Bull Environ Contam Toxicol (2011) 87:545–549
DOI 10.1007/s00128-011-0369-x

Enrichment Factor and Profiles of Elemental Composition of PM 2.5 in the City of Guadalajara, Mexico

Leonel Hernández-Mena · Mario Murillo-Tovar · Martín Ramírez-Muñíz · Edith Colunga-Urbina · Iliana de la Garza-Rodríguez · Hugo Saldarriaga-Noreña

Received: 3 May 2011 / Accepted: 15 July 2011 / Published online: 12 August 2011

Abstract In this study, the Enrichment Factors and elemental composition profiles of the PM2.5 were used to suggest the emission sources. The selected sites were Miravalle and Centro, and in both cases there were high values lead, Cadmium, Cobalt, Chromium, Cupper, Molybdenum, Nickel, Antimony, Selenium and Zinc for EF (>5), suggesting an anthropogenic origin. The remaining elements (Iron, Magnesium, Manganese, Strontium and Titanium) had Enrichment Factors <5, attributable to a geological origin, probably due to the suspension of particles from motor vehicles or wind. Comparing the elemental composition profiles of the two sites allowed establishing similarities with some reference profiles (SPECIATE database Version 4.2-EPA) from sources such as Paved Road Dust (PRD) and Industrial Soil (IS) and profiles of combustion sources such as Diesel Exhaust (DE). Through the estimation the Enrichment Factors and of the elemental composition profiles of two different sites in the city, it was possible to suggest not only the general type of emission source (geological or anthropogenic), but also more specific sources based on elemental composition of PM2.5.

Keywords Enrichment factor · PM2.5 · Elemental composition profiles

L. Hernández-Mena · M. Murillo-Tovar · M. Ramírez-Muñíz
Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco, Guadalajara, Mexico

E. Colunga-Urbina · I. de la Garza-Rodríguez · H. Saldarriaga-Noreña (✉)
Facultad de Ciencias Químicas, Universidad Autónoma de Coahuila, Saltillo, Coahuila, Mexico
e-mail: hugosaldarriaga@uadec.edu.mx; hsaldarriaga@unam.mx

The City of Guadalajara with its metropolitan area is the second largest urban area of Mexico according to the National Institute of Statistics and Geography 2000 (INEGI for its acronym in Spanish 2000). One of the main pollutants affecting air quality are the fine particles less than or equal to 2.5 μm (PM2.5). Vehicle emissions are a major source of PM2.5, followed by the soil, secondary aerosols, industry, etc. (Mugica et al. 2009). PM2.5 not only differ in composition, but also on characteristics such as solubility, persistence in the atmosphere, reactivity, biological properties (toxicity and carcinogenicity), chemical structure and elemental composition, where its toxicity depends on the emission sources and their aerodynamic diameter (Kim and Jaques 2000; Götschi et al. 2005). PM2.5 is a major risk factor for human health as it is associated with the presence of inflammatory markers and oxidative stress in the lungs, where the effects depend on the concentration and emission sources (Duvall et al. 2008; Romieu et al. 2008). Fine particles are more strongly associated with increments in mortality than coarse particles, when considering the mass concentration (Schwartz et al. 1999). Furthermore, these effects depend on the content of their chemical constituents, including trace elements such as heavy metals, whose presence is attributable to the toxicity of the particles (Schwela 2000; Sharma and Maloo 2005).

One of the tools that can help determine the emission sources of PM2.5 components is the estimate of the Enrichment Factor (EF), which allows distinguishing between potential sources of components of geological or anthropogenic origin (Duan et al. 2006; Haritash and Kaushik 2007; Chen et al. 2008; Saldarriaga-Noreña et al. 2009). Therefore, with the purpose of complementing previous studies realized in the city of Guadalajara about the chemical characterization of the PM2.5, was carried out this study. Which complemented the estimated EF with elemental composition profiles of reference obtained from the SPECIATE database Version 4.2 (USEPA 2008). These tests lead us to suggest specific emission sources that affect the elemental composition of fine particles in two different places of the city.

Materials and Methods

In order for complement the previous studies that have been conducted on the composition of PM2.5 in the city of Guadalajara, the selected sites were Centro and Miravalle, since there is information on their chemical composition. The samplings were carried out in Rupprecht and Patshnick Co. equipment model Partisol 2300 (New York, USA) at a flow for 16.6 L min^{-1} for periods of 24 h (12:00–12:00 p.m.) between January and June 2008. The analytical methodology is well explained by Saldarriaga-Noreña et al. 2009. Briefly, the determination of the elements was made by ICP-MS equipment (Model ELAN 6100, Perkin Elmer. USA). The analytical method validation was carried out using certified reference material SRM 1648 (National Institute of Standards and Technology, Gaithersburg, MD, USA). The recoveries of the elements ranged from 80% to 120%, with variations below 10% (except Zn with 20%), these percentages were used to correct the concentration of each species in the real samples. For the elements quantification (Pb, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Sb, Se, Sr, Ti and Zn) we prepared calibration curves in a concentration range between 1 and 100 ng μL^{-1}, all showed correlation coefficients equal to or greater than 0.999.

The mass data elements were validated using percentiles of 10 and 90%, from these, and considering all the sampling period, we estimated the average contributions that these make to the average mass particles. A least square linear regression analysis between the profiles of elemental composition of study sites and six reference profiles for PM2.5 emissions published by the USEPA, allowed us establish the similarity between them and define the main sources of emissions of the PM2.5 elements the in the city. The reference composition profiles were estimated as averages from all cases included in the database PM2.5 SPECIATE Version 4.2 for each source.

Results and Discussion

One way to estimate the possible sources of the elements associated with the PM2.5 can be carried out by calculating the Enrichment Factor (EF) established by Taylor (1964), the calculation takes as reference the mean abundances of each element in geologic material (mg L^{-1}). For this analysis, EF was used as the reference element. The way to estimate the EF is:

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

where X is the element of interest, while (X/Y) air and (X/Y) crust refer to the ratio between the concentrations of the element of interest (X) with respect to EF (Y) in the air and geological material, respectively. If the estimated value for EF is approximate to the unit, soil and geological materials are the dominant sources of fine particles. On the other hand, if EF is greater than 5, the element of interest is originated from anthropogenic emission sources. For the EF we used both the geological concentration and the air of K (data not shown) as a reference. Both sites showed high values (>5) for Pb, Fe, Cd, Co, Cr, Cu, Mo, Ni, Sb, Se and Zn, suggesting that they come from anthropogenic emission sources (Table 1). The remaining elements (Fe, Mg, Mn, Sr and Ti) had <5, indicating that come from other sources, which may include re-suspension of particles of geological origin, either by passing motor vehicles or the wind (Jones and Harrison 2004; Haritash and Kaushik 2007). The EF results in both sites and the order of abundance established from the mass determined for (Fe > Ti > Zn > Mg > Pb), reported by Saldarriaga-Noreña et al. 2009, suggest that particles of geological origin also have an important influence on the elemental composition of PM2.5 in the city of Guadalajara, mainly due to the contribution of Fe, Ti, and Mg. However, some of the least abundant species, but with an EF greater than 5, are mainly attributed to different anthropogenic activities (including Pb, Co, and Cu); the EF value for Zn was also originated from anthropogenic sources and was the third most abundant element in the two sites. These results are congruent with other studies that used the same tool of analysis. In this respect, Duan et al. (2006) in a study in the city of Beijing, found that species such as Fe, Ti and Mg are mainly related to natural sources such as geological materials, while Zn, Cu, Se, and Pb, due to their higher EF value are believed to be derived from different sources such as anthropogenic. In Shanghai, through EF value estimation, Chen et al. (2008) indicate that Cd, Cu, Pb, Zn, and Sb come from different sources to the geological material and at least the first four are also incorporated into the atmosphere by multiple combustion processes. Dutkiewicz et al. (2006) reported that Zn and Pb are associated with vehicle emissions and are used in non-ferrous alloys in the area of Queens, New York. They also mentioned that measurements for Ni and Co on this site may be due to emissions from combustion of residual oil. The presence of Se in New York may be associated with primary sources such as coal combustion, which indicates the transportation of these sources outside of this city. It is noteworthy that despite the introduction of unleaded gasoline in our country for several years, this species was the fifth and seventh most abundant in Miravalle and Centro, respectively. The same situation was observed for Sharma and Maloo (2005) who indicated that the presence of Pb in fine particles in air ambient can represent a high health risk.

To complement the EF results and be more specific in suggesting possible sources of the PM2.5 emissions, based on elemental composition, we performed a least squares linear regression analysis between the elemental profiles of PM2.5 in Miravalle and Centro (for the whole period), with a widely used reference like the SPECIATE database Version 4.2 of the USEPA. This database includes data records, collected from scientific publications by the literature and research organizations, on the pollutants' profiles in both gas phase and particles from specific sources; in this case, with particular interest on the profiles of elemental composition of PM2.5. It is because of anthropogenic activities that characterize at Centro and Miravalle, and the EF values of the most abundant species (Fe > Ti > Zn > Mg > Pb), it was decided to establish the relationship with the following profiles obtained from the database: Gasoline Exhaust (GE), Diesel Exhaust (DE), Tire Wear (TW) Paved Road Dust (PRD), Industrial Soil (IS) and Residual Oil Combustion (ROC). For Miravalle, which is characterized by near avenues with high traffic flow, high industrial activity, areas without vegetation (dry season occurs in the first half of the year), and residential areas nearby, the elementary profile was more closely related to those of sources such as PRD ($r^2 = 94\%$), DE (72%), and IS (68%), all significant (at least $p < 0.001$ in all cases). For the Centro site, which is a business area, with residential land use and increased vehicular activity, including public transportation, the elemental profiles of PRD, DE and SI sources showed r^2 values of 89, 75 and 66%, respectively (at least $p < 0.001$ in all cases). The r^2 values for PRD and IS in the latter site were slightly lower than those observed in Miravalle, suggesting a lower impact of these sources in the elemental composition profile of the particles at Centro, it is important to note that in the latter site, the DE profile source was slightly higher ($r^2 = 0.75$), compared to Miravalle, suggesting that this activity, attributed to diesel vehicles, has a slightly greater impact on the elemental composition of the particles. In both sites there were no significant correlations with basic profiles of GE, ROC, and TW ($p > 0.05$), so these three sources have less impact in defining the elemental composition of fine particles. Figure 1 compares the basic profiles of the study sites with the best correlation profiles for PRD, DE, and SI sources. In this figure, is important to note that the contributions of Fe, Mg, Mn, and Zn for the reference profile of IS source and Fe in the PRD profile, were very high compared with those estimated in Miravalle and Downtown, this may reflect some characteristics of these sources, particularly with regard to the abundance of elements of geological origin.

Table 1 Enrichment factors (EF) estimated for elemental species associated to PM2.5 in the study sites during the first half of 2008

Element	E F	
	Miravalle	Centro
Pb	**204.51**	**147.8**
Cd	**1862.61**	**3488.8**
Co	**10.07**	**13.2**
Cr	**17.5 2**	**34.1**
Cu	**64.16**	**88.2**
Fe[a]	0.94	0.9
Mg	0.29	0.4
Mn	1.69	1.7
Mo	**143.37**	**189.7**
Ni	**6.83**	**9.8**
Sb	**3448.54**	**2452.2**
Se	**4487.77**	**7349.6**
Sr	4.95	4.9
Ti	2.85	2.6
Zn	**157.01**	**183.0**

In bold those whose EF values >5

[a] Calculated from the geological concentration of PM2.5 and potassium (K)

The results of the EF estimation for each species and the least square linear regression analysis between the elemental composition profiles at Centro and Miravalle determined with the reference profiles, indicate that the most abundant elements (except Zn and Pb) in these two sites with EF <5, are most likely derived from sources such as PRD and IS. Perhaps the resuspension of geological materials by vehicles and buses as well as by the winds of the area, are related to the presence of Fe, Ti and Mg in the PM2.5 at these locations. In addition, the DE profile is also one of the most consistent with the profiles determined for Miravalle and Centro, which may explain the contribution of species with a value of EF >5, among which the presence of Zn and Pb is remarkable. It is reasonable that the PRD and IS have coincided with the profile determined in Miravalle since this site is characterized by developing a strong industrial activity, which represents a vehicular load that could re-suspend particles and leave a large area without vegetation. In the case of the Centro site, the elemental profile match with the PRD and IS sources, cannot be explained only by the vehicular re-suspension, but also by the transport of pollutants from nearby sites with some kind of industrial activity through wind and re-suspension, which are most likely are involved.

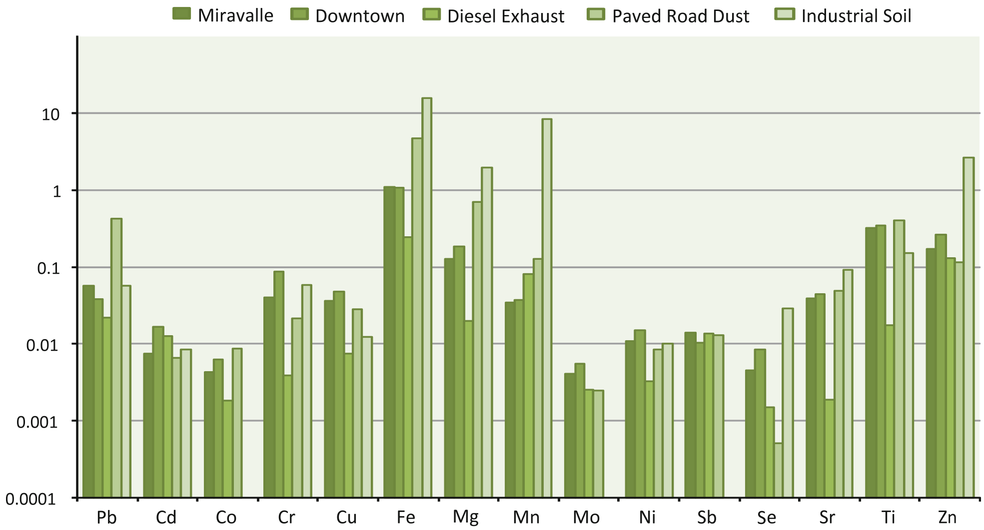

Fig. 1 Profiles of elemental composition of PM2.5 determined for two sites in the city of Guadalajara in the first half of 2008 and profiles of elemental composition of reference from three specific sources: *DE* Diesel exhaust, *PRD* Paved road dust, *IS* Industrial soil, estimated from the SPECIATE database version 4.2. The visual comparison is made through a logarithmic scale of the contribution (%) for the mass of PM2.5

Thus, the determination of elemental composition profiles of PM2.5 in two places in the city of Guadalajara, which share some anthropogenic activities as emission sources, but at the same time are distinguished by the presence and intensity of other sources, as the case of Miravalle, and high industrial activity, has allowed to establish similarities with some reference profiles of sources such as PRD and DI, and also with profiles derived from combustion sources such as the DE profile. The estimated profiles of elemental composition of PM2.5 and its relation to the reference profiles obtained from the SPECIATE database version 4.2, goes beyond the general sources suggested by the estimation of enrichment factors, thus acquiring an additional value by defining more specifically the emission sources based on their elemental composition. This study may be one of the first foundations for further research on the contribution given by each of these probable sources to the elemental composition of PM2.5 in the city of Guadalajara, using tools such as the Chemical Model Mass Balance (CMB).

In summary, this study used tools such as the estimation of enrichment factors and the profiles of elemental composition of PM2.5 in two places in the city of Guadalajara, to suggest not only the sources of general emission (geological or anthropogenic) which is made through the EF, but also to propose more specific sources through the relationship of these profiles with those considered as reference profiles obtained from a widely used source of information as the SPECIATE database Version 4.2. The elemental composition profiles for PM2.5 at Centro and Miravalle positively correlated with the profiles of sources such as PRD, IS, and DE, with and slight variations. It should be noted that although the basic components contribute little to the PM2.5 mass, its composition profiles allow us to approach most probable sources of emissions that affect the composition of fine particles in the city of Guadalajara.

Acknowledgments The authors would like to express their appreciation to Sandra Bravo and Rosalva Cuevas for their collaboration in the analysis of inorganic ions, to Winston Smith of the Peace Corps for the revision of this paper and to the Secretaría de Medio Ambiente para el Desarrollo del Estado de Jalisco (SEMADES), for allowing the installment of the equipment in their locations. Special thanks also to Consejo Nacional de Ciencia y Tecnología (CONACyT) for the financial support in this project.

References

Chen J, Tan M, Li T, Zheng J, Zhang Y, Shan Z, Zhang G, Li Y (2008) Characteristics of trace elements and lead isotope ratios in PM2.5 from four sites in Shanghai. J Hazard Mater 156:36–43

Duan FK, He KB, Ma YL, Yang FM, Yu XC, Cadle SH, Chan T, Mulawa PA (2006) Concentration, chemical characteristics of PM2.5 in Beijing, China: 2001–2001. Sci Total Environ 355: 264–275

Dutkiewicz V, Qureshi S, Husain L, Schwab J, Demerjian K (2006) Elemental composition of PM2.5 aerosols in Queens, New York: evalutation of sources of fine-particles mass. Atmos Environ 40:347–359

Duvall MR, Norris AG, Dailey AL, Burke MJ, McGee KJ, Gilmour IM, Gordon T, Devlin BR (2008) Source apportionment of particulate matter in the US and associations with lung inflammatory markers. Inhal Toxicol 20:671–683

Götschi T, Hazenkamp-von Arx EM, Heinrich J, Bono R, Burney P, Forsberg B, Jarvis D, Maldonado J, Norbäck D, Stern BW, Sunyer J, Torén K, Verlato G, Villani S, Künzli N (2005) Elemental composition and reflectance of ambient fine particles at 21 European locations. Atmos Environ 39:5947–5958

Haritash AK, Kaushik CP (2007) Assessment of seasonal enrichment of heavy metals in respirable suspended particles matter of a sub urban Indian city. Environ Monit Assess 128:411–420

Instituto Nacional de Estadística Geografía e Informática (INEGI) (2000) Sistema Municipal de Bases de Datos, SIMBAD. Censos poblacionales y vehiculares 2000

Jones AM, Harrison RM (2004) The effects of meteorological factors on atmospheric bioaerosol concentrations – a review. Sci Total Environ 326:151–180

Kim CS, Jaques PA (2000) Respiratory dose of inhaled ultrafine particles in healthy adults. Phil Trans R Soc Lond A 358: 2693–2705

Mugica V, Ortiz E, Molina L, De Vizcaya-Ruiz A, Nebot A, Quintana R, Aguilar J, Alcántara E (2009) PM composition and source reconciliation in Mexcio city. Atmos Environ 43:5068–5074

Romieu I, Barraza A, Escamilla C, Almstrand Ch, Díaz D, Sly P, Carin A (2008) Exhaled breath malondialdehyde as a marker of effect of exposure to air in children with asthma. J Allergy Clin Immunol 121:903–909

Saldarriaga-Noreña H, Hernández-Mena L, Ramírez-Muñíz M, Carbajal-Romero P, Cosío-Ramírez R, Esquivel-Hernández B (2009) Characterization of trace metals of risk to human health in airborne particulate matter (PM2.5) at two sites in Guadalajara, Mexico. J Environ Monit 11:887–894

Schwartz J, Norris G, Larson T, Sheppard L, Claiborn C, Koening J (1999) Episodes of high coarse particle concentration are not associated whit increased mortality. Environ Health Persp 107: 339–342

Schwela D (2000) Air pollution and health in the urban areas. Rev Environ Health 15:13–42

Sharma M, Maloo S (2005) Assessment of ambient air PM10 and PM2.5 and characterization of PM10 in the city of Kanpur, India. Atmos Environ 39:6015–6026

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. Geochem and Cosmochem Acta 28:1273

United States Environmental Pollution Agency (USEPA) (2008) SPECIATE Version 4.2, http://www.epa.gov/nrmrl/news/012010/news012010-s.html