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Elemental Contribution to the Mass of $PM_{2.5}$ in Guadalajara City, Mexico

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Abstract The seasonal behavior of the mass of $PM_{2.5}$ and its elemental components and their contribution to the mass of the particles is described for two different sites in Guadalajara City. The average mass of the particles for the entire study period at the two sites, Centro and Miravalle (1.3 and 1.8 mg, respectively), showed significant differences ($p < 0.05$), while differences ($p < 0.05$) between seasons (rainy and dry season) only occurred at Miravalle. The total elemental contribution to the mass of the particles was 1.97% in Miravalle and 2.05% at Centro, with Iron and Titanium the largest contributors and most abundant elements for both sites. Likewise, the monthly contribution per element with respect to the monthly mass of all elements was estimated. The results revealed that the elements that present the biggest contribution to this mass were Iron, Titanium, Zinc and Magnesium. Iron was the largest contributor at both sites. At Miravalle, the contribution oscillated between 56 and 58% from January to June, while at Centro it oscillated between 55 and 40% for the same period of time.

Keywords Elemental composition: $PM_{2.5}$ · Health · Trace elements

The Metropolitan Zone of Guadalajara (MZG) is the second largest urban area and one of highest population growth rates (Instituto Nacional de Estadística y Geografía (INEGI) 2005) of Mexican cities, with a population of approximately 4.1 million people. This population phenomenon is attributed to the establishment of various industrial complexes and the ever growing demand for goods and services to fulfill the population's needs, which have led to a notorious increase in traffic density. It is estimated that about 1.3 million vehicles daily circulate throughout the MZG. These factors have significantly increased pollutant emissions to the atmosphere, which has caused a deterioration in air quality and could have a repercussion in the quality of life for the inhabitants. Recent estimations have shown emissions to be about 1,389,047 tons/year of diverse pollutants originating primarily from the transport sector, due to fossil fuels consumption, followed by industrial emissions and services in the urban area (Programa para el mejoramiento de la Calidad del Aire en la Zona Metropolitana de Guadalajara (PROAIRE) 1997–2001). In general, vehicle emissions are the main contributing source to fine particles or $PM_{2.5}$, followed by soil, secondary aerosols, industry and combustion during food preparation (Mugica et al. 2009). Such pollutants could be present in a gas or particulate phase; the latter, also known as suspended particles, are classified by their aerodynamic diameter as coarse, fine and ultrafine (Finlayson-Pitts and Pitts Jr 2000).

Fine particles, or PM2.5, are one of the pollutants that have generated the most concern in Guadalajara City as well as in other parts of the world, even though annual emissions are less than 1% of the total. Their physical and chemical properties encompass different types of effects in the environment and health of the population potentially exposed. Fundamentally, they have the property for depositing and coming in contact with the internal tissue of the lung, carrying to the lung a complex mixture of thousands of compounds. A number of these compounds present diverse physical and chemical properties, with different degrees of

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reactivity, toxicity and carcinogenicity (Götschi et al. 2005). They enter into the alveolar zone, where there is no mucus protection layer and where the time to evacuate the deposited particles is much greater than in the rest of the respiratory system (Finlayson-Pitts and Pitts Jr 2000). Therefore, the probability of interaction or the entrance of these components into the metabolism increases. The toxicity of the particulate material depends on the relative contribution of the sources of emission and on their aerodynamic diameter (Kim and Jaques 2000). Every day more evidence reinforcing the hypothesis of the association between the effects upon health and the chemical composition of the particulate matter is found (Dagher et al. 2006; De Kok et al. 2006; Billet et al. 2007). In this sense, the $PM_{2.5}$ fraction has been demonstrated to be an important risk factor for health since it induces the presence of inflammatory and toxicological markers in the lungs, whose degree of adverse effect depends not only on the concentration but also on the source of emissions (Duval et al. 2008). In terms of mass concentration, fine and ultrafine particles are strongly associated with the increments in mortality when they are compared with coarse particles (Schwartz et al. 1999). These effects of fine particles on public health depend on the content of some of their chemical components. Among these are some trace elements, especially some heavy metals, whose presence renders them more toxic (Sharma and Maloo 2005). The fraction of metals in particles, although it is usually very low in terms of mass, could represent a substantial part of the toxicity of the suspended particles (Schwela 2000). Despite this, in MZG, there is currently scarce information that supports the aforementioned presence of metals and that also tackles the analysis of the degree of exposure of the population to this kind of toxic pollutants.

The aim of the present research study is to describe the behavior per site and per season of the mass of $PM_{2.5}$ as well as to analyze elemental components and their contribution to the composition of fine particles, in order to know the degree of exposure to trace and heavy elements, which due to their known toxicity represent a risk to MZG inhabitants' health.

Materials and Methods

The selected particle collection sites were Centro and Miravalle, which is located in the southern MZG. At these sites data on the levels and variation of $PM_{2.5}$ are known, and there is also information, mainly inorganic, about their composition. Likewise, at these two sites the Atmospheric Monitoring Network of Guadalajara City (Red de Monitoreo Atmosférico de la Ciudad de Guadalajara (RAMAG) has automatic monitoring equipment for some of the meteorological parameters (relative humidity, temperature, wind velocity and direction). The samples of $PM_{2.5}$ were taken using low volume Rupprecht and Patshnick Co. equipment model Partisol 2300 (New York, USA) which operated at 16.6 L min^{-1} for periods of 24 h (12:00–12:00 pm) between January and June, 2008. The methodology followed to analyze the samples has been extensively detailed by Saldarriaga-Noreña et al. (2009). Briefly, an acid extraction was carried out (30 mL HNO_3–HCl 2.6:0.9 M) in PTFE tubes by means of an ultrasonic bath for 30 min at 60–70°C; the acid extracts were adjusted to 50 mL and were analyzed by ICP-MS (Model ELAN 6100, Perkin Elmer, USA); the analytic system was calibrated by using calibration curves ($r > 0.999$) prepared in an acid solution of similar composition to the one of the samples. The instrumental detection limits for all analyzed metals were near to 0.0001 μg mL^{-1}, except for Fe and Mg which were 0.016 and 0.002 μg mL^{-1}, respectively. The validation of the analytical method was carried out using certified reference material SRM 1648 from the National Institute of Standards of Technology (NIST, Gaithersburg, MD, USA). Recovery of elements ranged from 80 to 120% with variations below 10%, except for Zn which was less than 20%.

The Shapiro–Wilk test was applied to the whole set of data in order to confirm their normal distribution. In the same manner, the data considered in this research study were validated by applying the percentiles from 10 to 90%, calculating basic parameters such as mean, standard deviation, median, maximum and minimum. The Mann–Whitney test was used to establish the significant differences in the levels of particles and their elemental components among sites and seasons. All the statistical analyses were carried out using STATISTICA 6 software.

Results and Discussion

The statistical analysis of the mass of the particles reveals that there were significant differences in their levels between sites when considering the entire sampling period, with the higher levels at Miravalle ($p < 0.05$). Also, from the data analysis per season (Dry Season (DS, January–May) and Rainy Season (RS, June), it is inferred that the median of the $PM_{2.5}$ at Miravalle showed a significant difference between seasons, presenting a higher amount of particles in DS ($p < 0.05$). At Centro, due to the variation in the levels of particulate matter in DS, differences with respect to RS ($p > 0.05$) could not be established. From these results, it can be highlighted also that at Centro there were relatively constant levels of mass of $PM_{2.5}$ during the first half of the year. The results from a research study on the levels of $PM_{2.5}$ for the same sites during 2007, carried out by Saldarriaga-Noreña et al. (2009), shows consistency toward what was found in the research study herein, because they demonstrate that there was a higher level of particles during DS at Miravalle, and also show that there were no differences between DS and RS for Centro. The difference in mass of the $PM_{2.5}$ observed between seasons at Miravalle could probably be due to rainfall and to the higher relative humidity during RS. In fact, a regression analysis performed between the mass of $PM_{2.5}$ and relative humidity showed an inverse relationship, which is non significant (data not shown), but it did show statistical differences in the levels of precipitation between DS and RS at the studied sites ($p < 0.0001$, in both cases). The higher relative humidity during RS favors an increase in the mass of particulate matter in the coarse fraction of the aerosol due to the hygroscopic growth condensation phenomenon of the particles, while the abundant rainfalls also facilitate removal processes (Chandra et al. 2006). So, both phenomena contribute to the reduction of the mass of the $PM_{2.5}$ particles. However, at Miravalle, the extent of the impact of this factor could be increased due to the properties of the predominant components of the particles. It has been documented that sulfates and nitrates are chemical species that provide the increment in the hygroscopy of particles (Friedlander and Yeh 1998; McMurry 2000). This is consistent with what was found by Hernández-Mena et al. (2010), who reported a larger presence of sulfates in the $PM_{2.5}$ from Miravalle during DS in 2007 than at Centro where there were no differences between these two seasons. On the other hand, low wind velocity favored the accumulation and minor dispersion of the pollutants at both sites, probably without causing a significant effect on the seasonal nature of the mass at Miravalle, since most of the wind velocity values are below 2.1 m s^{-1}, which are relatively slow winds. At Centro, the low values of wind speeds represented a higher percentage (78%) than the ones from Miravalle, nonetheless, the similarity in conditions renders this factor less helpful in explaining the seasonal nature of the mass of the $PM_{2.5}$ at Miravalle and its behavior at the city center (Centro).

Elements such as Fe and Ti were the most abundant ones at both sites, followed by species such as Zn and Mg. At both sites, Fe was the most abundant element; its average mass at Miravalle was 18,739.8 ng, while at Centro it was 14,517.7 ng. The average mass of all elements exhibited a downward trend from January until June only at Miravalle, while for both sites a similar pattern was found in the following degree of abundance: Fe > Ti > Zn > Mg. This was followed by elements such as Pb, Cr, Cu and Sr, all of which oscillated between 500 and 1,000 ng, and with the other species underneath this interval (Table 1).

The comparison between sites, regarding abundant elements, showed that the mass of Fe and Ti at Miravalle was significantly different (higher) than Centro ($p < 0.001$ in both cases), and that less abundant species such as Pb, Mn, Sb and Sr also had higher levels at Miravalle (at least $p < 0.001$ for all cases). Nevertheless, species such as Cd, Cr and Se had higher mass levels at Centro (at least $p < 0.01$ in all cases). These results contributed to the fact that the total sum of the monthly averages of the mass of the elements during the period of the research study is also greater ($p < 0.01$) at Miravalle due to the presence of those species, reaching the 35,648 ng in February.

Table 1 Mass of elemental components (ng) associated with $PM_{2.5}$ (mg) for two sites in Guadalajara City during the first half of 2008

Miravalle						
	n	Mean	Median	Minimum	Maximum	SD
$PM_{2.5}$	31	1.790	1.720	1.240	2.390	0.380
Pb	30	996.45	896.21	278.74	2216.31	538.32
Cd	35	139.62	139.28	5.30	355.24	81.06
Co	32	94.38	145.03	9.03	152.48	66.34
Cr	25	656.54	607.56	29.99	1172.95	321.47
Cu	33	601.2	527.8	81.5	1135.9	293.5
Fe	34	18739.8	20401.6	2678.1	28983.8	6329.4
Mg	32	2306.1	2247.2	820.7	4569.9	902.2
Mn	32	601.8	600.5	273.2	936.3	169.1
Mo	33	80.6	108.5	17.3	128.6	44.8
Ni	34	191.9	185.3	70.9	414.1	77.2
Sb	32	258.5	244.2	59.1	648.6	131.0
Se	34	84.1	92.3	28.0	149.1	32.2
Sr	32	696.3	747.5	319.0	1070.2	211.3
Ti	32	6124.5	6145.5	3037.1	8634.8	1615.3
Zn	34	3825.1	3034.4	673.0	13565.4	3061.2
Sum		34603.1	35749.1			
Centro						
	n	Mean	Median	Minimum	Maximum	SD
$PM_{2.5}$	33	1.300	1.300	0.800	1.900	0.300
Pb	35	558.0	417.0	115.5	3855.0	651.1
Cd	33	202.6	164.9	42.4	431.9	102.6
Co	34	95.8	140.6	10.9	147.5	61.9
Cr	30	988.9	846.4	261.9	2324.3	567.5
Cu	35	640.4	472.9	44.3	2781.3	561.3
Fe	33	14517.7	14531.5	8193.8	22222.6	3652.1
Mg	34	2583.4	2212.6	1260.8	8225.4	1296.7
Mn	33	475.6	434.2	305.8	697.0	109.9
Mo	34	82.6	111.3	14.4	136.6	45.3
Ni	34	213.0	207.1	132.3	411.8	57.0
Sb	33	142.4	145.4	53.6	231.3	46.9
Se	35	106.7	106.9	19.5	240.6	38.9
Sr	33	530.4	551.9	295.1	861.4	140.7
Ti	33	4365.3	4300.9	2766.5	6769.7	1045.4
Zn	33	3453.8	3053.7	1273.1	7874.7	1708.5
Sum		29160.4	28832.0			

n sampling size, *SD* standard deviation

Regarding the behavior of the elements between seasons, at Miravalle, it was observed that Pb, Co, Fe, Mg, Mo, Ni, Sb, Se and Ti had higher levels of mass (at least $p < 0.05$ for all cases) during DS, while at Centro Cd, Co, Cr, Cu, Mo and Sb were the ones with higher mass during the same season (at least $p < 0.03$ for all cases). Co, Mo and Sb were the elements that showed differences in the mass of the particles between DS and RS at both sites. The apparent incongruence between similar levels of mass of the particles between seasons at Centro and the higher levels of Cd, Co, Cr, Cu, Mo and Sb during DS can be explained since those species are not the ones that contributed the most to the mass of the $PM_{2.5}$. This behavior coincides with the one from a study made in 21 cities in Europe for some of the species under study, where the expected pattern of higher concentrations was found during winter months for Cu, Mn, Pb and Ti in most of the cities (Götschi et al. 2005). These results suggest that probably the meteorological conditions that predominate during DS (lower temperatures, low relative humidity and scarce rainfalls) could have favored higher particle levels, especially at Miravalle, as well as a higher quantity of some elemental species associated with the particles, including, two of the most abundant such as Fe and Ti.

The presence of the elements considered in this research study was handled as a contribution (in %) to the mass of the $PM_{2.5}$ per sampling. From January to June, similar contributions were observed between sites; at Miravalle the median was 1.97%, while at Centro it was 2.05%. At Centro, those components have a slightly larger contribution to the mass of the particles ($p < 0.03$), although at Centro significantly lower particle masses were measured. Of the elements in general (except Cd, Cr and Se), the contribution that these make to the mass of the $PM_{2.5}$ was greater at Centro than at Miravalle. These results suggest that other components, either organic or inorganic, are found in a slightly less proportion inside the $PM_{2.5}$ at Centro, while at Miravalle those same components are probably more abundant. The analysis of the variation of the elemental contribution to the mass of the particles for 24 h periods shows that at Centro, at the beginning of May, there are days with much higher proportions than the other days, a time period which without a doubt contributed to the observed differences between sites, when considering the entire period of the study.

Likewise, the monthly contribution per element as a part of the total monthly mass of all elements was estimated. The ones that showed an important contribution to that mass (Fe, Ti, Zn and Mg), are represented individually in Fig 1a and b, while those elements whose contributions were lower than 5% were combined and comprised another group (others); their contributions are shown in different figures for each site. In this manner, the appreciation of

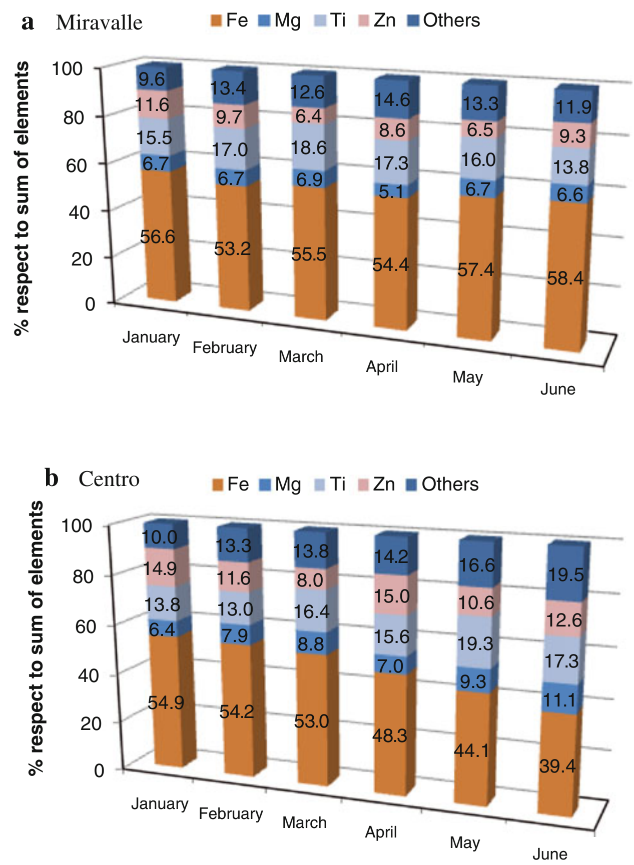

Fig. 1 Contribution of the most abundant elements associated with $PM_{2.5}$ with respect to the total mass of elements. In both sites, it is evident that Fe is the main elemental specie during the research study time period

how Fe was the biggest contributor becomes clearer, oscillating between 56 and 58% from January to June at Miravalle and showing low variation throughout time, while at Centro it oscillated between 55 and 40% for the same period, but with a clear downward trend, mainly between April and June. In a chemical composition and source of particulate matter research study undertaken in Mexico City, Fe was determined to be an important component of soil (Mugica et al. 2009). Also, in a previous research study in Guadalajara City during 2007 (Saldarriaga-Noreña et al. 2009), through the estimation of the Enrichment factor, it was pointed out that Fe had a geologic origin. Ti had the second biggest contribution with values between 13.8 and 17.6% at Miravalle and between 13 and 19.3% at Centro. The group of elements identified as "others" reached contributions of up to 20% during June at Centro.

In summary, the results indicate a clear season driven behavior of the mass of particles in Miravalle, which is likely caused by environmental conditions that favor the accumulation of pollutants and by the nature of the chemical composition of the particles with significant concentrations of sulfates and nitrates, thereby favoring their hygroscopic properties, which resulted in a smaller amount of suspended particles during the rainy Season (RS). On the contrary, at Centro the mass was maintained almost constant without any apparent significant effects stemming from the environmental conditions throughout both seasons. The analysis of the elemental composition revealed that Fe and Ti were the most abundant species at both sites, with mass values oscillating between 10,000 and 20,000 ng (Table 1). Likewise, the calculus of the contribution of the total concentration of the elements to the mass of the $PM_{2.5}$ shows that it is practically the same for both sites: 1.97 and 2.05% for Miravalle and Centro, respectively. These values suggest that the $PM_{2.5}$ in Guadalajara City is probably influenced by other chemical species of organic and inorganic compounds that are different from the metallic species which contribute significantly to the total mass of the particles. These other chemical species define the thematic to be developed in future research studies to obtain such information and support the approach of this hypothesis. Therefore, it is evident that there is the need to measure another type of chemical species that have not been currently determined in Guadalajara's Metropolitan Area.

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