAMV), between September and November 2009.
Methodology: A simultaneous sampling campaign was conducted in the Toluca and Mexico Valleys on alternate days from September-22 to November-29, 2009. From the samples collected, their gravimetric concentration was obtained, and S, Cl, K, Ca Ti, V, Mn, Fe, Ni, Cu, Zn, and Pb were determined using the particle-induced X-ray emission technique (PIXE).
Results: The health risk by inhalation of $PM_{2.5}$ with a higher result for the metropolitan area of the Toluca Valley (2.09 for adults, 6.25 for children from 6-12 years old, and 6.58 for children from 2-6 years old) in contrast with that of the metropolitan area of the Mexico Valley (1.67 for adults, 5.20 for children from 6-12 years old, and 5.28 for children from 2-6 years old).
Conclusion: These results are perhaps due to the higher concentration of Cl and Mn for the MATV. Additionally, the air parcels from sampling site MAMV go to MATV and thus contributes to an increased health risk from inhalation of $PM_{2.5}$. There are health risks for the inhalation of $PM_{2.5}$ in the MATV and MAMV study areas. The risk only considers the elemental risk. There are no similar studies for this comparison between MATV and MAMV in the literature.

Keywords: Toluca; Mexico; PIXE; Health; risk, $PM_{2.5}$

1. INTRODUCTION

Since energy is the ability to do work, then there are two main types of energy: potential energy (position or state) and the other is kinetic energy (action or movement). Both types of energy transform each other and become part of other forms of energy depending on the source from which they come, we can speak of electrical, nuclear or radioactive, chemical, magnetic energy. Since 1896 and thanks to the French physicist Henri Becquerel discovered the phenomenon known as radioactivity, which is the property of some atoms (such as radium, polonium and thorium) to emit energy spontaneously. Later studies determined the nature of this energy, consisting of the emission of particles and photons, and the first letters

of the Greek alphabet were used to designate them as radiation: alpha, beta and gamma. The study of the atomic nucleus both theoretically and experimentally gave rise to a new branch of science called nuclear physics and the experimental study of these systems was initially done by studying the collisions of nuclei with projectiles produced by radioactive sources. The need to have instruments to generate projectiles with which the experimenter could control the type of particle (protons, deuterons, alphas, etc.) as well as their energy and flow (electric current) was the origin of the invention of these instruments, which were called particle accelerators. Today these accelerators have a wide range of applications, such as in the field of atmospheric pollution [1]. As described in this work.

Human health and quality of life have been impaired by air pollution in urban areas. Numerous studies have shown associations between morbidity, mortality, and air quality [2-4]. One possible explanation for this scenario is particulate matter (PM) in the fine fraction $PM_{2.5}$ (particles ≤ 2.5 micrometers in aerodynamic diameter), that has been linked to increased asthma episodes, tachycardia, heart attacks, and premature death [5-9].

In Mexico, the scenarios caused by $PM_{2.5}$ are not different from other countries [10-15], in the metropolitan area of the Toluca Valley (MATV), in the metropolitan area of the Mexico Valley (MAMV). In both areas, health statistics reflect the morbidity and mortality caused by this pollutant.

The statistics for health effects have worsened due to various factors, including the fact that there are no reliable evaluation measurements for studying the potential impacts of the pollution on the health of the population. The measurements carried out to date are for the single variable of the gravimetric concentration, since it is the only factor with available measurement standards. This variable does not represent the actual risks that the population is exposed to when inhaling this $PM_{2.5}$. Therefore, the elemental composition of $PM_{2.5}$ is not measured, and neither the volatile organic compounds (VOCs), nor the bacteria, fungi nor other substances that naturally adhere to these particles, so it is not possible to consider their health effects.

Several studies have been conducted to determine the health risk to the population due to $PM_{2.5}$ inhalation: In our country, Díaz and Domínguez (2009), assessed the risk to the health of the inhabitants of the metropolitan zone of the City of Mexico posed by the chemical elemental contamination present in $PM_{2.5}$ particles. PIXE (particle induced X-ray emission), analysis of particles identified 18 elements, thereby achieving an elemental characterization. In order to calculate the risk posed by each element, the dose of elemental exposure was considered in relation to the corresponding reference dose. This gave an elemental risk of less than 1 for the three age groups; however, when the additive risk is considered for each age group a value exceeding 1 is obtained. Hence, although no individual element represents a public health risk, a consideration of the total risk for each of the age groups shows that members of the population are at high risk of contracting any one of the diseases that can be caused by the elements present in $PM_{2.5}$ [16].

Saldarriaga-Noreña at al. In Saltillo, Mexico, conducted a study from September to December 2012 and January-February 2013, at the School of Chemical Sciences of the Autonomous University of Coahuila, a total of 13 samples were taken. The risk assessment indicated that heavy metals present in $PM_{2.5}$ represent a potential health hazard for the population exposed to the inhalation of respirable suspended particles [17].

Internationally in Canada an investigation of levels and potential sources affecting ambient fine particulate matter ($PM_{2.5}$) and associated risk to public health was undertaken at two Canadian oil sands communities (Fort McKay and Fort McMurray) using a 4-year dataset

(2010–2013). Geometric mean concentrations of $PM_{2.5}$ at Fort McKay and Fort McMurray are not considered high and were 5.47 μg/m^3 (interquartile range, IQR = 3.02–8.55 μg/m^3) and 4.96 μg/m^3 (IQR = 3.20 – 7.04 μg/m^3), respectively. Carcinogenic risks of trace elements were below acceptable (1×10^{-6}) and/or within tolerable risk (1×10^{-4}), and non-carcinogenic risks were below a safe level of concern (hazard index = 1). Source-specific risk values were also estimated and were well below acceptable and safe level of risks. Further work would be needed to better understand the contribution [18].

In Nanjing, China to understand the impact of pollution control measures on the ambient fine particle ($PM_{2.5}$), two sampling campaigns before and after the release of pollution control measures (BPCM: Jan.–Nov. 2014 and APCM: Nov. 2015–Jul. 2016) were conducted. Chemical compositions, sources, regional transport, and potential health risks of $PM_{2.5}$ for the two distinguishable periods were compared. Results showed that the annual averaged $PM_{2.5}$ concentrations in Nanjing decreased by 12.4 % from BPCM (100 ± 54.3 μg m^{-3}) to APCM (87.6 ± 56.4 μg m^{-3}). Chemical mass closure showed that secondary inorganic aerosols (SIA) contributed most to the $PM_{2.5}$ mass (50.7 % and 47.1% for BPCM and APCM), followed by carbonaceous components (30.8% and 33.8%) for both the two periods. Health risk assessment showed that the non-carcinogenic risk and carcinogenic risk of $PM_{2.5}$ bound heavy metals decreased by 50.0 % and 58.3 %, respectively. These results indicated that the $PM_{2.5}$ pollution control measures were effective in Nanjing, for both reducing the mass concentrations and health risks of $PM_{2.5}$. Further attention should be paid to the reduction of the secondary inorganic aerosols and industrial process, due to their high contribution to $PM_{2.5}$ mass and health risks. This study also highlighted the impact of regional transport of coal combustion emission from north China on south cities, which should be controlled more strictly especially in winter of China [19].

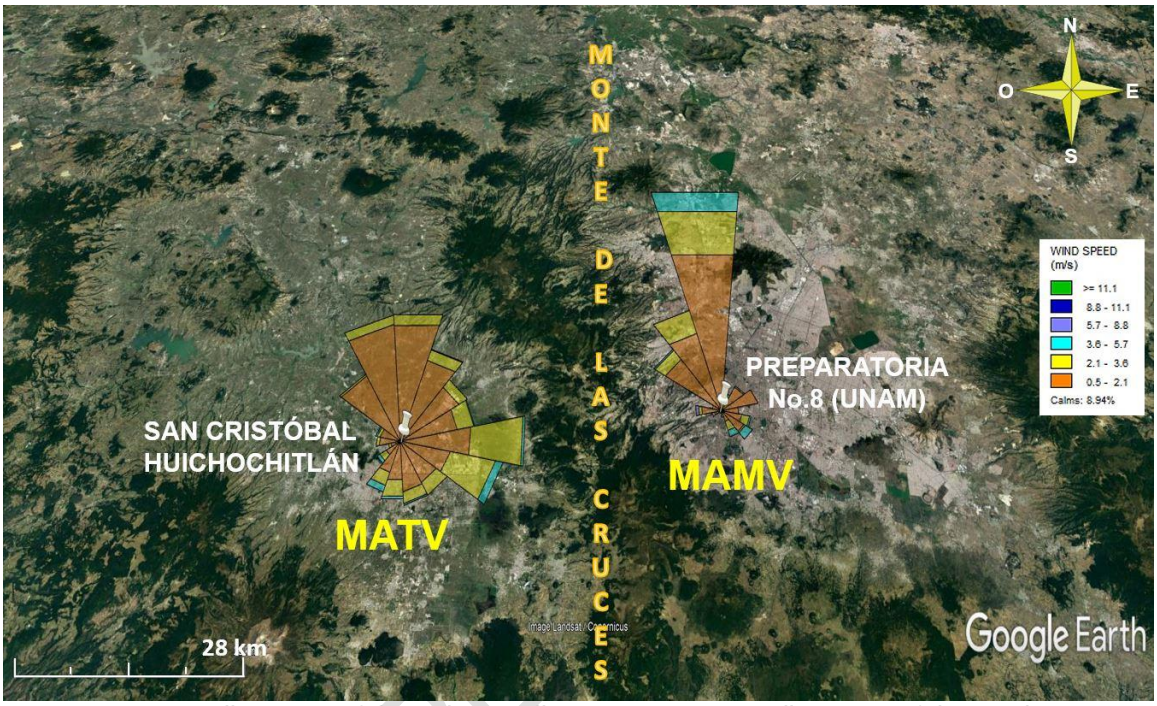
Too in China, Liang et al. they studied the contamination and health risks for residents in the vicinity of a tailing pond in Guangdong southern China. Water, soil, rice, and vegetable samples were collected from the area in the vicinity of the tailing pond. Results showed that surface water was just polluted by Ni and As, while groundwater was not contaminated by heavy metals. The concentrations of Pb, Zn, Cu, Cd, Ni, and As in the paddy soil exceeded the standard values but not those of Cr. In vegetable soils, the concentration of heavy metals was above the standard values except for Ni and As. Soil heavy metal concentrations generally decreased with increasing distance from the polluting source. Leafy vegetables were contaminated by Pb, Cr, Cd, and Ni, while the non-leafy vegetables were contaminated only by Cr. There was a significant difference in heavy metal concentrations between leafy vegetables and non-leafy vegetables. Almost all the rice was polluted by heavy metals. Diet was the most significant contributor to non-carcinogenic risk, which was significantly higher than the safe level of 1. The total cancer risk was also beyond the safe range ($10^{-6} – 10^{-4}$). Results revealed that there is a risk of potential health problems to residents in the vicinity of the tailing pond [20].

The aims of this study were to determine the elemental composition of $PM_{2.5}$, and the health risks it presents to the MATV and MAMV populations in order to generate scientifically reliable results and provide decision-making tools for reducing the emission of air pollutants, such as $PM_{2.5}$, and to implement risk management strategies for the population.

2. MATERIAL AND METHODS

This work was developed under the following methodology:
Study sites in the MATV and MAMV. For the selection of study sites (Fig. 1), the Reference Codes of the US EPA [21] require that sites be representative of the area where

they are located, provide comparable data with other stations, be useful at least throughout the period of the study, be permanently accessible, have safe electric power, be conditioned to withstand extremes of temperature, and be free of trees and buildings (one 10 m distance around the sampling site is recommended). It is recommended for the sampling site to be 20 m away from sources of industrial, commercial, and mobile emissions. The height of sampling collection should be from 6 to 45 m.



MATV: metropolitan area of the Toluca Valley; MAMV: metropolitan area of the Mexico Valley)

Fig. 1 Study sites (MATV and MAMV). a) Prevalence of winds in the MATV [22]; b) Wind lines in the MAMV [23]

The MATV consists of 22 municipalities, which comprise an area of 2669.6 km^2, corresponding to 11.9% of the state territory, with a population of **2,166,024** and a population density of 811.3 habitants /km^2 [24]. The average altitude of the municipalities is 2610 masl (meters above sea level), ranging from 2560 to 2740 masl. The MATV is located in the central part of the Mexico, between 18°59'07'' and 19°34'47'' north latitude parallels and 99°38'22'' and 99°56'13'' west longitude from the Greenwich Meridian. According to the Köppen climate classification modified by García, five types of climates are present: subhumid, warm, temperate semiarid, cold, and semi-cold [22]. The sampling site is Manuel Hinojosa Giles elementary school, located at the corner of Paseo de la Luz and Manuel Hinojosa Giles without number, Town of San Cristóbal Huichochitlán, ZIP Code 50100, between Paseo de la Luz and República Del Salvador streets. This is a subrural area, with little industrial activity and medium traffic flow. Due to the wind (Fig. 1a), pollutants generated in San Mateo Atenco, in the industrial zone of el Cerrillo, Airport Boulevard, and the central market converge in this area. The MATV is 280 masl higher than the MAMV, which also means that the combustion processes operate poorly and emit greater amounts of pollutants into the atmosphere due to the low oxygen content. This area receives intense solar radiation that accelerates the photochemical formation of air pollutants, with similar effects to those present in the MAMV. The MATV is also affected by anticyclonic systems,

which also increase the photochemical capacity of the atmosphere. In addition, these systems induce decreased wind speed near the soil surface, which inhibits vertical and horizontal air movements, preventing the dispersion of pollutants [22-23]**.**

In the MATV, the State of Mexico Health Institute (Instituto de Salud del Estado de México) [25], presented the following statistics for mortality and morbidity at the time of this study: for children between the ages of 1 and 4 years, asthma and asthmatic conditions (0), cerebrovascular disease (10), pneumonia and bronchopneumonia (1,990) acute respiratory infections (763,058). For children between the ages of 5 and 9 years old, asthma and asthmatic conditions (7,079), cerebrovascular disease (9), pneumonia and bronchopneumonia (748), acute respiratory infections (574,682). For adults aged 65 years and older, asthma and asthmatic conditions (650), cerebrovascular diseases (1276), pneumonia and bronchopneumonia (1025), and acute respiratory infections (126,158).

The study site in the MAMV is located in the western portion of the city, at a height of 2330 masl, with a high traffic flow, high population density, and high industrial activity. Due to the wind direction, as shown in Fig. 1b, pollutants generated in the industrial area of Naucalpan and Xalostoc converge in this area [23]. The sampling site was the No. 8 National Preparatory School (Escuela Nacional Preparatoria No. 8) of the National Autonomous University of Mexico (Universidad Nacional Autónoma de México) located in Av. Lomas de Plateros without number, at the corner of Francisco P. Miranda Colonia Merced Gómez Delegación Álvaro Obregón C.P. 01600.

The MAMV's high altitude causes combustion processes to operate poorly and emit a larger amount of pollutants into the atmosphere; this occurs because of the low oxygen content of the air, which is approximately 23% lower than at sea level, as well as the mountain range that surrounds it, which causes the stagnation of pollutants. Due to its latitudinal position that the MAMV receives intense solar radiation that accelerates the formation of photochemical air pollutants, such as ozone and secondary particles. Additionally, its location at the center of the country is affected by anticyclonic systems throughout the year, which keep the sky clear and increase the photochemistry capacity of the atmosphere. These systems also induce the wind speed to decrease near the soil surface, which inhibits vertical and horizontal air movement, preventing the dispersion of pollutants.

In the MAMV, as described by the National Epidemiological Surveillance System (Sistema Nacional de Vigilancia Epidemiológica: SINAVE) [26], morbidity and mortality statistics at the time of study included infectious respiratory diseases, streptococcal pharyngitis and tonsillitis (M= 125, F=147), acute respiratory infections (M= 558028, F=728255), pneumonia and bronchopneumonia (M= 3 106 F= 3 206), influenza (A H1N1) [M= 1 072, F= 1 060], and seasonal influenza (M= 407, F= 478)

Sample collection.

The samples were collected simultaneously in the MATV and MAMV on alternate days from September 22 to November 29, 2009, using the methodologies described by Martinez, Romieu and Korck [27-28]. $PM_{2.5}$ TCR TECORA brand samples and 47 mm glass fiber filters were used. Thirty samples were collected for each site during 24 h each. Due to the high cost of sampling, 30 samples were considered at each sampling site, which is the minimum statistically acceptable number of samples.

Sample analysis

Gravimetric analysis.

Gravimetry (mass concentration) was performed according to the methods described by the US EPA [29], in the Metrology Laboratory of the National Institute of Nuclear Research,

using a Sartorius Mettler Toledo model BP211D electronic scale. Before weighing, each sampling filter was conditioned at 21°C and 35% relative humidity for 48 h.

Elemental Analysis.
The samples obtained in the study sites were analyzed by particle-induced X-ray emission (PIXE), which has an atomic origin, is multi-elemental, non-destructive, rapid, and highly sensitive. The analysis was conducted in a Tandem Van de Graaff accelerator at the Instituto Nacional de Investigaciones Nucleares (ININ). For this, a proton beam was used with energy of 2.5 MeV, a current of 5 nA, and a load of 6 μC was deposited on the samples. An Ortec HPGe (High-Purity Germanium) X-ray detector (resolution 180 eV at 5.9 keV, located at an angle of 135° with respect to the incoming beam direction) collected the X-rays. The detector sensitivity curve was determined using thin film standards (MicroMatter® Co., Deer Harbor, WA, USA).

Natural and Anthropogenic Component.
Natural and anthropogenic components considering the enrichment factor (FE) were obtained according to Duce and Díaz [30-31]

$$FE = \frac{\left(\frac{\mathrm{X}}{\mathrm{Fe}}\right) aerosol}{\left(\frac{\mathrm{X}}{\mathrm{Fe}}\right) \mathrm{crust}}$$

Where X is the variable for the element of interest, and Fe is the abundance of this element in the earth's crust as well as the abundance of it in the sample. The FE from 0 to less than 10 is considered natural, between 10 and 500 is considered enriched, and more than 500 is considered highly enriched. Thus, elements with factors higher or equal to 10 must be considered as anthropogenic.

Elemental risk by $PM_{2.5}$ Inhalation in the MATV and MAMV
For the risk calculation, the methodology used by Diaz [12] was followed. The exposure dose (ED) of the population (obtained from atmospheric sampling), exposure factors (EF), and reference dose (RD) and/or minimal risk indicated (MNR) were needed. In the calculation children between the ages of 2 and 6 years, from 6 to 12 years old and adults older than 70 years, were considered as sensitive population groups.

Exposure Dose (ED).
For the ED calculation, elemental concentrations obtained through the PIXE technique and exposure factors taken from US EPA [32] were used, according to Peña, ATSDR, US EPA and Diaz [12, 33-35].

The exposure dose was calculated using the expression:

$$Exposure\ Dose\ \left(\frac{\boldsymbol{mg}}{\boldsymbol{kg}\ \boldsymbol{day}}\right) = \frac{(\mathrm{C})(\mathrm{IR})(\mathrm{RR})(\mathrm{AR})\mathrm{EF})(\mathrm{ED})}{(\mathrm{AT})(\mathrm{BW})}$$

Where:
C = Concentration of the pollutant in the medium (mg/m^3)
IR = Inhaled air rate (m^3/day).
RR = Retention rate for the inhaled air
AR = Absorption rate of inhaled air
EF = Exposure frequency (days)
ED = Exposure duration (years)
BW = Body weight (kg)
AT = Averaging time

Calculation of Elemental Risk (R).

With the ED calculated as above and RD and/or minimum risk level (MRL) obtained from ATSDR [36] and US EPA [35] references, the $PM_{2.5}$ elemental risk was calculated using the following expression:

$$Risk\ (R) = \frac{\text{ED}\ (\frac{\frac{\text{mg}}{\text{kg}}}{\text{day}})}{\text{RD}\ (\frac{\frac{\text{mg}}{\text{kg}}}{\text{day}})}$$

Or the concentration of the pollutant (mg/m^3) and the MRL in the expression:

$$Risk(R) = \frac{(\text{C})\text{pollutant concentration}\ (\text{mg/m3})}{\text{MRL}\ \ (\text{mg/m}\mathbf{3})}$$

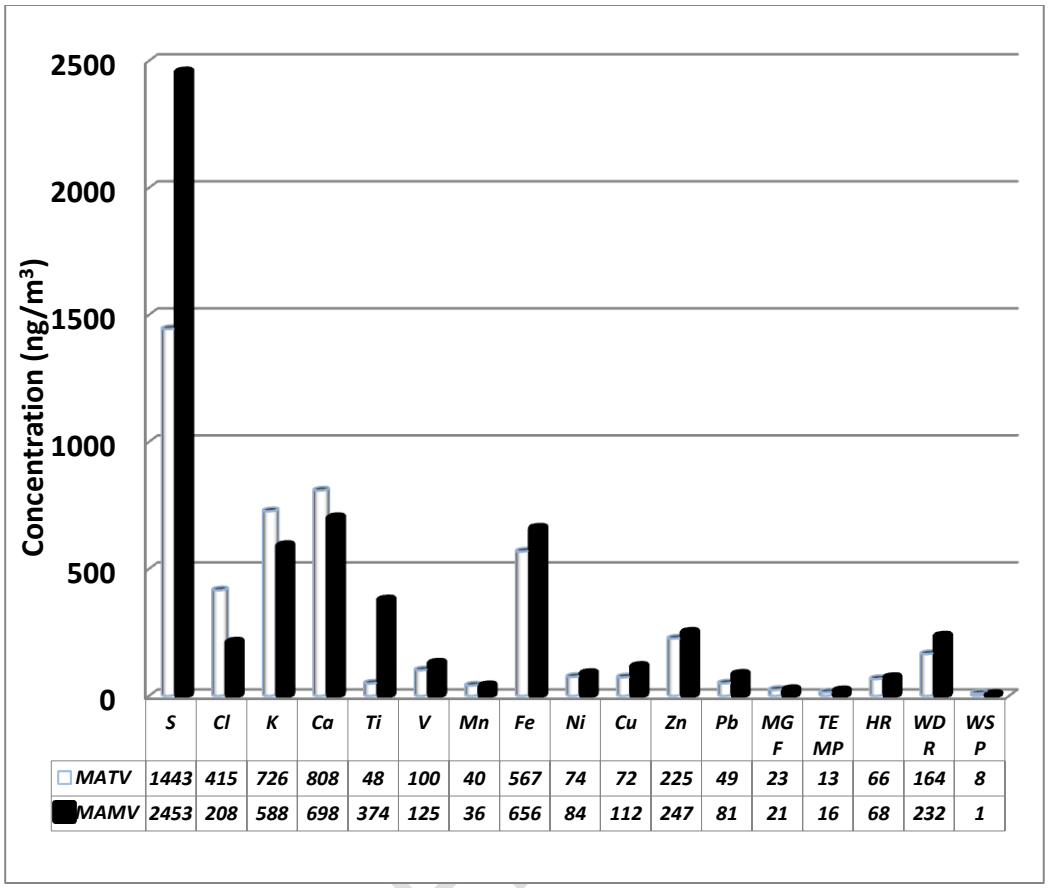
3. RESULTS AND DISCUSSION

Table 1 Descriptive statistics of the elemental composition of $PM_{2.5}$ present in the MATV and MAMV

		MATV					MAMV				
Element	MDL	N	Min	Max	Mean	Typical Deviation	N	Min	Max	Mean	Typical Deviation
				ng/m^3					ng/m^3		
S (Sulfur)	134	30	143	3253	1443	787	30	168	5700	2453	1706
Cl (Chorine)	109	30	134	852	415	182	30	109	669	208	119
K (Potassium)	68	30	310	1783	726	339	30	223	1025	588	188
Ca (Calcium)	52	30	318	1428	808	316	30	268	1166	698	180
Ti (Titanium)	31	2	32	64	48	NM	3	56	1009	374	NM
V (Vanadium)	26	30	38	168	100	41	30	29	507	125	118
Mn (Manganese)	20	30	20	77	40	14	30	20	117	36	21
Fe (Iron)	15	30	171	1276	567	291	30	108	1099	656	205
Ni (Nickel)	6	30	40	147	74	22	30	50	145	84	28
Cu (Copper)	4	30	34	118	72	23	30	39	485	112	85
Zn (Zinc)	8	30	45	920	225	187	30	65	455	247	93
Pb (Lead)	43	2	47	51	49	NM	3	46	146	81	NM
MGF		30	1	44	23	13	30	1	94	21	20
TEMP		30	9	17	13	2	30	12	20	16	2
HR		30	48	88	66	8	30	51	91	68	10
WDR		30	75	207	164	32	30	152	340	232	57
WSP		30	5	17	8	3	30	1	3	1	1

MDL: minimum detection limit, NM: Not Measurement, MGF: Mass gravimetric Fine, N: Number of occurrences, WDR: Wind direction, WSP: Wind speed, HR: Relative Humidity, TEMP: Temperature.

Table 1 presents descriptive statistics on the MATV and MAMV for: gravimetric concentration, elemental concentration determined by PIXE, minimum detection limit of the analytical technique, meteorological parameters, and presence of these elements (N) in each sample. In Fig. 2, the concentration of the elemental composition of the MATV and MAMV is observed.



	S	Cl	K	Ca	Ti	V	Mn	Fe	Ni	Cu	Zn	Pb	MGF	TEMP	HR	WDR	WSP
MATV	1443	415	726	808	48	100	40	567	74	72	225	49	23	13	66	164	8
MAMV	2453	208	588	698	374	125	36	656	84	112	247	81	21	16	68	232	1

Fig. 2 Concentration levels of the elemental composition of the MATV and MAMV

The meteorological parameters of temperature and relative humidity were similar at both sites, but slightly higher in the MAMV, whereas the wind speed in the MATV was higher for the study period than that of the MAMV.

From these concentrations and in accordance with the methodology described. Fig. 3 shows the anthropogenic and natural components obtained to determine their origin and nature.

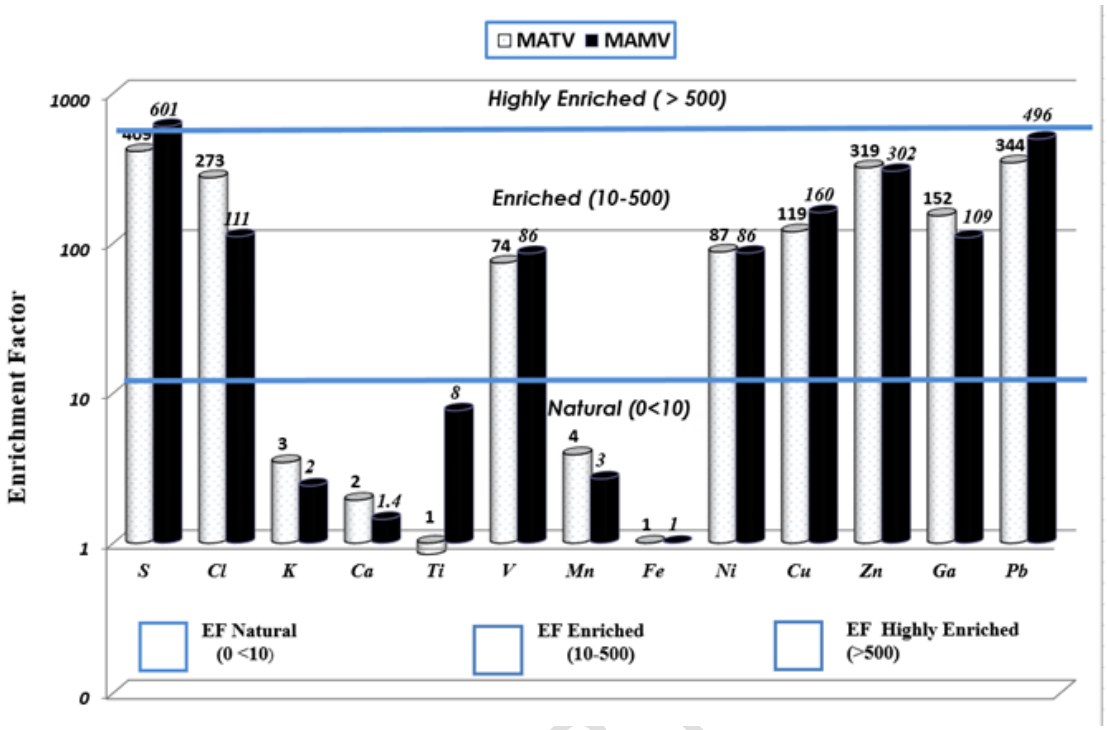


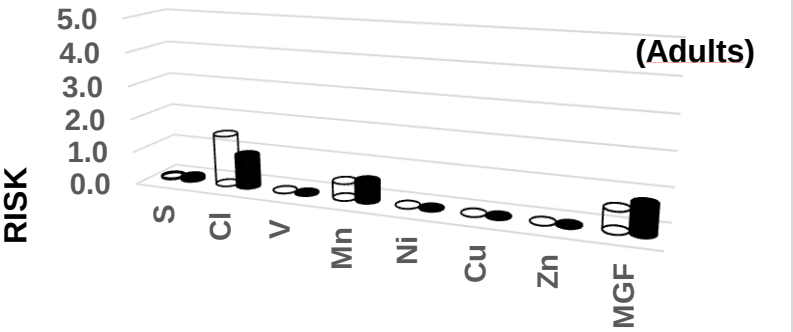
Fig. 3 Comparison of natural and anthropogenic components in MATV and MAMV

For the evaluation of the health risks of inhaling the elemental composition of the elements present in the $PM_{2.5}$ fraction, to which the population is exposed during breathing, the following characteristics were considered:

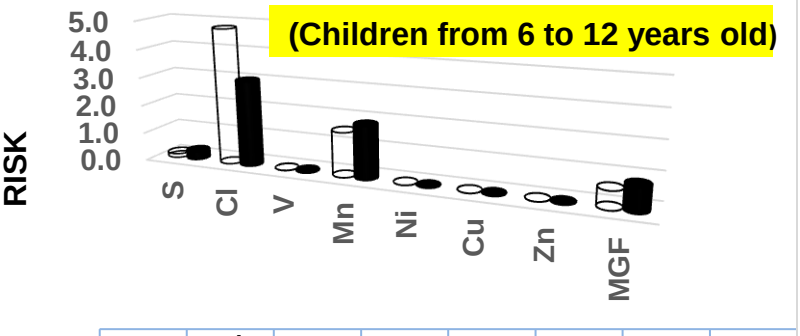
a) Route of exposure: inhalation.
b) More sensitive groups: children aged from 2 to 6 years, from 6 to 12 years and adults aged 70 years or older.
c) The elements present in all samples (30) and those that possess RD or MRL: for the MATV (S, Cl, V, Mn, Ni, Cu, and Zn), for the MAMV (S, Cl, V, Mn, Ni, Cu, and Zn).
d) The risk assessment of exposure to these pollutants inhaled by sensitive population groups was determined following the methodology described. The results are shown in Table 2 and represented graphically in Fig. 4.

Table 2. Health risk for sensitive population classes of the MATV and MAMV.

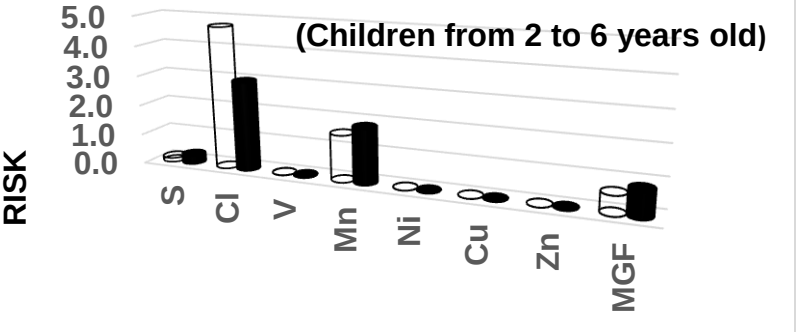
RISK = ED/RD= dimensionless						
MATV				**MAMV**		
ELEMENTS	**Adults (70 years)**	**Children (6–12 years)**	**Children (2-6 years)**	**Adults (70 years)**	**Children (6–12 years)**	**Children (2-6 years)**
Sulfur	**0.044**	**0.136**	**0.134**	**0.091**	**0.283**	**0.279**
Chlorine	**1.538**	**4.800**	**4.729**	**0.968**	**3.020**	**2.975**
Vanadium	**0.003**	**0.008**	**0.008**	**0.007**	**0.022**	**0.022**
Manganese	**0.503**	**1.571**	**1.547**	**0.597**	**1.864**	**1.836**
Nickel	**0.001**	**0.002**	**0.002**	**0.001**	**0.002**	**0.002**
Copper	**0.001**	**0.001**	**0.001**	**0.003**	**0.003**	**0.003**
Zinc	**0.0002**	**0.0007**	**0.0007**	**0.0002**	**0.0005**	**0.0005**
MGF	**0.631**			**0.846**		
Total Exposition (*)	**2.09**	**6.52**	**6.42**	***1.67***	***5.20***	***5.12***
(*) Risk of developing an adverse effect by exposition to elemental composition the $PM_{2.5}$ particles. MGF. - Mass gravimetric Fine, not considered in the total sum.						



	S	Cl	V	Mn	Ni	Cu	Zn	MGF
☐ MATV	0.044	1.538	0.003	0.503	0.001	0.001	0.000	0.631
■ MAMV	0.091	0.968	0.007	0.597	0.001	0.003	0.000	0.846



	S	Cl	V	Mn	Ni	Cu	Zn	MGF
☐ MATV	0.136	4.800	0.008	1.571	0.002	0.001	0.001	0.631
■ MAMV	0.283	3.02	0.022	1.864	0.002	0.003	0.000	0.846



	S	Cl	V	Mn	Ni	Cu	Zn	MGF
☐ MATV	0.134	4.729	0.008	1.547	0.002	0.001	0.001	0.631
■ MAMV	0.279	2.975	0.022	1.836	0.002	0.003	0.000	0.846

Fig. 4 Health risk for sensitive population classes of the MATV and MAMV

Discussion.

Table 1 shows the variation of elemental concentrations obtained from each of the study areas, and Fig. 2 best distinguishes its variation. Considering the average (mean) values of concentrations in three levels, high, medium, and low, the highest value corresponded to S in both the MATV (1443 ng/m^3) and the MAMV (2452 ng/m^3). This is probably due to the greater influence of industrial sources in the MAMV as well as the prevailing winds in the MATV, as posited by Diaz [37].

For the MATV, the medium level corresponded to Cl, K, Ca, and Fe, and for the MAMV, this level corresponded to K, Ca, and Fe. In both areas, the groups were very similar, but they differed in the presence of Cl, which may be due to the greater proximity of the MATV's sampling site to the industrial area. Low levels of V, Mn, Ni, Cu, and Zn were observed in the MATV, while low levels of V, Mn, Ni, Cu, and Zn for the MAMV. Table 1 show that the elemental concentrations were almost the same in both areas.

Ti and Pb were also obtained, although Ti was present in only in 2 samples for the MATV and 3 for the MAMV, and Pb was present in 2 samples for the MATV and 3 samples for the MAMV. These results are probably due to extraordinary events, such as biomass burning [38] and industrial processes, respectively.

The average gravimetric concentration in the study period for the MATV (23 µg/m^3) appears higher than that in the MAMV (21 µg/m^3), These values were exceeded only twice comparing them with those established in the Official Mexican Norm [39] for $PM_{2.5}$ (45 µg/m^3 in 24 hours average) for the MAMV: October 1, 2009 (94 µg/m^3) and October 6, 2009 (64 µg/m^3). In 2 days was close to, but did not exceed the OMN limit: November 17, 2009 (44 µg/m^3) and 28 November (42 µg/m^3). However, the highest values that were closest to the OMN value limits for the MAMV occurred on October 1, 2009 (43 µg/m^3), October 6, 2009 (38 µg/m^3), November 17, 2009 (38 µg/m^3) and 28 November (44 µg/m^3). These results indicate that it is possible that the behavior of air pollution is similar in both areas. However, if compared with the limits of the standard set by WHO [40], which establishes a 25 µg/m^3 average for 24 hours, then the limits for the MAMV were exceeded in 9 days, and the limits for the MATV were exceeded in 13 days. Results also show that the gravimetric concentration MATV is greater than that of the MAMV.

Comparing the elemental concentrations obtained in this study with similar works by other authors [41-42] in the MAMV, in which they use sampling equipment for $PM_{2.5}$, and sample collection is performed with Teflon filters and the same analysis technique (PIXE), we note that the values have the same tendency In 2004, in the MAMV, 10 elements were determined. In this work, we identified 14. S was the element with the highest concentration of micrograms per cubic meter. Results for MATV obtained in this study compared with those obtained [41] also have the same tendency, that is, sulfur has the highest concentration, and the other elements present variations of the same tendency. Despite presenting the same trends, it must be emphasized that the results of this study are generally higher than those obtained in previous years for both locations. The same references show that gravimetric concentration in 2009 for both sites was very similar and was even the same for the MATV in 2007. Only the data for the MAMV in 2004 were approximately 27% higher.

As for the meteorological parameters of both sites at the time of study, the relative humidity was only two units apart. The temperature in the MAMV temperature was 4 degrees warmer than in the MATV. This occurrence may be due to the fact that the MAMV is more urbanized

than the MATV. The wind speed had greater variation in the MATV, which favors the dispersion of pollutants and may lead to slightly lower concentrations of some elements in this area.

To determine which pollutants can be considered natural or anthropogenic, their enrichment factors were obtained. The data show that the natural components for the MATV and MAMV were the same (K, Ca, and Mn). The anthropogenic components were also the same for both zones (S, Cl, V, Ni, Cu, and Zn), indicating that human activity is similarly contaminating both areas. These results agree with those obtained by Diaz [31], who determined the natural (K, Ca, Ti, Cr, Mn) and anthropogenic (S, Cl, V, Ni, Cu, Zn, and Pb) components in the western portion of the MATV.

In calculating the risk to health presented in Table 2 and represented graphically in Fig. 4, it was revealed that the values of S, V, Ni, Cu, and Zn values for both study areas were less than one for the three sensitive classes of the population and therefore not at risk from inhalation of these pollutants in $PM_{2.5.}$ In both areas, the Cl presents health risks for the three sensitive classes of the population, being higher in the MATV; in this area, the risk is higher in children aged 6 to 12 years (4.80) and 2 to 6 years (4.73), while the risk is lower for adults (1.5). In the MAMV, the risk posed by Cl showed the same behavior as in the MATV, being greater for children aged 6 to 12 and 2 to 6 years (3.020) and (2.98), respectively, and lower for adults (0.97). These results show that the risk is greater in the MATV due to the higher concentration of Cl in this area. Another element that presents considerable risk is Mn for the MATV, it is also higher for children aged 6–12 and 2–6 years (1.57) and (1.55), respectively, and lower for adults (0.50). For the MAMV, Mn presents major risks for children aged 6 to 12 years (1.86), 2 to 6 (1.84) and lower risks for adults (0.60). Overall for Mn, the MAMV presents health risks for all three sensitive groups.

The high levels of chlorine, sulfur and Mn shown in the risk table (Table 2) are due to the high concentrations of these elements in the zones, which also cause high absorption doses. The high concentrations of these elements originate from the different sources present in the zones, such as vehicular and industrial sources. Since both zones are influenced by high vehicular traffic and a great variety of industries whose emissions are carried by the winds to the study sites.

The values of S, V, Ni, Cu, and Zn values for both study areas were less than one for the three sensitive classes of the population and therefore not at risk from inhalation of these pollutants in $PM_{2.5,}$ despite this finding, these elements do not act alone in the atmosphere because breathing is not selective. However, as the potentiation of health risks is not known for each element taken in by breathing, an approach to determining this value is the sum of the risks of each element, which gives us a total exposure value. This total exposure is the risk of an adverse effect. Table 2 shows that total exposure values were higher in the MATV than in the MAMV, and it was largest in the sensitive classes of children aged 2 to 6 and 6 to 12 years, while it was lower for adults. There are no studies presented for the MATV in the literature; only Flores, made an estimate of the risk of exposure of suspended particles in the Valley of Toluca, but they used another methodology [10]. For the MAMV, obtained the health risk for the three sensitive classes of the population of the area to the west of the Valley of Mexico, in 2005, Cuajimalpa, DF, for children aged 2 to 6 years (1.79), 6 to 12 years (1.81) and for adults (1.15). In this area, the risk was less than that obtained from this work [12]. This is justified by the fact that the western zone generates less pollution and is also free from the influence of pollution generated and driven by winds from areas of Xalostoc and Naucalpan. In contrast to the results of this study, the increased risk was for children aged 6 to 12. However, it should be noted that in both studies, the difference between the risks of age groups 2 to 6 and 6 to 12 was only a few hundredths. Thus, both

classes can be considered as having the same risk.

The results of this study indicate the existence of health risks from inhalation of $PM_{2.5}$ as corroborated in the literature [43]. Among the various adverse health effects on the population are the events caused by Cl: mild irritation of the nose (1–3 ppm), eye irritation (5 ppm), throat irritation (5–15 ppm), immediate chest pain, vomiting, impaired breathing and cough (30 ppm), and death from exposure to 1000 ppm (exposure of several minutes). Mn can also cause symptoms such as headaches, pain in the respiratory tract, hallucinations, forgetfulness, damage to the nervous system, Parkinson disease, pulmonary embolism, and bronchitis [44-45]. According to the results obtained in this study, the harmful effects to health caused by Cl and Mn have the highest possible occurrences in the study areas. Fig. 5 shows the SINAVE statistics for diseases suffered by the population in both study areas in the same period of study. It shows that, for both sites, tuberculosis and otitis events were approximately equal, while for the MATV, pharyngitis, tonsillitis, and acute respiratory infections are higher than in the MAMV. Pneumonia, bronchopneumonia, influenza (H1N1), and seasonal influenza present more major events in the MAMV than in the MATV. This behavior agrees with average concentrations and risk values obtained in this study. However, to fully justify the relationship between pollutants and disease, studies should be carried out directly on individuals.

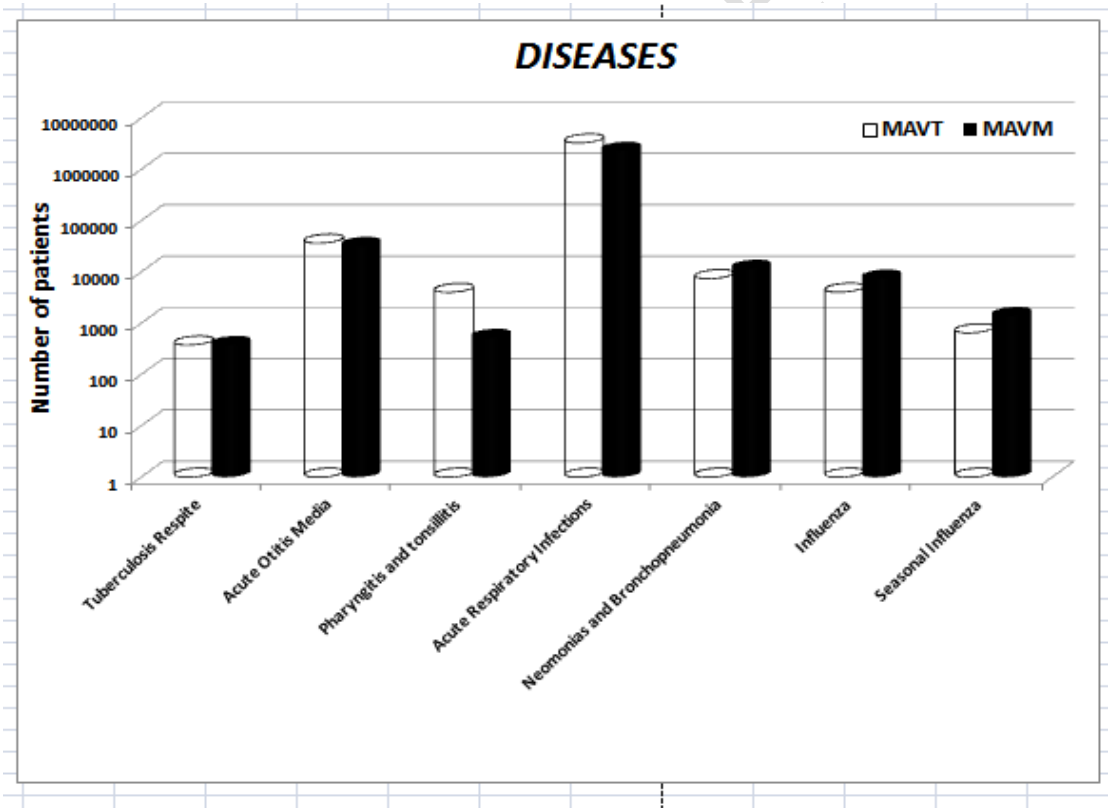


Fig. 5 Statistics for diseases suffered by the population in both study areas

In addition, an exploratory study was done (October 1, 2009, day of higher concentration in this study), by calculating back trajectories from the site monitoring to characterize the flow of air and its relation to the weather conditions in order to identify regions of origin of air parcels [37]. This indicated that air parcels from the original site sampling (Plateros National Preparatory School No. 8_UNAM) MAMV is directed to the MATV crossing the Monte de Las

Cruces, reaching San Cristóbal Huichochitlán, which can justify the fact that, on certain days in the MATV, pollution is greater than that of the MAMV and thus contributes to increased health risk by inhalation of $PM_{2.5}$. This justifies the finding that the day of higher gravimetric concentration (94 $\mu g/m^3$) in the Valley of Mexico agrees with the day of higher gravimetric concentration in the Toluca Valley. To corroborate the latter behavior, it is suggested that more study points at the MATV are needed.

4. CONCLUSION

In this research work, the objective was achieved by determining the health risk by inhalation of the elemental chemical composition present in $PM_{2.5}$ in the metropolitan areas of the Toluca and Mexico Valleys. For this purpose, a sampling campaign was carried out simultaneously in both sites, with the samples obtained the elemental chemical composition was determined using the atomic technique called PIXE (Proton Induced X-Ray Emission) and with the elemental concentrations the natural and anthropogenic component was obtained as well as the health risk by inhalation of $PM_{2.5}$. From the results obtained in this research work, concluded that there is an increased risk of contracting a respiratory disease due to $PM_{2.5}$ inhalation in the MATV when compared to the MAMV, the risk calculated in this study only considers the elemental risk and the samples obtained present VOCs, bacteria, fungi, and other substances, for these, the risk was not considered. This study provides a sampling point in both areas, and to clarify these results, the authors recommend increasing the points of study, calculating the risk to health, as has been discussed here, is a fundamental tool for assessing risks to which the population is exposed, therefore, it would be ideal to include the strategies for pollution control in the assessment.

CONSENT (WHERE EVER APPLICABLE)

Not applicable

ETHICAL APPROVAL (WHERE EVER APPLICABLE)

Not applicable

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge.

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