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Chemical characterization and Health Risk Assessment of metals associated to airborne particulate matter $PM_{2.5}$ in Saltillo, México

Caracterización química y evaluación del riesgo para la salud de los metales asociados a las partículas atmosféricas PM2.5 en Saltillo, México

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Hugo Saldarriaga-Noreña
Centro de Investigaciones Químicas, Instituto de Investigación en Ciencias Básicas y Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Colonia Chamilpa, C.P. 62209;
E-mail: hsaldarriaga@uaem.mx

Silvia Montiel-Palma
Instituto de Ciencias Básicas e Ingeniería, Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca-Tulancingo km 4.5, Pachuca 42184, México
E-mail: silvia_montiel@uaeh.edu.mx

Rebecca López- Márquez
Centro de Investigaciones Químicas, Instituto de Investigación en Ciencias Básicas y Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Colonia Chamilpa, C.P. 62209;
E-mail: rbk_137@hotmail.com

Josefina Vergara-Sánchez
Laboratorio de Análisis y Sustentabilidad Ambiental, Escuela de Estudios Superiores de Xalostoc, Universidad Autónoma del Estado de Morelos, C.P. 62715, Ayala, Morelos, México
E-mail: vergara@uaem.mx

Mario Alfonso Murillo-Tovar
CONACYT- Centro de Investigaciones Químicas, Instituto de Investigación en Ciencias Básicas y Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Colonia Chamilpa, C.P. 62209
E-mail: mario.murillo@uaem.mx

ABSTRACT
This study was carried out from September to December 2012 and January-February 2013, in the Faculty of Chemical Sciences of the Autonomous University of Coahuila, in total 13 samples were taken. On that period, dry weather predominated, with an average temperature of 17.0 °C, relative humidity of 52.0% and wind speed of 3.5 m s^{-1}. The mean concentration for $PM_{2.5}$ was 36.0 μg m^{-3}. The most abundant metal in $PM_{2.5}$ was Fe, with an average concentration of 1386.4 ng m^{-3} and the lowest concentration was obtained for Cd with 4.1 ng m^{-3}. On the other hand, within the ionic species the most abundant were sulfates (3569.0 ng m^{-3}), while ammonium was the least abundant species (490.9 ng m^{-3}). The ion balance indicated that during the study period the suspended particles had acidic characteristics, which means that the amount of cations was not sufficient to neutralize the sulfates, nitrates and chlorides. Finally, the risk assessment indicates that of heavy metal in the $PM_{2.5}$, represent a potential danger for the health of the population exposed to the inhalation of breathable suspended particles.

Keywords: suspended particles, metallic and ionic species, risk assessment

RESUMEN

Este estudio se realizó de septiembre a diciembre de 2012 y enero-febrero de 2013, en la Facultad de Ciencias Químicas de la Universidad Autónoma de Coahuila, en total se tomaron 13 muestras. En ese periodo predominó el clima seco, con una temperatura promedio de 17.0 °C, humedad relativa de 52.0% y velocidad del viento de 3.5 m s-1. La concentración media de PM2,5 fue de 36,0 µg m-3. El metal más abundante en las PM2.5 fue el Fe, con una concentración media de 1386,4 ng m-3 y la menor concentración se obtuvo para el Cd con 4,1 ng m-3. Por otro lado, dentro de las especies iónicas las más abundantes fueron los sulfatos (3569,0 ng m-3), mientras que el amonio fue la especie menos abundante (490,9 ng m-3). El balance iónico indicó que durante el periodo de estudio las partículas en suspensión tenían características ácidas, lo que significa que la cantidad de cationes no era suficiente para neutralizar los sulfatos, nitratos y cloruros. Por último, la evaluación de riesgos indica que los metales pesados presentes en las PM2.5 representan un peligro potencial para la salud de la población expuesta a la inhalación de partículas suspendidas respirables.

Palabras clave: partículas en suspensión, especies metálicas e iónicas, evaluación de riesgos

1 INTRODUCTION

Saltillo is the capital of the state of Coahuila of Zaragoza, México. It is located north of México in the southeast region of the same state, 400 km south of the border with Texas (United States) and 846 km from México City, at coordinates 101° 59'17" longitude W and 25° 23' 59" latitude N, it has an altitude of 1,600 meters above sea level and an area of 6,837 km^2, limits to the north with the municipality of Ramos Arizpe; to the south with the states of San Luís Potosí and Zacatecas; at the east with the municipality of Arteaga and Nuevo Leon state and to the West with the municipalities of General Cepeda and Parras.

The 47.4% of the territory of Coahuila, has a climate classified as very dry semi-warm. While its capital Saltillo represents the 4.64% of the State total area, classified as dry tempered. Along with the municipalities of Ramos Arizpe and Arteaga makeup the Metropolitan Area, which has a population of about 823,000 inhabitants. In its surroundings have been established several industrial zones, among which stand out the automotive industry (INEGI 2010a). Likewise, in surrounding areas mining activity is intense, mainly extraction of fluorite, copper, barite ($BaSO_4$), gold, silver, lead, zinc, strontium, magnesium and manganese. Also, the extraction of gypsum, iron, dolomite, lime, cement, all of them constitute the most important economic activities for this region (Corona et al. 2006; SGM 2012). This suggests that atmospheric aerosols in this zone have a complex composition.

$PM_{2.5}$ is constituted as a complex mixture of many different chemical resulting from distinct origin, either natural or anthropogenic, and from both primary and secondary particles, thus diverse sources and multiple atmospheric processes are involved in the formation of $PM_{2.5}$. The occurrence of inorganic ions and heavy metals is due to multiple atmospheric routes, and many of them are primarily present in fine particles (Cabada et al. 2004; Pan et al. 2015). In $PM_{2.5}$, sulfate, nitrate and ammonium are the more abundant ionic species (Young-Ji et al. 2008); these can also indicate contribution either by direct emission or atmospheric reactions due to photochemical processes via gas-particle reactions involving their oxygenated precursors (NO and SO_2) (Sitaras and Siskos 2008; Sharma et al. 2007; Bari et al. 2003). Meanwhile, trace metals are minor components, and their origin is mainly by direct emission, either anthropogenic or/and geological (Wang et al. 2005).

The airborne particulate matter represents a potential hazard to population in polluted urban areas, as it has been demonstrated by several epidemiological studies (Englert 2004; Kappos et al. 2004). The exposure to respirable fraction particles with a size smaller than 2.5 μm ($PM_{2.5}$) have showed the most significantly association with increase of the mortality by lung cancer and cardio-respiratory diseases by long-term exposure (Pope et al. 2002).

For Saltillo Metropolitan Zone, there are no studies that have determined the chemical composition associated with suspended particles less than or equal to 2.5 µm. For this reason, it is important to generate scientific information to establish the current levels of some chemical compounds that could be associated with impacts on health and the environment in this region.

2 EXPERIMENTAL

2.1 SAMPLING SITE AND METEOROLOGICAL CONDITIONS

The sampling was conducted from September until December 2012, and January-February 2013 in the Faculty of Chemical Sciences of the Autonomous University of Coahuila, 10 meters above ground level. This place is located between Boulevard Venustiano Carranza and the Salvador González Street (26° 56′ 44.52″ N, 101° 24′ 57.6″ W) (Figure 1), which has a large vehicular flow. During the sampling period the climate conditions was dry-warm (average temperature was 17.0 ºC), being the month of December the coldest, with average temperature of 12.5 °C, the average relative humidity (% RH) was 52% and the average wind speed was moderate with 3.5 m s^{-1}.

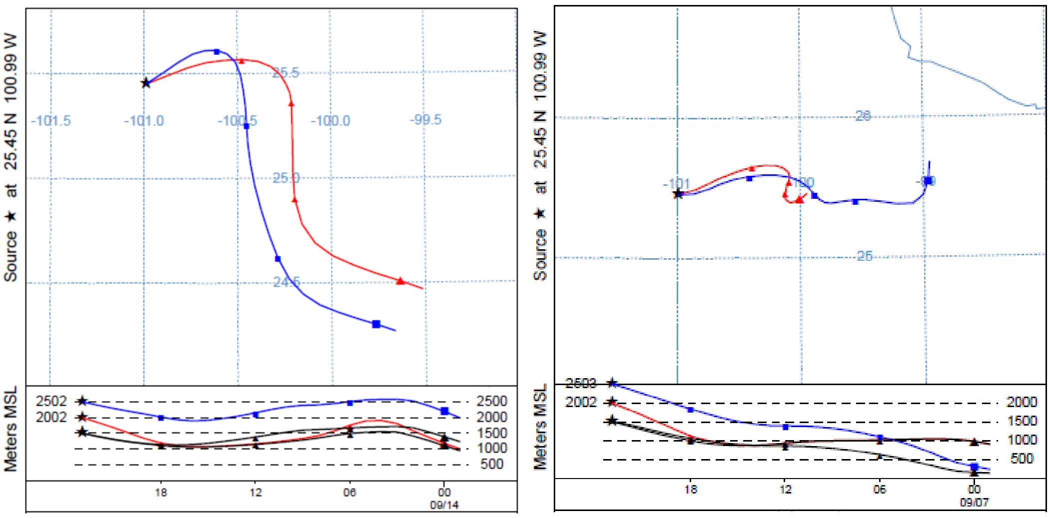
Figure 1. Location of the study area (INEGI 2010a)

2.2 WIND TRAJECTORIES

To determine the behavior of winds in the studied area, HYSPLIT4 model trajectories, obtained from the NOAA (National Oceanic and Atmospheric Administration), was used (Draxler and Rolph).

During the study period, the winds came mainly from the southeast and east, 66 % and 15 %, respectively. Which probably suggests that part of the air pollutants identified in the Autonomous University of Coahuila came from Zacatecas, Tamaulipas, San Luis Potosí and Nuevo León states. However, other possible local sources could be the emissions from the industrial parks located around the city (Figure 2).

Figure 2. Behavior of wind trajectories in Saltillo, Coah., during September to December 2011. Source: 25°45′N, 100°99′W, heights: 500, and 1000 m above ground level (a.g.l.)



2.3 CONCENTRATION OF $PM_{2.5}$

Samples were collected using two low volume equipment simultaneously, (Air Metrics-Minivol) for 24 h (12:00-12:00), at a flow rate 5.0 l min^{-1}, one for ion analysis (Nylon filters, MAGNA®, diameter 47 mm, pore size 0.2 µm) and the other for metal analysis and gravimetric determination (Teflon filters PALL® diameter 47 mm, 0.2 µm pore size). Prior to sampling, the filters were conditioned under controlled conditions of relative humidity (45% +/- 5%) and temperature (22 +/- 3 °C) for at least 24 h before sampling. The concentration of $PM_{2.5}$ (µg m^{-3}) was obtained by dividing the mass by the volume of filtered air, adjusted to standard conditions of temperature and pressure (25 °C and 760 mm Hg). After obtaining the mass of $PM_{2.5}$, the samples were stored in Zip-Lock® polyethylene bags and stored in a refrigerator at ~ 5 °C until chemical analysis.

2.4 QUALITY CONTROL OF THE ANALYTICAL METHODOLOGY

2.4.1 Limits of detection and quantification

The limit of detection (LOD) and quantification (LOQ) of the method were calculated in according with IUPAC, for which it was prepared a blank of reagents and analyzed ten times. The LOD can be defined as the analyte concentration that provides a signal equal to the target signal (Y_B), plus three times the target standard deviation ($\boldsymbol{S_B}$) (IUPAC 1997).

$$\mathbf{LOD} = \boldsymbol{Y_B} + \mathbf{3}^* \boldsymbol{S_B} \qquad (1)$$

Meanwhile de LOQ is defined as the analyte concentration that provides a signal to the target signal (Y_B) plus ten times the target standard deviation ($\boldsymbol{S_B}$).

$$\mathbf{LOQ} = \boldsymbol{Y_B} + \mathbf{10}^* \boldsymbol{S_B} \qquad (\mathbf{2})$$

2.4.2 Evaluation of the methodology efficiency

2.4.2.1 Metallic species

The analyzed metals were Pb, Cd, Co, Cu, Fe, Mn, Mo, Ni, Sb, and Zn, using atomic absorption spectroscopy. For the calibration of the equipment, multicomponent curves were performed, ranging from 1.0 to 100 ng mL^{-1}. The correlation coefficients (r) for all the elements were greater than 0.999.

In order to ensure the quality of the results, laboratory targets (materials and reagents) were made. The evaluation of the efficiency of the extraction methodology using the reference material NIST 1648a, as follows: the material was conditioned in a desiccator for five days, four replicates of this one were weighed (13.5, 11.2, 9.7 and 10.1 mg). The extraction of each one of the samples was carried out in PTFE tubes, using 30 mL of a solution of nitric and hydrochloric acid, HNO_3: HCl (2.6: 0.9 M), in an ultrasonic bath for 3 hours at a temperature of 60-70 °C. The extracts were filtered and adjusted at final volume of 50 mL, with the same solution. The percentages of recovery were evaluated by comparing the amount of metals obtained in each of the extracts against the value reported by NIST certificate.

The average recovery ranged from 77.5 to 118.5 % for Mg and Pb, respectively. The repeatability as a relative standard deviation (RSD) was below 20%, indicating good efficiency and precision of the method, considering the criteria established in the **EPA IO-3.5** method, which recommends for this type of matrix recovery range between 75 and 125 %, and the precision of the method less than 20% (US EPA 1999). The concentration of the metals in the real samples were corrected with laboratory blanks and percentages of recovery.

The LODs ranged from 0.0002 (Mg) to 0.0272 (Ni) µg mL^{-1} and the LOQs between 0.0008 and 0.0906 µg mL^{-1} (Table 1).

Table 1. Limit of detection and quantification (µg mL^{-1}), percentage of recovery for each analyzed metallic

	LOD	**LOQ**	**% Recovery**	**RSD[a]**
Cd	0.0014	0.0048	86.5	15.8
Cu	0.0023	0.0077	79.4	10.5
Zn	0.0006	0.0022	80.1	7.8
Fe	0.0048	0.0159	84.5	11.7
Mn	0.0024	0.0081	97.2	1.2
Ni	0.0272	0.0906	86.3	19.8
Pb	0.0087	0.0289	118.5	10.8
Mg	0.0002	0.0008	77.5	6.8

[a] RSD: Relative standard deviation

2.4.2.2 Ionic species

Calibration curves for all species were constructed in a range of concentration between 0.0625 and 10 µg mL^{-1}. The analyzed ions were: Cl^-, NO_3^-, PO_4^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} y Mg^{2+}, by ion chromatography (Metrohm model 861 Advanced Compact with conductivity detector). The anions were analyzed with chemical suppression using a Dionex-IonPac AS18-4 µm column, the mobile phase used consisted of a solution of sodium carbonate-sodium bicarbonate (0.35: 0.1 M), at a flow of 1.0 mL min^{-1}. Meanwhile, the cations were determined without chemical suppression, using a Dionex IonPac CS16 column, the mobile phase was a 26.0 mM meta-sulfonic acid solution at a flow of 1.0 mL min^{-1}.

Laboratory blanks were collected for the deionized water used for the extraction of ionic species, as well as the mobile phases and filters. The efficiency of the extraction was carried out as follows: at each site were chosen three different days, in which two samples were taken simultaneously, one of the filters was enriched with 500 µL of a multi-standard solution consisting of Cl^-, NO_3^-, PO_4^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} y Mg^{2+}, at a concentration of 2.5 µg mL^{-1}, were allowed to stand in Petri dishes for 24 h, then the filters were taken into polypropylene tubes and extracted using 8.0 mL of deionized water in an ultrasonic bath for 1 hour. The extracts were filtered through 0.45 µm nylon membranes and then transferred to vials for analysis.

The percentage recovery for anions ranged from 95.4% (NO_3^{-1}) to 96.3% (SO_4^{2-}), the % RSD were below 20%. For the cations the percentages were between 94.2% (K^+) and 120.0% (NH_4^+) and the RSD were below 10%. LOD for the anions ranging from 0.0025 (NO_3^-) to 0.0031 (SO_4^{2-}) µg mL^{-1} and for cations between 0.0013 (NH_4^+) and 0.0084 (K^+) µg mL^{-1} (Table 2).

Table 2. Limit of detection and quantification (µg mL^{-1}), percentage of recovery for each analyzed ionic species

	LOD	LOQ	% Recovery	RSD[a]
Cl^-	0.0028	0.0094	95.9	12.1
NO_3^-	0.0025	0.0082	95.4	13.5
SO_4^{2-}	0.0031	0.0101	96.3	14.7
Na^+	0.0022	0.0072	96.0	8.2
NH_4^+	0.0013	0.0042	120.0	9.8
K^+	0.0025	0.0084	94.2	9.1
Ca^{2+}	0.0022	0.0073	99.2	8.4

[a] RSD: Relative standard deviation

2.5 HUMAN HEALTH RISK ASSESSMENT

2.5.1. Exposure Assessment

According to the USEPA Integrated Risk Information Database (IRIS) and International Agency for Research on Cancer (IARC), pollutants were divided into non-carcinogens and carcinogens (US EPA 1989; US EPA 2001). Average daily dose (ADD, mg kg^{-1} day^{-1}) is employed for non-carcinogenic elements, such as Cu, Pb and Zn, while lifetime average daily dose (LADD, mg kg^{-1} day^{-1}) is used for carcinogenic elements, such as Cr, Ni, and. In this study, “human population” was divided into three groups: adult females, adult males and children.

Initially, the ADD to which the population is exposed, was calculated using the following equation:

$$\textbf{ADD or LADD} = (C x I_R x E_F x E_D)/(B_W x A_T) \quad (3)$$

C: measured metal concentration (mg x m^{-3})
IR: respiration rate (m^3 x d^{-1}), 20 and 7.6 for adults and children, respectively (US EPA 2011)
EF: exposure frequency (d x a^{-1}), 365
ED: duration of exposure (a), 26 and 6 for adults and children (US EPA 2011)

B_W: average weight of the individual by gender and age, 68.7, 78.4 and 15 for women, men and children, respectively
AT: average total exposure time (year), 70 for all in the case of carcinogenic and toxic metals of 30 and 6 for adults and children, respectively (US EPA 2011; Gao et al. 2016).

Given that in Mexico, information for some of these parameters is not available, reference data were taken for the United States, Norway and China (SFT 1999; US EPA 2011; Gao et al. 2016).

2.5.2 Risk assessment for non-carcinogenic metals

The non-carcinogenic risk of a single contaminant in an exposure pathway was evaluated by the hazard quotient (HQ). If $HQ < 1$ indicates that the risk of non-carcinogenic effects are not significant and sometimes may be neglected. Conversely, If $HQ \geq 1$ indicates that non-carcinogenic effects are possible, with a probability that tends to increase as the value of HQ increases (US EPA 2001).

$$\mathbf{HQ = ADD/RfD)} \tag{4}$$

ADD: Exposure (mg kg^{-1} d^{-1})
RfD: Reference dose (mg kg^{-1} d^{-1}); Pb (0.0035), Cu(0.0143), Zn (0.3) (US EPA 1989; Gao et al. 2015)

2.5.3 Risk assessment for carcinogenic

The incremental lifetime cancer risk (ILCR), is the probability of an individual developing any type of cancer from lifetime exposure to carcinogenic hazards. Thea cancer risk is calculated by using the following equation:

$$\mathbf{ILCR = LADD \times SF} \tag{5}$$

where SF is the slope factor (mg kg^{-1} day^{-1}).
LADD: Exposure (mg kg^{-1} d^{-1})
SF: slope factor (mg kg^{-1} d^{-1}); Ni (0.84) (Gao et al. 2015)
If $ILCR > 10^{-6}$; carcinogenic effects
If $ILCR < 10^{-6}$; acceptable level (no concern) (US EPA 2001)

2.6 STATISTICAL ANALYSIS

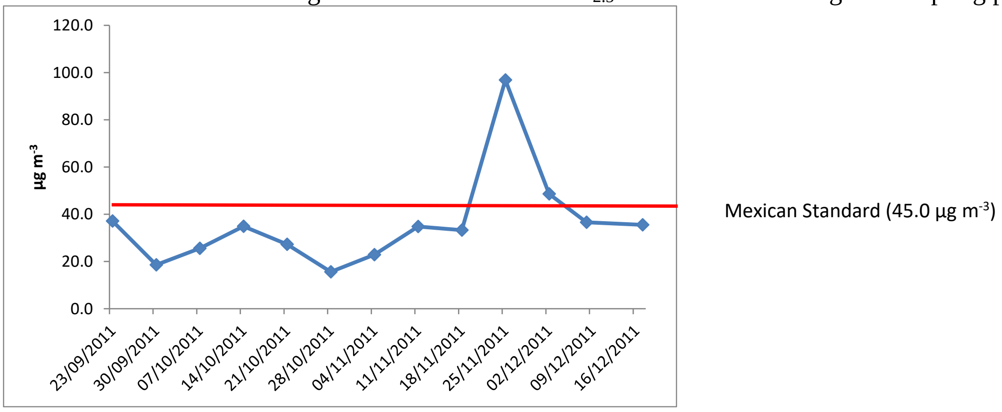
The normality of the data was assessed using the Shapiro-Wilk test, which suggested the use of non-parametric statistics for the analysis of the results. Spearman correlation analyzes with the "*r*" were applied to the total data set. On the other hand, linear regression analysis by least squares were applied to evidence the existence of chemical neutralization processes between anions and cations present in the particles. Likewise, an analysis of principal components and cluster were carried out to establish possible associations between analyzed variables. All these tests were realized with the Statgraphics Centurion XVI software.

3 RESULTS AND DISCUSSION

3.1 CONCENTRATION OF $PM_{2.5}$

During the studied period, the mean concentration for $PM_{2.5}$ was 36.0 (min 15.6 µg m^{-3}, max 96.9 µg m^{-3}). It should be mentioned that only two days passed the limit established by the Official Mexican Standard (**NOM-025-SSA1-2014**), for a period of 24 h (45.0 µg m^{-3}) (NOM-025-SSA1-2014). However, 77% of the cases exceeded the limit fixed in the WHO air quality guidelines (45.0 µg m^{-3}, 24 h) (WHO 2005). Among the possible sources of $PM_{2.5}$ in this zone could be mentioned the vehicular activity, likewise must take into account the great industrial activity that is developed around and the resuspension of dust from the mining areas surrounding the city. The wind direction during this period indicated that the majority of air mass came from southeast and east, which suggests that probably the mining zones located in the municipality of Arteaga, and San Luis and Zacatecas states, are partially affecting $PM_{2.5}$ concentration in the studied area. (Figure 3).

Figure 3 Behavior of the $PM_{2.5}$ concentration during the sampling period



When comparing these results with those obtained in other urban areas of the Mexican Republic, it is observed that the average concentration was above that reported for the Metropolitan Zone of the Valley of Mexico (24.8 µg m^{-3}), (Fourth report of data and trends of air quality in 20 Mexican cities, 2016), in the same period of study, but below that reported for the Metropolitan Area of Guadalajara (Saldarriaga et al. 2009) and the Metropolitan Area of Monterrey, (Fourth report of data and trends of air quality in 20 Mexican cities, 2016), 42.1 and 38.3 µg m^{-3}, respectively. An important aspect to consider with the observed results in Saltillo, is that the temperature decreased between November and December, as well as less favorable conditions for dispersing pollutants were observed and a possible increase in the consumption of fossil fuels, could have been associated with higher concentrations of particulates. In these months, it is frequent that masses of cold and dry air arrive to Saltillo, causing decreases in temperature, frost and some stratification of the atmospheric layers, thus enhancing the phenomenon of thermal inversion and fostering higher levels of pollutants in the atmosphere (SINAICA 2014).

3.2 CONCENTRATION OF METAL SPECIES IN $PM_{2.5}$

Seven metals were identified in the collected particles in Saltillo (Cu, Zn, Fe, Mn, Ni, Pb, and Mg). The most abundant specie was Fe (average concentration 1386.4 ng m^{-3}), followed by Mg (1207.7 ng m^{-3}) and Zn 298.9 ng m^{-3} (Table 3).

Table 3 Descriptive statistics of the analyzed metal species (ng m^{-3})

	Media	**SD[a]**	**Minimum**	**Maximum**	**Median**
Cu	18.9	18.6	4.1	82.2	12.3
Zn	298.9	163.9	98.6	690.5	277.4
Fe	1386.4	1011.5	197.3	3908.5	1097.3
Mn	19.7	11.4	4.1	41.1	16.4
Ni	108.5	72.7	8.2	332.9	94.5
Pb	91.2	62.2	8.2	176.7	111
Mg	1207.7	1307.7	49.3	4547.6	532.2

[a] SD: standard deviation

Elements such as Zn, Fe and Ni were determined in 100 % of the analyzed samples, followed by Cu (77.0 %), Pb (69.3 %) and Mn (15 %). In Mexico the only metal that is regulated by the environmental laws is Pb (NOM-026-SSA1-1993). Its maximum average quarterly concentration is 1500 ng m^{-3}, this value was not exceeded during this period (91.2 ng m^{-3}). Several studies conducted around the world have shown that Fe, Mg, Zn and Pb come from natural and anthropogenic sources (Allen et al. 2001; Fukai et al. 2007). For example, it is known that Fe and Mg are primarily crustal elements, while Zn and Cu are primarily anthropogenic (Odabasi et al. 2002). The combustion of fossil fuels is the main source of Be, Co, Hg, Mo, Ni, Sb, Se, Sn, Cu, Zn and V (Rajšić et al. 2008; Pacyna 1998). Metallurgical processes generate large amounts of As, Cd, Cu, Ni and Zn (Pacyna 1986). While the vehicle emissions emit significant quantities of Pb, Fe, Cu, Zn, Ni and Cd (Pacyna 1986). Saltillo is surrounded by desert areas, industrial zones and mining activities, this situation may be one of the possible reasons of high levels of particles and elements such as Fe, Mg, Zn, Ni and Cu, considering that to the southeast of the state there are some mines, specifically in the municipality of Arteaga and Zacatecas sate, meanwhile that in Tamaulipas and Nuevo León states, a great variety of industrial activities are developed.

The calculation of the enrichment factor (EF) was carried out with the intention to evaluate the possible sources of the metallic species. The estimation of EF is based on the average abundances of the elements in geological material, EF was performed according to Taylor 1964 (Fe was used as reference element) (Taylor 1964):

$$EF_{crust,\,X} = (X/Y)_{air}/(X/Y)_{crust} \quad (6)$$

Where “X” is the targeted element, and (X/Y) air and (X/Y) crust refer to the concentration ratios of element “X” with respect to “Y” (reference element) in air and in crust, respectively. It has been established that a value of $EF < 5$ corresponds to a trace metal from the soil, a value of $5 < EF < 100$ is a natural and anthropogenic mixture and if $EF > 100$ is considered anthropogenic origin (Chester et al. 1993a; Herut et al. 2001) (Table 4).

The results revealed that atmospheric concentrations of Zn are mainly from anthropogenic emissions (EF > 100), the high enrichment of non-crustal sources could be explained by either industrial activities (Chester et al. 1993a), or vehicular traffic, because Zn and Pb are markers of vehicular emissions. Meanwhile Cu, Mg clearly have a natural origin and are derived from the soil, the presence of the latter elements in the $PM_{2.5}$ is likely due to the resuspension of dust either by wind or vehicular traffic (EF<10). Probably the resuspension of dust and the mining activity that surround the city, may be affecting the PM composition. It is also known that in urban areas emissions from fossil fuels mainly contribute Pb, Fe, Cu, Zn, Ni and Cd, while the abrasion of the wheels of the vehicles and the brakes emit significant amounts of Zn. Likewise, is known that, Cu, Ni and Zn come from the metallurgical industry, which is congruent with the characteristics of the studied area, which has an important vehicular and metallurgical activity (Wålhin et al. 2006).

Table 4 Enrichment factor for the metals identified in Saltillo, during the studied period

	EF
Mg	2.1
Cu	9.2
Fe	15.3
Pb	32.6
Ni	63.2
Zn	171.0

3.3 CONCENTRATION OF IONIC SPECIES IN $PM_{2.5}$

The descriptive statistics of concentrations of ionic species in the period of study at Saltillo are presented in Table 5, which includes averages, standard deviations, median, maximum, and minimum values. Sulfates, nitrates, chloride and ammonium were the most abundant.

Table 5 Descriptive statistics of anions and cations concentrations associated to PM2.5 (ng m^{-3})

	Mean	**SD[a]**	**Minimum**	**Maximum**	**Median**
NH_4^+	490.9	249.8	135	1124	441.4
Na^+	495.8	447.9	291.1	2011.2	332.5
K^+	140.4	46.2	112.8	233.7	144.7
Ca^{2+}	918.8	1063.4	356	4682.2	590.2
Cl^-	1062.3	631	285.4	2887	1009.1
NO_3^-	2078.6	1497.6	391.1	5801.6	1742.8
SO_4^{2-}	3569.0	2677.0	791.6	9635.6	2818.4

[a] SD: standard deviation

Several studies have reported that sulfates and nitrates constitute more than 50 % of the mass of $PM_{2.5}$. Sulfates, nitrates and ammonia are related to the formation of secondary aerosols in which their oxidant precursors, nitrogen oxides (NOx) and sulfur dioxide (SO_2), respectively (Clapp and Jenkin 2001; Ito et al. 2004). These precursors come mainly from the combustion processes of petroleum-derived (Wang et al. 2005). This suggests that in the site of study the sources of anthropogenic origin, specifically industrial and vehicular emissions contribute in an important way (Báez et al. 2007; Hagler et al. 2007; Yang et al. 2005). The presence of species such as calcium and magnesium, is mainly associated with a geological origin (by re-suspension of dust due to winds or vehicular traffic), indicating a contribution in a lower proportion of natural sources to the chemical composition of the $PM_{2.5}$ on this site (Rattigan et al. 2006; Ghio et al. 1999). Also, the presence of potassium may have a geological origin or burning of biomass (Hagler et al. 2007). Meanwhile the presence of chloride is attributed to coal cars, vegetation burning and incineration (Ghio et al. 1999).

3.4 CORRELATIONS BETWEEN IONIC SPECIES

The degree of association between the anion and cation species, was evaluated by calculating the Spearman's rank correlation (r) and using the entire data set.

Ammonium correlated significantly with calcium, chlorides, nitrates, and sulfates (***p < 0.05***), meanwhile, sodium correlated with potassium, magnesium, chlorides and sulfates, as well as potassium with magnesium and chlorides. Positive correlations probably suggest that the species analyzed come from similar sources, but also indicate the presence of chemical processes in the atmosphere, such as the neutralization between anions and cations. For example, the correlation between ammonium and chlorides (**NH_4Cl, *r= 0.61***), nitrates (**NH_4NO_3, *r = 0.65***) y sulfates (**$(NH_4)_2SO_4$, *r = 0.56***), these indicates the process of neutralization between species that occurred during the studied period (Table 6).

Table 6 Spearman correlations for ionic species

	NH_4^+	**Na^+**	**K^+**	**Ca^{2+}**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**
NH_4^+	1.00						
Na^+	***-0.52***	1.00					
K^+	-0.06	0.43	1.00				
Ca^{2+}	-0.47	0.13	0.14	1.00			
Cl^-	***0.61***	0.10	***0.85***	0.44	1.00		
NO_3^-	***0.51***	0.30	0.29	0.13	0.20	1.00	
SO_4^{2-}	***0.56***	***0.62***	0.21	0.17	0.02	0.10	1.00

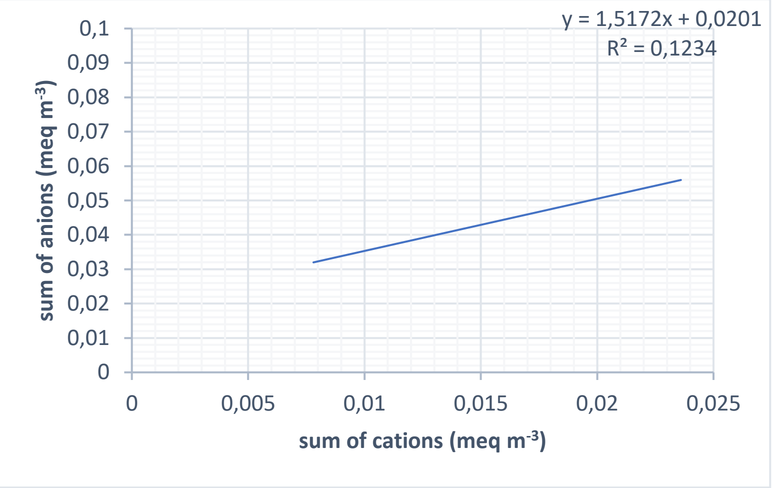
Bold and italic values – $p < 0.05$

Neutralization processes in the atmosphere depend on some environmental factors such as temperature, humidity, solar radiation, as well as the availability of its precursors. For example, the presence of NH_4NO_3 in the suspended particles suggests relatively low ambient temperatures and high relative humidity. On the other hand, high temperatures favor the decomposition of ammonium nitrate until the formation of nitric acid (Jang et al. 2002).

3.5 ION BALANCE

The degree of acidity or basicity of the suspended particles in the studied site, was evaluated by a linear regression analysis with the least squares method, between the total sum of anions *vs* the total sum of cations. The slope value was (***1.51)***, which indicates that the amount of cations was not sufficient to neutralize the anions during the sampled period, giving acid characteristics to the suspended particles. It is important mentioning that this result will depend on the number of species considered for the calculation (Figure 5).

Figure 5. Ion balance between the sum of cations vs the sum of anions



Respect to the acidic characteristics observed in the particles analyzed in this study, it should be emphasized that the acidity of atmospheric aerosols facilitates the solubility of some metals, which confers a high degree of toxicity to the respirable particles. This, given the high degree of penetration of $PM_{2.5}$ in the respiratory system (Wålhin et al. 2006). It has also been reported that acidic sulfate aerosols act as catalysts in the formation of secondary aerosols, which to a certain extent may be regulating the formation of photochemical smog at the site studied (Clapp and Jenkin 2001).

3.6 PRINCIPAL COMPONENT ANALYSIS

In order to obtain the possible sources of the species that contribute to the formation of the $PM_{2.5}$ in Saltillo, a principal component analysis (PCA) with Varimax rotation was performed. The principal components (PC) were selected with eigenvalues greater than 1.0.

The analysis showed that 82.6 % of the total variance of data was explained in five PC. PC1 explained 26.6% of the total variance, consisting mainly of Na^+, Mg^{2+}, SO_4^{2-}, Zn and Pb, grouping species that come from natural and anthropogenic sources. PC2 explained 21.9%, the highest weight species were Fe and Ni, which groups as possible sources metallurgical and mining activities; while the PC3 explained 15.4%, and it consisted of K^+ and Cl^-, both considered as markers of biomass burning. PC4 represented

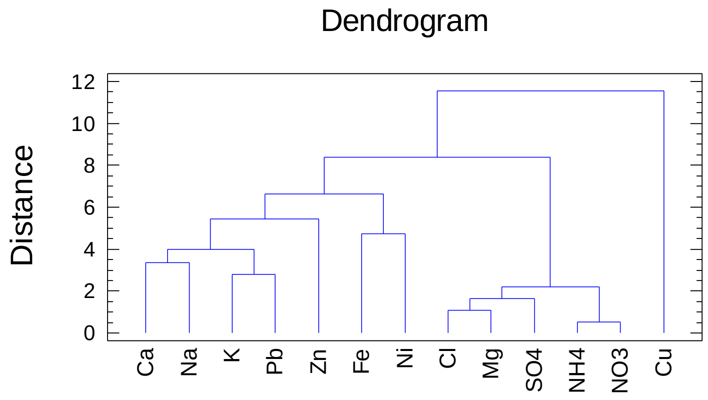
10.9%, constituted of NH_4^+ and Ca^{2+}, indicating that they come from a mixture of natural and anthropogenic activities. Finally, PC5 explained only 7.8%, made up mainly of Cu, and according to the EF can come from natural sources (Table 7).

Table 7 Principal Component Analysis

Components	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cumulative variance (%)	26.6	21.9	15.4	10.9	7.8
Eigenvalues	3.5	2.9	2.0	1.4	1.0
NH_4^+	0.02	-0.51	0.45	**0.63**	0.09
Na^+	**0.92**	0.19	-0.04	0.08	0.15
K^+	-0.06	-0.12	**0.93**	-0.08	0.08
Ca^{2+}	-0.07	0.03	-0.03	**-0.85**	0.02
Mg^{2+}	**0.66**	0.07	0.56	-0.06	0.15
Cl^-	0	0.05	**0.79**	0.37	0.34
NO_3^-	-0.15	-0.77	0.09	0.27	0.04
SO_4^{2-}	**0.76**	-0.31	0.24	0.29	0.02
Cu	0.02	0.18	-0.08	0.02	**0.91**
Zn	**0.81**	0.12	-0.03	-0.17	0.23
Fe	-0.08	**0.85**	0.21	0.12	0.08
Ni	-0.02	**0.78**	-0.22	0.04	0.32
Pb	**0.57**	-0.35	0.21	-0.53	0.12

On the other hand, to complement the PCA, a Cluster analysis was performed by the Ward correlation method, in order to establish possible associations among the analyzed species. The dendogram shows a first subgroup consisting of calcium, sodium, potassium and lead, suggesting that the species come from similar sources, specifically natural sources. Meanwhile, iron, nickel and zinc have formed a second group, from natural and anthropogenic sources, which is congruent with that observed in *EF* (Figure 6). The third group consists mainly of sulfates, nitrates and ammonium, species of secondary origin and the most abundant in the present study, they are derived from precursors originating from various combustion processes, especially from petroleum derivatives.

Figure 6 Ward's method for cluster analysis



3.7 HUMAN HEALTH RISK ASSESSMENT

3.7.1 Non-carcinogenic risk through the Inhalation Exposure Pathway

Tables 8 and 9 exhibited relevant exposure for metals entering the human body through of the inhalation. Due to the lack of basic data of local exposure parameters in México, USA's and China parameters were used in previous researches to conduct health risk assessment.

Table 9 shows the non-carcinogenic risks of detected metals via the inhalation exposure pathway during the whole sampling period, at the different populations in the studied site. The non-carcinogenic risks via inhalation were the highest to children, followed by adult females and then adult males. For all three population groups, the non-carcinogenic risks via inhalation showed the next trend: Pb > Cu > Zn. The monthly average risk level of non-carcinogenic heavy metals for exposure through the respiratory system, reveals that Pb was the only metal that has a value greater than 1.0 (4.8 children, 2.39 females, 2.20 males), which suggests the high vulnerability to adverse effects on health of children by the inhalation of suspended particles in this region.

Table 8 The risk associated with non-carcinogenic heavy metals in the human population of Saltillo

	Pb HQ,dimensionless			**Cu HQ,dimensionless**			**Zn HQ,dimensionless**		
	Females	**Males**	**Children**	**Females**	**Males**	**Children**	**Females**	**Males**	**Children**
22/09/2011	4.63	4.25	9.3	0.1	0.09	0.21	0.21	0.19	0.42
29/09/2011	3.55	3.26	7.13	ND[a]	ND[a]	ND[a]	0.05	0.05	0.1
06/10/2011	ND[a]	ND[a]	ND[a]	0.13	0.12	0.26	0.07	0.07	0.15
13/10/2011	3.03	2.78	6.08	0.21	0.2	0.43	0.09	0.09	0.19
20/10/2011	1.29	1.18	2.59	0.03	0.02	0.05	0.09	0.08	0.18
27/10/2011	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	0.03	0.03	0.06
03/11/2011	0.21	0.19	0.42	0.05	0.05	0.1	0.06	0.05	0.11
10/11/2011	ND[a]	ND[a]	ND[a]	0.08	0.07	0.16	0.04	0.03	0.08

17/11/2011	2.82	2.59	5.65	0.05	0.05	0.1	0.06	0.06	0.12
24/11/2011	3.34	3.07	6.71	0.08	0.07	0.16	0.11	0.11	0.23
01/12/2012	3.13	2.88	6.29	0.08	0.07	0.16	0.14	0.13	0.29
07/12/2011	2.92	2.68	5.87	0.05	0.05	0.1	0.11	0.11	0.23
16/12/2011	0.21	0.19	0.42	0.13	0.12	0.26	0.09	0.08	0.18
12/01/2012	ND[a]	ND[a]	ND[a]	0.1	0.09	0.21	0.19	0.17	0.37
19/02/2012	ND[a]	ND[a]	ND[a]	0.1	0.09	0.21	0.08	0.07	0.16
26/01/2012	ND[a]	ND[a]	ND[a]	0.08	0.07	0.16	0.06	0.06	0.12
09/02/2012	1.18	1.09	2.38	0.53	0.49	1.06	0.12	0.11	0.24
Mean	**2.39**	**2.20**	**4.80**	**0.12**	**0.11**	**0.24**	**0.09**	**0.09**	**0.19**

[a] ND: no detected

3.7.2 Carcinogenic risk through the Inhalation Exposure Pathway

Meanwhile Table 9 shows the carcinogenic risks from Ni through inhalation exposure. The ILCR were greater than 1 x 10 $^{-6}$ for the three groups. The results indicate that in the studied area, there is a high possibility that the population exposed for long periods of time to develop some type of cancer.

Table 9 The risk associated with carcinogenic for Ni in the human population of Saltillo

	Ni		
	ILCR dimensionless		
	Females	**Males**	**Children**
22/09/2011	0.004	0.004	0.002
29/09/2011	0.004	0.003	0.001
06/10/2011	0.004	0.003	0.001
13/10/2011	0.004	0.003	0.001
20/10/2011	0.003	0.002	0.001
27/10/2011	0.002	0.002	0.001
03/11/2011	0.001	0.001	0.001
10/11/2011	0.001	0.001	0.001
17/11/2011	0.002	0.002	0.001
24/11/2011	0.003	0.003	0.001
01/12/2012	0.003	0.003	0.001
07/12/2011	0.003	0.003	0.001
16/12/2011	0.003	0.003	0.001
12/01/2012	0.005	0.004	0.002
19/01/2012	0.011	0.01	0.004
26/01/2012	0.007	0.006	0.003
09/02/2012	0.005	0.005	0.002
Average	**0.004**	**0.003**	**0.001**

4 CONCLUSIONS

The obtained results in this study revealed that maxima concentrations of $PM_{2.5}$ in Saltillo, it was measured between November and December, in these months the ambient temperature decreases significantly, what increases the consumption of fossil fuels and at the same time environmental conditions are less favorable for the dispersion of pollutants, it which probably allowed higher concentration of PM. The same situation occurred with the concentration of ionic and metal species, which confirms the incidence of such species in the composition of the PM in this site.

The metal species most abundant were Fe followed by Mg and Zn, which suggests a mixture of sources, both of natural and anthropogenic origin. This behavior was verified with the calculation of the EF, which indicated that Mg and Fe come fundamentally from natural sources and Zn from anthropogenic sources.

Meanwhile the ionic species showed that sulfates, nitrates, ammonium and calcium were the most abundant, indicating that these species are derived from anthropogenic precursors or natural sources, specifically calcium. The ion balance showed that during the studied period particles presented acidic characteristics, which may facilitate the solubility of metals present in the ambient air, probably incorporating them into the pulmonary alveoli. Likewise, the results suggest possible events of acid rain, which directly affect bodies of water, vegetation and structures.

For its part, the wind trajectories indicated the incidence of Zacatecas, San Luis, Tamaulipas and Nuevo León states, in the chemical composition of PM in Saltillo, considering that during the study, winds come from south and southeast meanly.

Finally, the risk analysis of non-carcinogenic elements by the inhalation of $PM_{2.5}$, indicates that the children population is the most susceptible to negative effects on health. Meanwhile the carcinogenic risks to all populations through inhalation exposure exceeded the threshold ranges. Therefore, the carcinogenic and non-carcinogenic risks to all population age groups from $PM_{2.5}$-bound metals concentrations must be considered, by the authorities responsible for the care of the environment, so that they continue to follow up on this problem.

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