

Article

Potential Sources of Trace Metals and Ionic Species in PM_{2.5} in Guadalajara, Mexico: A Case Study during Dry Season

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Abstract: This study was conducted from May 25 to June 6, 2009 at a downtown location (Centro) and an urban sector (Miravalle) site in the Metropolitan Zone of Guadalajara (MZG) in Mexico. The atmospheric concentrations of PM_{2.5} and its elemental and inorganic components were analyzed to identify their potential sources during the warm dry season. The daily measurements of PM_{2.5} (24 h) exceeded the WHO (World Health Organization) air quality guidelines (25 µg·m⁻³). The most abundant element was found to be Fe, accounting for 59.8% and 72.2% of total metals mass in Centro and Miravalle, respectively. The enrichment factor (EF) analysis showed a more significant contribution of non-crustal sources to the elements in ambient PM_{2.5} in Centro than in the Miravalle site. Particularly, the highest enrichment of Cu suggested motor vehicle-related emissions in Centro. The most abundant secondary ionic species (NO³⁻; SO₄²⁻ and NH₄⁺) and the ratio NO³⁻/SO₄²⁻ corroborated the important impact of mobile sources to fine particles at the sampling sites. In addition, the ion balance indicated that particles collected in Miravalle experienced neutralization processes likely due to a higher contribution of geological material. Other important contributors to PM_{2.5} included biomass burning by emissions transported from the forest into the city.

Keywords: PM_{2.5}; trace metals; enrichment factor; ionic species; emissions sources

1. Introduction

In urban environments, epidemiological studies suggest that particulate matter (PM) is an environmental pollutant with adverse effects on human health. In addition, the more meaningful association between PM exposure and occurrence of diseases are found for smaller airborne particles [1]. Short- and long-term exposure to particles with an aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$) is linked to an increased risk of cardiopulmonary and lung cancer mortality [2,3] and reduced life expectancy [4]. Also, associations between chemical characteristics and PM toxicity tend to be stronger for the smaller PM size fractions [5]. Although air quality standards are used to control and manage exposure to its concentrations and emissions, a detailed understanding of the chemical composition of $\text{PM}_{2.5}$ is essential, since chemical substances not only play a crucial role in toxicity but also could be employed as a fingerprint to identify its origin [6].

$\text{PM}_{2.5}$ is constituted as a complex mixture of many different chemical substances resulting from distinct origin, either natural or anthropogenic, and from both primary and secondary particles with diverse effects on human health. Because diverse sources and multiple atmospheric processes are involved in the formation of $\text{PM}_{2.5}$, its chemical characterization must be based on simultaneous chemical analysis. Since occurrence of inorganic ions and heavy metals is due to multiple atmospheric routes, and many of them are primarily present in fine particles [7,8], these are very frequently analyzed to identify sources of $\text{PM}_{2.5}$. In $\text{PM}_{2.5}$, sulfate, nitrate and ammonium are the more abundant ionic species [9]; 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) [10–12]. Their occurrence in the urban environment can influence bioavailability of metals and exposure to fine particles may increase deposition of toxic compounds in the lungs [13,14]. Conversely, trace metals are minor components, and their origin is mainly by direct emission, either anthropogenic or/and geological [15]. With respect to their toxicity, transition metals such as Fe and Cu contribute to the oxidative capacity of PM [16]. Indeed, the ferrous ions in particle matter (PM) play an important role in the generation of hydroxyl radicals [17], a reactive oxygen species (ROS) that act synergistically with other PM-related chemical species. They can damage membrane lipids, proteins and DNA, which can alter respiratory immune responses in exposed individuals [18] and result in cell death via either necrotic or apoptotic processes and eventually cause and/or aggravate lung diseases [19]. Moreover, the element Zn has shown correlation with pulmonary inflammation by inhalation toxicology studies using animal models [20], and those elements with the lowest atmospheric concentration, such as Cd, Co, Cr, Ni and Pb, are known to be animal or human carcinogens [21].

The Metropolitan Zone of Guadalajara (MZG) that comprises Guadalajara City is located in the Atemajac valley in the western Mexican territory and has the second largest population in Mexico with around 4.4 million inhabitants in an urban area of about 2734 km^2 [22]. Because the industry and vehicular traffic activities have rapidly risen from the nineties, the city of Guadalajara currently experiences a high stress on the environment, particularly in urban and peri-urban areas. There are frequent episodes of poor air quality in its urban area due to high atmospheric concentrations of ozone and particulate matter exceeding the Mexican 24-h standards, mainly occurring during dry seasons [23]. Therefore, the identification of emission sources is essential to finding effective methods to control exposure to air pollutants [24]. In addition, this can contribute to a better understanding of their formation mechanism in urban areas. So far, the earliest studies undertaken to identify sources suggest that $\text{PM}_{2.5}$ in Guadalajara results from a mixture of anthropogenic and biogenic sources [25–28]. However, analysis of information on how particles are specifically emitted and how they respond to variations in their environment during the warm dry season is scarce.

Hence, the present study aims, with a short and intensive campaign, to identify the potential emission sources of $\text{PM}_{2.5}$ collected at a downtown site and an urban site in Guadalajara City, based on spatial variation and the elemental and inorganic ions composition analysis during a dry season.

2. Methods

2.1. Monitoring Sites and Meteorological Conditions

The PM_{2.5} measurements were made on the flat roofs of two local health facilities: Centro (CEN), situated in the downtown, and Miravalle (MIR), located to the southwest in the Metropolitan Zone of Guadalajara (Figure 1). Both sites have atmospheric monitoring stations operated by the Jalisco State Government. The meteorological parameters used in this study were obtained from those stations. Centro is an urban site with commercial and services activities and surrounded by heavily traveled paved curbed surface streets with light duty vehicles and heavy-duty diesel buses. In addition to infrastructure streets and similar types of vehicles as those traveling in Centro, Miravalle is located 100 m from a major arterial street with fast vehicular traffic and a rapid transport system for passengers, and is surrounded by dense residential areas and some industrial facilities. In addition, Miravalle is an urban site with nearby green areas and an inactive volcano, called Cerro del Cuatro, about 270 m above surrounding ground level, located to the south-southwest (~2 km).



Figure 1. Locations of the sampling sites, CEN (Centro) and MIR (Miravalle).

During the sampling period (May 25 to June 6, 2009), the climate presented dry–warm characteristics and moderate winds. While in Miravalle the wind speed ranged from 0.1–9.1 m·s⁻¹, in the Centro station it was between 0.1–5.5 m·s⁻¹. The relative humidity (RH) ranged 11%–82% and 16%–88% at Centro and Miravalle, respectively. In both, the temperature range was 17 °C–33 °C. It was observed that the wind came from the west and west-southwest at the CEN and MIR sites, respectively (Figure 2).

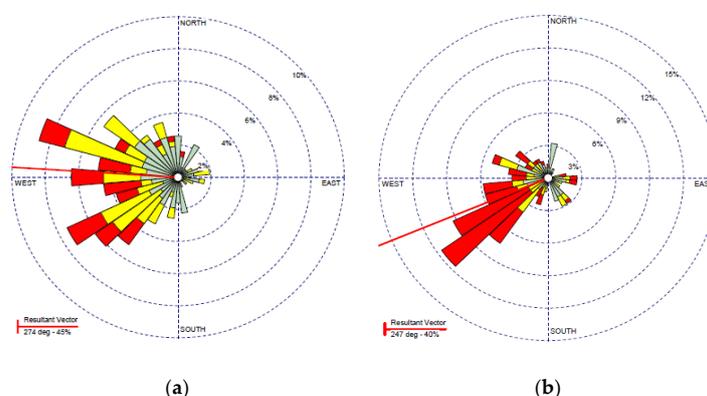


Figure 2. Wind roses during the study period in CEN (a) and MIR (b) sites. Wind speed (m/s): ≥3.6, 2.1–3.6 and 0.5–2.1.

2.2. Sampling and Chemical Analysis

In order to carry out the chemical characterization of PM_{2.5}, the samples were obtained every third day using a Partisol 2300 sampler (Rupprecht and Patashnick Co.). The particles were collected simultaneously for 24 h (12:00–12:00) at 16.6 L·min⁻¹ flow on Nylon (MAGNA) membrane filters and at 10 L·min⁻¹ flow on PTFE (PALL) discs (47 mm diameter and 0.2 µm pore size) for ions and elements analysis, respectively. The respective field and laboratory blanks were included daily in each individual sample set. The filters were conditioned and stabilized under controlled relative humidity (45 ± 5%) and temperature (about 22 °C) before and after the sampling for about 24 h. The concentrations of PM_{2.5} in ambient air (µg·m⁻³) were obtained from the ratio of the particle weight on the PTFE filter to its corresponding air sampling volume drawn through a cartridge filter holder corrected to EPA's [29] standard temperature and pressure (25 °C and 760 mm Hg). The mass of each filter, with and without samples, was accurately measured in triplicate on a micro analytical balance SE2F (Sartorius) with a readability of 0.1 µg. Only mass averaged measurements with a repeatability less than 0.01% were included. As the mass of particles was validated and successfully recorded, filters were put in Petri dishes and stored in polyethylene zip-lock bags at ~5 °C until chemical analysis.

The details of the samples' chemical analysis are described in Saldarriaga *et al.* [27] and Hernández *et al.* [28]. Briefly, for the analysis of metals, the PTFE filters were extracted in an ultrasonic bath for 3 h at about 60 °C–70 °C, using 50 mL of HNO₃–HCl (2.6:0.9 M). The determination of the elements was carried out by ICP-MS equipment (ELAN Model 6100, Perkin Elmer, USA). For the quantification a multicomponent calibration curve was used for Pb, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Sb, Se, Sr, Ti and Zn with determination coefficients (r²) greater than 0.999, performed on a range of 1.0 to 100 ng·mL⁻¹. The concentrations of the elements in real samples were corrected with blanks and the recoveries (80%–120%) obtained by extraction from SRM 1648 (NIST) [27]. The ion analysis was performed with the Nylon filters; samples were extracted with Milli-Q water (18.2 MΩ) in an ultrasonic bath (Branson 5510) for 1 h. The aqueous extracts were passed through a nylon micropore membrane (0.45 µm diameter) and the ionic chemical species were separated and subsequently identified by an ion chromatographer (IC) 861-Advanced Compact with conductivity detector (Metrohm). The anions (SO₄²⁻, NO₃⁻, Cl⁻, PO₄³⁻ and NO₂⁻) were analyzed by chemical suppression with a Metrosep A Supp5—150 column (Metrohm); the mobile phase used was a carbonate solution of sodium–sodium bicarbonate (8.0:4.0 mM). The cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were determined without chemical suppression in a Metrosep C2_150 (Metrohm) column; the mobile phase was a solution of tartaric–dipicolinic acid (4.0:0.75 mM). For quantification of all species, calibration curves were performed at a concentration ranging 0.0625–10 µg·mL⁻¹ and with correlations coefficients (r²) also greater than 0.999.

2.3. Statistical Analysis

The normality of data per site was determined using the Shapiro-Wilk test. For the nonparametric and more robustness tests, the Mann-Whitney U and the Spearman correlation coefficient were employed to make comparisons between sites and for the evaluation of association between variables, respectively. These were only applied when at least three observations were obtained and validated. In addition to statistical analysis, the simple linear least squares regression was performed for the presence of neutralizing events between ions. All tests were conducted using the STATISTICS 6 software.

3. Results and Discussions

3.1. PM_{2.5} Levels

The epidemiological evidence has shown widely adverse effects of fine PM following both short-term and long-term exposures [30,31]. The results found in this study indicated that the urban

population in Guadalajara was exposed to short-term PM_{2.5} concentrations highly hazardous to health. Although the PM_{2.5} Mexican ambient quality standard (65 µg·m⁻³) was only exceeded once (Table 1), almost all individual PM_{2.5} concentrations measured (99%) exceeded the WHO Air quality guidelines [32] for that air pollutant (25 µg·m⁻³ 24-hour mean). For comparison, the PM_{2.5} average atmospheric concentrations in Guadalajara were higher than those in the Valley of Mexico (29 µg·m⁻³) and slightly higher than the ones found for the Monterrey (34 µg·m⁻³) Metropolitan Areas [33], which are Mexico’s first and third biggest urban zones, respectively. Nevertheless, spatial variation must also be taken into account before emission control actions, since the PM_{2.5} average air concentrations ± standard deviation found in Miravalle (58.0 ± 13.0 µg·m⁻³) were, on average, higher than those recorded in the Centro site (39.3 ± 12.0 µg·m⁻³). Saldarriaga-Noreña *et al.* [27] and Limon-Sanchez [34] similarly observed this spatial trend in May–Jun 2007 and 2008 in Guadalajara, indicating that, over that period, there has not been an effective action to mitigate this air pollution issue.

Since meteorological conditions reported by both monitoring stations were similar, it clearly shows that the high spatial variation could be attributed to differences between the emission sources in each study site. Thus, in addition to vehicular traffic intensity, in Miravalle those highest concentrations of PM_{2.5} could be attributed to the larger resuspension of dust from bare green areas surrounding the site during the dry season (Figure 1). The wind direction suggested emissions transport from the southwest. What most likely contributed to the ambient levels of PM_{2.5} found in Miravalle was either resuspended particles from the inactive volcano area located on this trajectory or the regional or long-range transport of air pollutants that traveled from areas situated to the southwest and southeast.

Table 1. PM_{2.5} (µg·m⁻³) and trace metals concentrations (ng·m⁻³) in Centro and Miravalle sites.

	Centro					Miravalle				
	n	Mean	SD	Median	Range	n	Mean	SD	Median	Range
PM _{2.5}	6	39.3	12.0	43.0	16.0–49.2	6	58.0	13.0	62.2	37.0–72.5
Pb	4	7.8	3.8	7.6	3.8–12.4	4	12.8	7.6	12.7	3.6–21.9
Cd	5	8.0	4.1	8.6	3.5–13.3	5	5.1	2.7	5.4	2.2–4
Co	-	n.d.	-	-	-	3	0.4	0.0	0.4	0.3–0.4
Cr	6	9.2	2.4	10.2	5.2–11.1	6	16.6	1.9	15.6	14.9–19.6
Cu	3	107.0	16.9	108.8	89.2–122.9	1**	-	-	-	-
Fe	6	410.3	142.3	445.2	183.9–580.0	6	653.7	236.8	588.6	345.4–961.1
Mg	5	65.2	32.5	56.5	30.8–116.1	6	102.8	61.0	98.8	42.4–193.7
Mn	6	9.8	3.6	10.2	3.5–14.4	6	16.1	5.2	17.6	7.4–21.2
Ni	1*	-	-	-	-	2	4.0	-	-	3.4–4.5
Sb	2	2.1	0.2	-	1.9–2.2	5	2.0	1.0	1.5	1.4–3.7
Se	3	3.6	0.5	3.8	3.0–4.0	4	1.8	0.8	1.8	0.8–2.8
Sr	6	3.9	1.9	3.5	1.6–6.9	6	5.4	2.5	5.2	2.7–9.1
Ti	6	11.4	5.9	12.2	2.2–19.1	6	21.8	8.4	20.5	10.4–32.0
Zn	5	47.5	37.8	36.3	14.4–107.7	6	30.1	16.2	30.2	5.0–53.6

* 6.9 ng·m⁻³; ** 33 ng·m⁻³; n: sample size; SD: standard deviation; n.d.: not detected.

3.2. Metals in PM_{2.5}

The elemental analysis was performed for 14 metals (Table 1). In both sites, iron was the element most abundance in the PM_{2.5}. In the Centro site, Fe accounts for 59.8% of total elemental mass, followed by Cu (15.6%), Mg (9.5%) and Zn (5.9%), while in Miravalle it was 72.2%, followed by Mg (11.4%) and Zn (3.3%). The other metals account for 9.1% at Centro and 9.4% at Miravalle or sometimes were not quantified. The environmental levels of trace metals are of the same order of magnitude as those already reported in the earliest studies [27]. It is a concern to health, since the most abundant elements are heavy metals characterized by their toxicity.

Thus, the characterization and identification of potential sources of trace elements within the fraction of PM_{2.5} in the Guadalajaran atmosphere could provide scientific evidence for setting up

an air control strategy to decrease health risks due to inhalation of suspended particles. The most abundant species indicated that both sampling sites have a mixture of natural and anthropogenic sources, since Fe and Mg are primarily crustal elements, while Zn and Cu are primarily anthropogenic elements [35]. Spatial variation analysis by the Mann-Whitney test showed that the contribution from natural sources to PM_{2.5} in the Miravalle site could be more important than anthropogenic ones, since the medians of crustal elements [36], such as Fe, Mg and Mn, were found to be significantly ($p < 0.05$) higher or higher (Ti) only in the Miravalle site. Close in proximity to Miravalle, surfaces devoid of vegetation may be one of the possible causes of high levels of particles and anthropogenic elements such as Fe and Mg at this site. On the other hand, the Centro site seems to have a more important contribution from anthropogenic sources because the median concentration of primarily anthropogenic Zn and two elements (Cd and Se) that are considered as partially anthropogenic [37] were greater here than in Miravalle (Table 1), although differences were not significant ($p > 0.05$). It might be due to the fact that the Centro site has a higher traffic intensity. The abundance of elemental species and the geological and anthropogenic origin coincides with those results previously found in 2007 at the same sites [27], including the atmospheric mean concentrations.

The analysis of potential sources contributing to metals in PM_{2.5} at both sites was based on the principle that the degree to which the trace elements are enriched or reduced in aerosols is related to a specific source. That Enrichment Factor (EF) is frequently used [38,39] and is a reliable analysis tool to determine the impact of the type of emission sources on the elemental composition of the particles. The estimation of EF is based on the average abundances of the elements in geological material. Iron is suggested to be used as a reference element [40]. The following expression (Equation (1)), proposed by Taylor [40], was used to calculate the EF:

$$EF = (C_{xp}/C_p)/(C_{xc}/C_c) \quad (1)$$

where C_{xp} and C_p are the concentrations of trace metal "x" and Fe in the aerosol, respectively, and C_{xc} and C_c are their average concentrations in soil. It has been established that a value of $EF < 10$ is an indicator of trace metal from the soil; if it is between 10–100, it is a natural and anthropogenic mixture. In contrast, a value of $EF > 100$ is considered to be of an anthropogenic origin [41,42].

The EF patterns were very similar at the two sampling sites, indicating that both non-crustal and crustal emissions are contributing to mass of PM_{2.5}. The EF analysis (Table 2) showed that atmospheric concentrations of Fe, Mg, Mn, Sr and Ti found in PM_{2.5} are likely from natural sources ($EF < 10$). Furthermore, it is indicated that Cr and Zn may come from natural and anthropogenic sources ($10 > EF < 100$) and Se, Cd, Sb and Cu are mainly from anthropogenic sources ($EF > 100$). Most elements from anthropogenic sources were more highly enriched in Centro than those found in the Miravalle site, suggesting that the Centro site is being more impacted by non-crustal pollution emissions than Miravalle. The higher enrichment of elements in Centro by non-crustal sources could be explained by either industrial activities, since Cd comes from metallurgical processes [43], or traffic, because Zn and Pb are markers of vehicular emissions [44]. In urban areas, road traffic (diesel engines and brake wear) could be the most important source of Cu [45]. Conversely, an earlier study suggested that geological sources significantly influenced the generation of PM_{2.5} as much in Miravalle as they did in Centro [27].

Table 2. Estimated values for EF.

Element	Centro	Miravalle
Pb	86.0	87.9
Cd	5464.7	2193.0
Co	n.c.	1.2
Cr	12.6	14.0
Cu	266.9	n.c.
Fe *	0.1	0.1
Mg	0.4	0.4
Mn	1.4	1.5
Ni	n.c.	n.c.
Sb	n.c.	907.6
Se	9795.1	3686.4
Sr	1.4	1.3
Ti	0.3	0.3
Zn	80.4	37.0

* EF calculated with crustal concentration of Ca; n.c.: not calculated.

3.3. Potential Sources of Ionic Species in PM_{2.5}

In both sampling sites, nitrate (NO₃⁻), sulfate (SO₄²⁻) and ammonium (NH₄⁺) were the dominant inorganic ions species followed by Ca²⁺, K⁺, Cl⁻ (Table 3). The environmental levels of inorganic species are of the same order of magnitude as those already reported in an earlier study [28]. The statistical analysis, via the Mann-Whitney U test, showed that the higher median concentration of NO₃⁻ was in Miravalle. This is unlike the sulfate and ammonium species that showed similar median concentrations between sites (p > 0.05).

Table 3. Atmospheric concentrations (µg·m⁻³) for ionic species.

Site	Mean	Standard Deviation	Median	Minimum	Maximum
Centro					
Na ⁺	0.29	0.05	0.28	0.22	0.35
NH ₄ ⁺	2.71	2.11	2.01	1.31	6.85
K ⁺	0.36	0.13	0.38	0.18	0.57
Ca ²⁺	0.98	0.10	1.01	0.82	1.07
Mg ²⁺	0.08	0.06	0.07	0.00 ₂	0.15
Cl ⁻	0.23	0.08	0.26	0.14	0.28
NO ₂ ⁻	0.05	0.02	0.04	0.03	0.08
PO ₄ ³⁻	-	-	-	-	-
SO ₄ ²⁻	3.21	1.26	2.85	1.92	5.57
NO ₃ ⁻	10.74	14.34	4.72	1.33	38.22
Miravalle					
Na ⁺	0.33	0.16	0.34	0.06	0.54
NH ₄ ⁺	4.18	5.41	2.22	1.36	15.19
K ⁺	0.38	0.30	0.25	0.18	0.97
Ca ²⁺	1.55	0.45	1.40	1.07	2.31
Mg ²⁺	0.05	0.05	0.06	0.05	0.12
Cl ⁻	0.36	0.06	0.35	0.30	0.42
NO ₂ ⁻	0.06	0.04	0.05	0.03	0.11
PO ₄ ³⁻	0.12	0.05	0.09	0.09	0.18
SO ₄ ²⁻	4.18	1.77	3.83	1.89	7.12
NO ₃ ⁻	24.07	33.27	7.02	1.70	83.92

In Miravalle, nitrate accounts for 68.2%, followed by sulfate (11.9%) and ammonium (11.9%) of the total mass of inorganic ionic species. In Centro, nitrate account for 57.3%, followed by sulfate (17.1%) and ammonium (14.5%). Overall, while the spatially similar abundance (Figure 3) indicated likely common sources, the most abundant anions showed the important role that secondary sources played in the chemical composition of PM_{2.5}. This is due to oxidation processes in the atmosphere that mainly form in the particle phase involving their directly emitted precursors, nitrogen oxides (NO_x), sulfur dioxide (SO₂) and ammonia (NH₃) [46]. However, the order followed by these major inorganic ions and the urban characteristics of the sites suggested that the contribution of vehicular emission to formation of nitrate is also important and substantial. Because a significant portion of nitrate came from the atmospheric conversion of nitrogen oxides (NO_x) and ammonia (NH₃) [47], the high emissions of nitrogen oxides from heavy traffic in the urban environment could enhance the formation of nitrate in both sites. In addition, vehicle emissions of NO_x and local combustion processes have been suggested as the biggest sources of nitrate in urban areas [48].

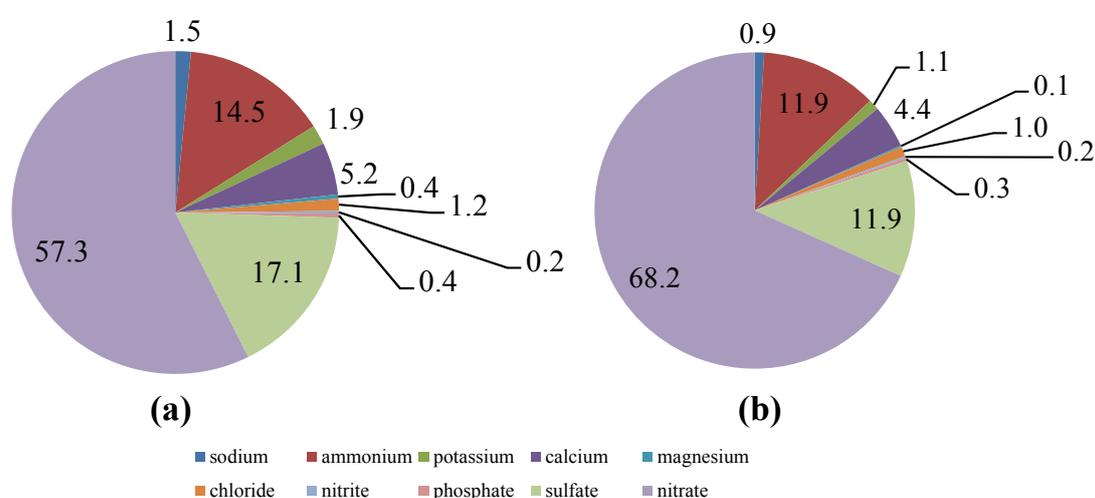


Figure 3. Relative contributions of ionic species to PM_{2.5} in CEN (a) and MIR (b).

Furthermore, higher NO₃⁻ mass than SO₄²⁻ suggested that the influences of motor vehicle emissions exceed those from coal combustion [49]. In this study, the average mass ratio (NO₃⁻/SO₄²⁻) at the Centro and Miravalle sites was 3.3 and 5.8, respectively. The high mass ratios indicated that mobile sources predominated significantly over stationary sources at both sites. These measured ratios were similar to those reported for urban areas such as Guangzhou (3.4–10.0), China [50] and for the city of Los Angeles (~2.0). The latter results emphasize that such findings may be due to no coal being used in this area [51]. These results were higher than the mass ratio observed for the city of Philadelphia (0.9), USA [52], which is due to that city having power plants that use coal as fuel. Nevertheless, the order of the less abundant ions Ca²⁺ > K⁺ > Cl⁻ also indicated a contribution to particles from natural sources either by geological origin or burning biomass, which could be attributed to the presence of Ca²⁺ and K⁺, respectively [53,54]. Therefore, the highest atmospheric concentration of Ca²⁺ in Miravalle could have resulted from dust resuspension due to surfaces being devoid of vegetation surrounding this sampling site, a frequent occurrence in the dry season. Conversely, higher K⁺ concentrations in Centro could have come from forest fires that occurred during the sampling period in the Primavera Forest located west of Guadalajara [55]. It was further noted that, during the sampling period, predominant westerly winds were observed, supporting the hypothesis that the K⁺ concentration could have been transported from the forest into the city.

The possible chemical forms of the ionic species were suggested by bivariate correlations with all the anions and cations analyzed. The correlation coefficients can be observed in Table 4. For Miravalle

NH₄⁺ with K⁺ and SO₄²⁻ correlated significantly ($p < 0.05$), while in Centro SO₄²⁻ and NO₃⁻ correlated with NH₄⁺. This indicated that compounds such as (NH₄)₂SO₄ and K₂SO₄ can coexist in Miravalle, while in Centro (NH₄)₂SO₄ and NH₄NO₃ are possible [56]. For the Centro site, a good correlation was observed between SO₄²⁻ and NO₃⁻ (0.76), which can likely be attributed to a similarity in formation conditions either from a shared emission source or a chemical conversion of their precursors through atmospheric processes [57].

Table 4. Correlation among inorganic ions (bold correlations are significant at $p < 0.05$).

	Cl ⁻	NO ₂ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Miravalle										
Cl ⁻	1.00									
NO ₂ ⁻	0.13	1.00								
PO ₄ ³⁻	-	-	1.00							
SO ₄ ²⁻	0.05	-0.20	-	1.00						
NO ₃ ⁻	-0.71	-0.53	-	-0.28	1.00					
Na ⁺	-0.68	0.17	-	-0.28	0.71	1.00				
NH ₄ ⁺	-0.47	-0.40	-	0.80	0.28	0.14	1.00			
K ⁺	-0.43	-0.50	-	0.77	0.18	-0.11	0.95	1.00		
Ca ²⁺	-0.46	0.61	-	-0.64	0.14	0.54	-0.48	-0.52	1.00	
Mg ²⁺	-0.18	-0.47	-	0.44	0.54	0.41	0.66	0.46	-0.54	1.00
Centro										
Cl ⁻	1.00									
NO ₂ ⁻	-0.32	1.00								
PO ₄ ³⁻	-0.69	0.11	1.00							
SO ₄ ²⁻	-0.19	-0.48	0.41	1.00						
NO ₃ ⁻	-0.66	-0.33	0.46	0.76	1.00					
Na ⁺	0.05	-0.23	-0.63	-0.25	0.06	1.00				
NH ₄ ⁺	-0.64	-0.34	0.51	0.82	0.99	-0.01	1.00			
K ⁺	-0.49	0.05	0.60	0.65	0.67	-0.61	0.70	1.00		
Ca ²⁺	0.18	0.60	-0.33	-0.95	-0.76	0.01	-0.81	-0.42	1.00	
Mg ²⁺	0.32	-0.14	0.43	0.06	-0.36	-0.80	-0.28	0.12	0.05	1.00

To evaluate the acidic nature of particles, a balance of ions was realized. Figure 4 shows the sum of cations plotted *versus* the sum of anions for each one of the sites sampled during the period of study ($\mu\text{eq}\cdot\text{m}^{-3}$). In Centro, the slope < 1.0 indicated that the concentration of anions was higher than that of the cations. Thus, those atmospheric particles had acidic properties during this sampling period. These results are consistent with those previously reported [28] for the Centro site in 2007, taking into account the same ionic species, while in Miravalle a slope of about 1.0 (1.08) was obtained, indicating neutralization processes, which is different than that observed during a previous study [28]. Thus, there were enough cations to neutralize the sulfate and nitrate present in the Miravalle environment, which likely originated either by contribution of additional cations from resuspended particles (Ca²⁺, Mg²⁺) or from being buffered by the higher average concentrations of NH₄⁺ found in Miravalle [58], which were almost two-fold of that measured in Centro (Table 4). Since NH₄⁺ formation on particles responds to variations in environmental conditions and availability of precursors [59], the similar atmospheric conditions found in Centro and Miravalle during the study suggested that the highest average atmospheric concentration of ammonium in Miravalle could be controlled by factors other than temperature and relative humidity. Therefore, there could be a contribution by secondary particles transported from traveled areas situated to the southeast; although the volcanic hill is a geographic barrier for the air mass from that direction (southwest), its elevation and the geography of the area could be causing some turbulence and channeling of winds near the study area [34].

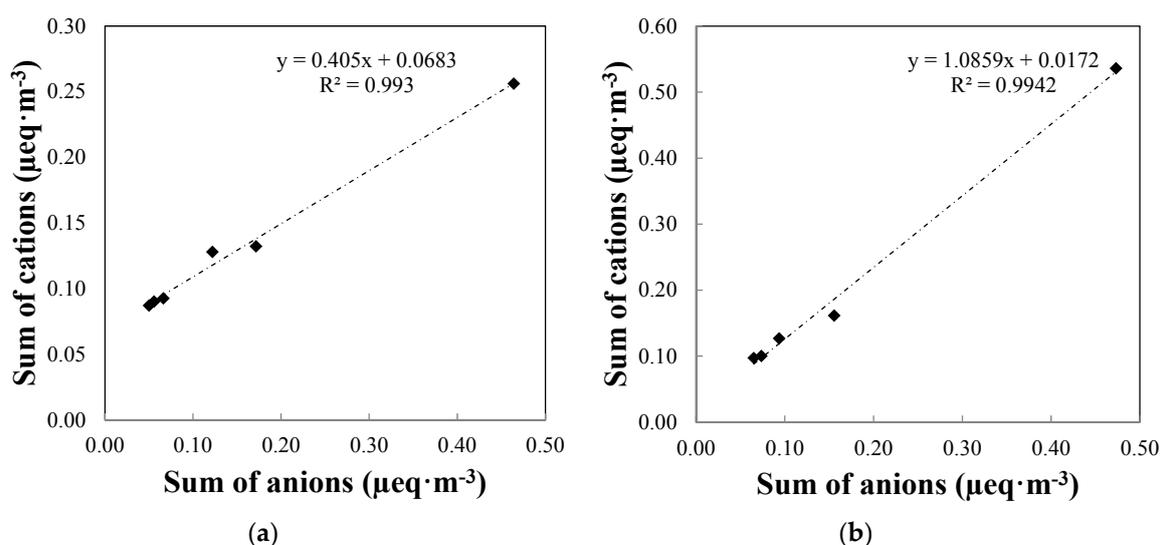


Figure 4. Ions balances for CEN (a) and MIR (b).

4. Conclusions

The results of this study suggested that anthropogenic and natural sources influenced the measured $\text{PM}_{2.5}$ in the Centro and Miravalle sites during the short warm dry season campaign realized in Guadalajara, Mexico. In addition to spatial variation, the chemical characterization of $\text{PM}_{2.5}$ allowed us to identify and distinguish some of the main emission sources contributing to particles in each site in the warm dry season in Guadalajara. The enrichment factor analysis indicated that road traffic mainly contributed to the $\text{PM}_{2.5}$ of Centro, and the highest abundance of K^+ suggested that biomass burning is an important source from the Primavera Forest located to the west. Despite the ratio ($\text{NO}_3^-/\text{SO}_4^{2-}$) indicating that the influences of motor vehicle emissions exceed those from the coal combustion in both sites, in Miravalle the resuspended particles from an inactive volcano (Cerro del Cuatro) to the southwest was suggested as significantly contributing to the mass of $\text{PM}_{2.5}$ and could have caused neutralization processes by a higher incorporation of cations on particles. Additionally, $\text{PM}_{2.5}$ at the Miravalle site apparently undergoes an impact from secondary particles of ammonium transported from areas located to the southeast, favored by a channeled-wind effect caused by elevations located to the southwest. Therefore, actions to be taken must focus mainly on both vehicular activity to reduce the emission of fine particles and undertaking campaigns of reforestation in the southwest of Guadalajara. In addition, for future studies the sampling must be seasonally extended and include analysis of sources based on other chemical species such as organic components.

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