Ionic species associated with PM2.5 in the City of Guadalajara, México during 2007

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Abstract Atmospheric aerosol particles were collected from January to December 2007 at two sites in the City of Guadalajara. The first site (Centro) is located in the downtown, which is characterized by high vehicular traffic, and the second site (Miravalle) is in the southern part of the city, characterized by emissions from high industrial and vehicular activity. Sulfates, nitrates, and ammonium were the most abundant ions at both sites. Similar concentrations of sulfates, nitrates, and ammonium were observed throughout the year at Centro while only sulfates and nitrates were similar at Miravalle. From the balance of anions and cations at the two sites, Centro was determined to have acidic particles, while at Miravalle, the particles were alkaline. Based on the analysis of the ammonium/sulfate molar ratios, it was determined that in Centro, there was not enough ammonium to neutralize the sulfate, while at Miravalle, ammonium practically neutralized all sulfate.

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Introduction

The City of Guadalajara is a municipality and the capital of the Mexican state of Jalisco as well as the focal point of the metropolitan area that bears its name: Metropolitan Zone of Guadalajara. Its territory is delimited in the north by the municipalities of Zapopan and Ixtlahuacan of River, in the east by Tonalá and Zapotlanejo, in the south by Tlaquepaque, and in the west by Zapopan. The City of Guadalajara is the second most populous city in Mexico with nearly 1,600,894 people (INEGI 2005) and possesses great vehicular and industrial activity, so it is affected by events of air pollution in some periods of the year. To determine some of the most abundant pollutants in these events, the collection of particulate matter equal to or less than 2.5 μm (PM2.5) was carried out during 2007 with the objective to analyze some ionic compounds. Inorganic species generally comprise between 25% and 50% of the aerosol mass (Gray et al. 1986), with sulfate, ammonium, and nitrate being the most abundant. Sulfates (SO_4^{2-}) and nitrates (NO_3^-) are generated mainly from the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x), respectively, which come from industrial emissions and the burning of

fossil fuels (Cope et al. 2004; Báez et al. 2007), and they contribute to the acidification of rainwater, which alters the composition of soils and aquifers and further deteriorates historical monuments, structures, and vegetation (Cope et al. 2004).

Anthropogenic components such as organic and elemental carbon, sulfates, and nitrates are present mainly in fine particulates. (Harrison 2004). It is precisely this fraction that has been shown in various epidemiological studies throughout the world to be associated with increased negative effects on the health of exposed populations (Pope et al. 2002; Pope and Dockery 2006). In the ambient air, the effects of these particles are measured by their ability to disperse or absorb radiation, which directly impacts global climate change and the influence they have on visibility (IPCC 2001; Watson 2002). The effects on human health are associated with the higher degree of penetration and retention of this size of particles in the respiratory tract, as well as its chemical composition complex (Claxton et al. 2004; Sugita et al. 2004; De Kok et al. 2006), establishing the importance of this study. In Guadalajara, no studies have been done to assess the chemical composition of PM2.5, and for this reason, the main goal of this study was to characterize the composition of inorganic ions present in aerosols collected at two sites. This information will become one of the foundations in research on the composition of PM2.5 in this region. Results will evaluate the variation in

chemical speciation throughout the year as well as determine the acidic or alkaline properties of particles.

Methodology

Sampling of PM2.5

Sampling of PM2.5 was carried out at two sites in Guadalajara. The first site is located in the downtown (Centro) and is characterized by high commercial influence and vehicular traffic both gasoline and diesel powered (Fig. 1). The other site (Miravalle) is located south of the city and is dominated by large industrial and vehicular activity, as well as resuspension of dust from soil. Particulate matter was collected using Partisol equipment (Rupprecht and Patashnick Co.) model 2300 operating at approximately $10 \, \mathrm{L \, min^{-1}}$ for 24 h (12:00–12:00) between January and December 2007 at both sites simultaneously; 72 and 74 samples were collected at the Centro and Miravalle sites, respectively. For the analysis of ions, nylon filters 47 mm in diameter with a pore diameter of 0.2 μm (MAGNA) were used.

Extraction and analysis

The nylon filters were placed in polypropylene tubes, and each one was extracted with 8 mL of

Fig. 1 Location of the sample sites Centro and Miravalle in the City of Guadalajara
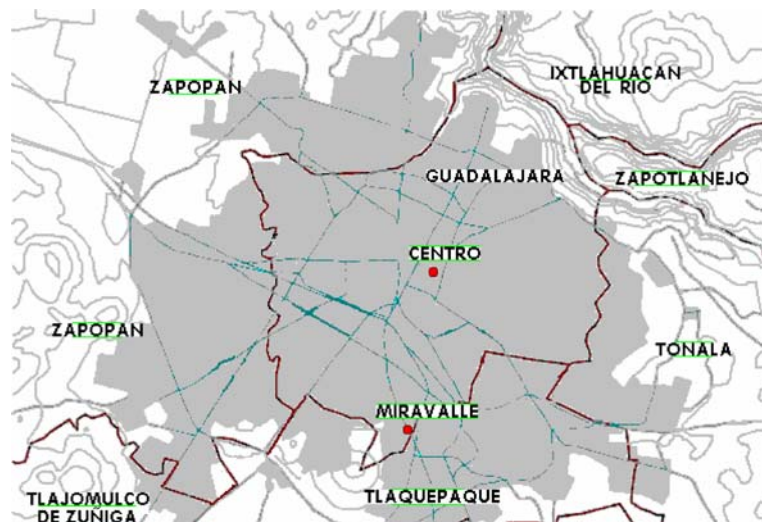
deionized water in an ultrasonic bath (BRANSON 5510) for 1 h at room temperature. Extracts were filtered through nylon membranes (0.45 μm pore diameter) and transferred to vials for chemical analysis by ion chromatography (CI, Metrohm model 861 Advanced Compact with conductivity detector). Ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) were analyzed without chemical suppression in a Metrosep C2_150 (Metrohm) column; the mobile phase was a solution of tartaric acid and dipicolinic acid (4.0:0.75 mM) at a flow rate of 1 mL min^{-1}; the injection volume was 50 μL. Chloride (Cl^-), sulfates (SO_4^{2-}), nitrates (NO_3^-), and phosphates (HPO_4^{2-}) were analyzed by chemical suppression with a column Metrosep A Supp5_150 (Metrohm), using as a mobile phase a solution of sodium carbonate–sodium bicarbonate (8.0:4.0 mM) at a flow rate 0.7 mL min^{-1}. The injection volume was 50 μL. Calibration curves for all species were constructed in a range of concentrations between 0.0625 and 10 μg mL^{-1}.

Statistical analysis

The absence of a normal distribution of data per site was evaluated by a Shapiro–Wilk test, while concentrations of comparisons between sites and annual seasons were performed using the Mann–Whitney U and Kruskal–Wallis tests, respectively. The association between the variables was evaluated using the Spearman rank-order correlation coefficient (r). The simple linear regression by least squares was used to demonstrate the presence of neutralization events among some ions. All these tests were carried out using the program STATISTICA 6.

Results and discussion

Seasonal variation of anions and cations

The descriptive statistics of concentrations of ionic species in the period of study at Centro and Miravalle sites are presented in Table 1, which includes averages, standard deviations, median, maximum, and minimum values. Sulfate, nitrate, and ammonium were the most abundant at both sites, suggesting that these components are important in the formation of secondary particles less than or equal to 2.5 μm, as well as the possibility of common sources for these species. Comparisons of concentrations during the year between sites indicate that K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} had higher concentrations in Miravalle ($p < 0.05$ in all cases), while NH_4^+ and NO_3^- did not present significant differences ($p > 0.05$). These differences allow the estimation that K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} concentrations were 1.32, 3.55, 11.67, 2.59, and 1.20 times higher, respectively, in Miravalle. Figure 2a–d shows the monthly behavior of anions and cations associated with PM2.5 collected at the study sites. In Mexico City, Moya et al. (2003) noted that ammonium and sulfate, which correlated with fine particles, were the dominant species during the year of study. In the same way, Rattigan et al. (2006) emphasized that sulfates and nitrates comprise an important fraction of the mass of PM2.5 in the eastern United States. These statements coincide well with the results obtained for some of the most abundant ionic species (sulfates, nitrates, and ammonium) in Guadalajara. Ito et al. (2004) reported for various sites in New York City (USA) that sulfates and nitrates explained almost 50% of the mass of PM2.5. Sulfate, nitrate, and ammonium are correlated with formation of secondary aerosols from their precursors such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2) by photochemical reactions (Finlayson-Pitts and Pitts 1986; Fosco and Schmeling 2006; Reiss et al. 2007). These precursors come mainly from combustion of gasoline and fuels containing sulfur, respectively (Clapp and Jenkin 2001; Isakson et al. 2003; Hodgson 2004), suggesting that some of the sulfates and nitrates originate in indirect ways from the same combustion processes. Zhao et al. (2007) reported that in urban areas, vehicle emissions of NO_x and local combustion processes are the biggest sources of nitrate. In addition, because NH^{4+} and Ca^{2+} neutralize SO_4^{2-} and NO_3^-, a positive correlation is expected between these variables, which would support their role in the formation of secondary aerosols. The variation in the concentrations of SO_4^{2-} between sites coincides with observed differences for SO_2 with higher concentrations in

Table 1 Descriptive statistics of anions and cations concentrations (nanograms per cubic meter) associated with $PM_{2.5}$ at two sites Centro and Miravalle in the City of Guadalajara during 2007

Species	n	Average (ng m^{-3})	SD	Median	Min	Max
Centro						
NH_4^+	72	1,668.1	907.6	1,574.6	4.4	3,841.5
Na^+	52	303.6	262.0	222.5	29.5	1,165.6
K^+	51	496.5	523.3	306.7	38.0	2,997.7
Ca^{2+}	72	356.5	407.6	182.9	0.06	1,767.0
Mg^{2+}	54	65.6	60.3	50.4	0.5	267.4
Cl^-	44	368.8	261.7	310.4	16.0	964.6
NO_3^-	70	2,366.0	1,617.1	1,967.0	339.4	7,324.6
HPO_4^{2-}	55	56.6	71.7	27.4	0.02	372.0
SO_4^{2-}	70	3,169.7	1,494.6	2,782.4	843.6	6,962.0
Miravalle						
NH_4^+	73	1,604.2	809.3	1,470.7	111.8	3,332.4
Na^+	52	274.7	201.4	238.2	6.1	1,104.9
K^+	55	656.1	541.2	444.7	26.0	2,044.6
Ca^{2+}	75	1,266.8	969.1	1,014.0	102.9	4,508.5
Mg^{2+}	74	766.2	1,032.3	187.8	7.2	3,009.2
Cl^-	69	957.8	874.5	570.8	5.7	4,103.1
NO_3^-	74	1,952.7	1,070.7	1,939.7	276.9	5,262.5
HPO_4^{2-}	62	79.1	136.8	28.5	0.3	707.8
SO_4^{2-}	74	3,810.3	1,697.1	3,764.8	1,194.6	9,021.8

n number of dates for the average estimation during study period, *SD* standard deviation, *Min* minimum, *Max* maximum

Miravalle (0.010 ± 0.005 ppm, $p < 0.05$), utilizing data from almost the entire study period (January–November). NO_2 did not have the same behavior as NO_3^- with higher concentrations at Centro ($p < 0.05$); this suggests that possibly, the formation of nitrate in Guadalajara is related to levels of NO or the sum of NO_2 and NO. Data from these pollutants were obtained from the Atmospheric Monitoring Automated Network of the City of Guadalajara that is operated by the Secretary of the Environment for Sustainable Development the state of Jalisco (SEMADES 2008). The conformed system for sulfate, nitrate, and ammonium in PM2.5 can respond in a non-linear way to changes in emissions from their precursors (Lonati et al. 2008), which could explain part of the behavior between nitrate and NO_2 levels in the air.

The period of study was divided into seasons in order to conduct a more detailed analysis of the behavior of the variations of the ion concentrations in PM2.5, and the annual report from pluvial precipitation (2007) for Guadalajara done by National Commission of the Water (CONAGUA 2008) was taken into account. The first dry season included the months from January to May (DS1), June to October (RS) were considered the rainy season, and the second dry season was from November to December (DS2). Under these criteria, Fig. 3a–d shows the behavior of the concentrations of anions and cations associated with PM2.5 at both sites, with significant differences in at least one of the seasons for Na^+, Ca^{2+}, and HPO_4^{2-} at Centro (Fig. 3a, b), whereas in Miravalle, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and HPO_4^{2-} showed significant differences (Fig. 3c, d). At Centro, the most abundant ions such as SO_4^{2-}, NO_3^-, and NH_4^+ had similar concentrations throughout the year ($p > 0.05$ in all cases), whereas Ca^{2+} and HPO_4^{2-} registered the highest concentrations in DS1; Na^+ was the unique component that showed elevated concentrations in RS ($p < 0.05$ in all cases). Although K^+ and Cl^- were not the most abundant ions at this site, neither had differences between seasons ($p > 0.05$ in both cases). For Miravalle, SO_4^{2-}, NO_3^-, and Na^+ did not present differences between seasons ($p > 0.05$), but NH_4^+, K^+, Ca^{2+}, Cl^-, HPO_4^{2-}, and Mg^{2+} were more abundant in DS1 and DS2 ($p < 0.05$ in all cases). Lonati et al. (2008) indicated
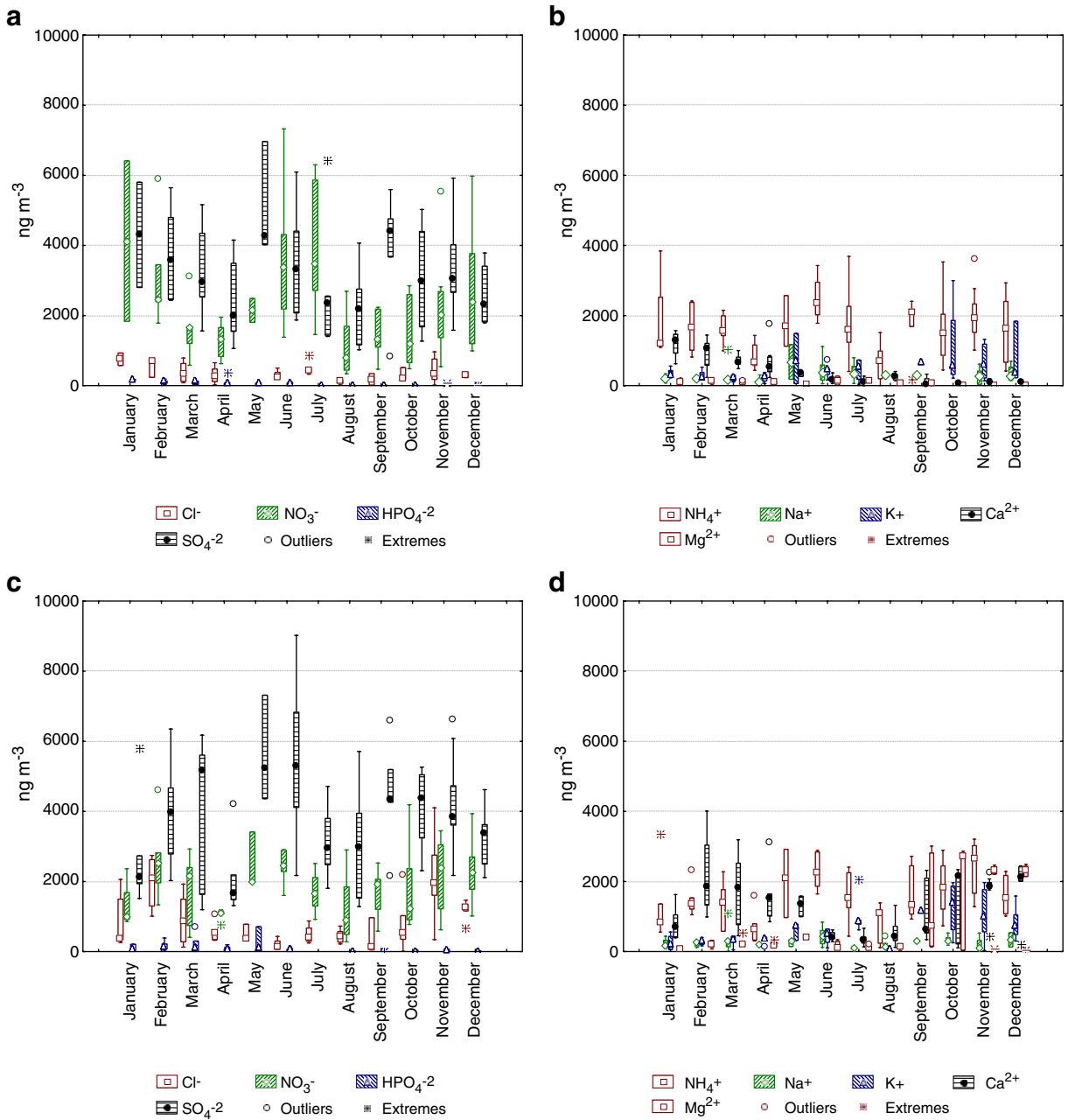
Fig. 2 Average monthly concentrations for anions and cations of Centro (**a** and **b**) and Miravalle (**c** and **d**) in the City of Guadalajara during 2007. *Squares* median, *box* percentiles 25–75%, *bars* range without outliers

that the seasonality of species such as NH_4^+ is due to conditions of high humidity and low temperature, which often occur during winter, which favors its formation. It was also noted that the lack of differences in concentrations of sulfates between seasons, as observed in Milan (Italy) and

in Guadalajara, can be explained by a high concentration of the precursor gas (SO_2) during the winter, while in summer, there are conditions that favor the oxidation of this precursor and increase the generation of secondary aerosols. These situations could occur at the two sites in Guadalajara.
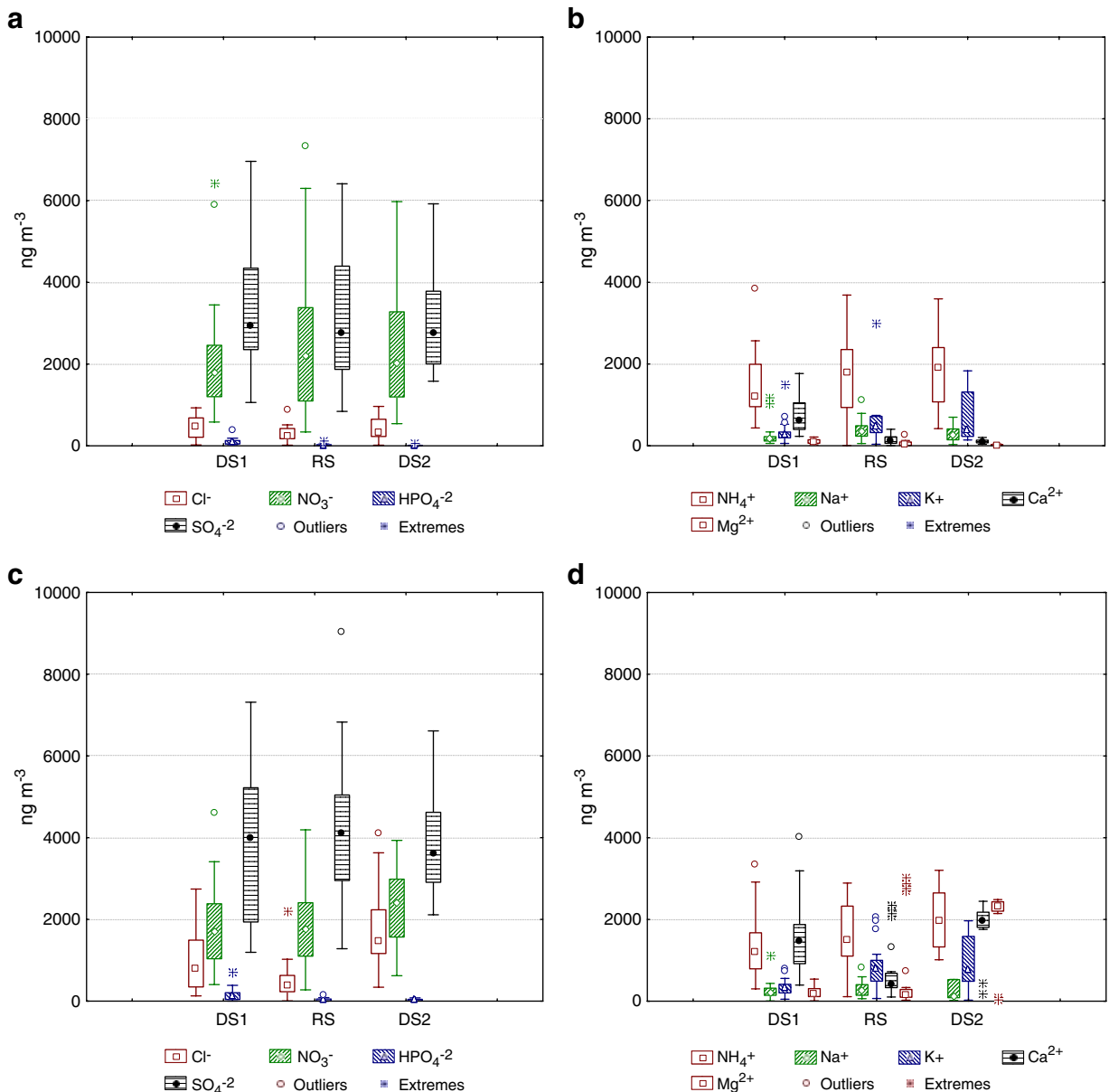
Fig. 3 Behavior between seasons of the concentrations of anions and cations associated with PM$_{2.5}$ at Centro (**a** and **b**) and Miravalle (**c** and **d**) during 2007. *DS1* first dry season (from January to May), *RS* rainy season (from June to October), *DS2* second dry season (from November to December). *Squares* median, *box* percentiles 25–75%, *bars* range without outliers

With some exceptions, the presence of the most abundant ions was constant throughout the year at both sites, and when comparing the differences between species, the less abundant species showed higher concentrations in DS1 followed by DS2. Aas et al. (2007) highlighted in a study carried out in different cities in China that concentrations of ionic species analyzed showed clear seasonal variation with higher concentrations during the winter. For Guadalajara, DS1 and DS2 relate largely to the winter season when there are decreases in temperature and conditions less favorable for the

dispersal of pollutants (PROAIRE 1997–2001). In general, there were no differences between the concentrations of the most abundant ions between sites (except for Ca^{2+} and SO_4^{2-}) and in different seasons (except in Miravalle NH_4^+). This suggests the existence of sources and common atmospheric processes and constants in the two study sites within Guadalajara, which are both marked by various anthropogenic activities. Moreover, absence of differences between seasons indicates that precursors and atmospheric conditions related to the generation of sulfates and nitrates are present throughout the year.

Correlations between species of ions associated to PM2.5

Table 2 contains the coefficients of correlation between concentrations of the species analyzed at Centro and Miravalle, respectively. For Centro, NH_4^+ correlated significantly with K^+, NO_3^-, and SO_4^{2-}, while in Miravalle, it correlated significantly with Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. In both cases, these ratios were positive although from moderate to low at both sites. The positive cor-

relations between SO_4^{2-} and NO_3^- with NH_4^+ indicate a possible common origin, although these associations also depend on the secondary characteristics of these pollutants and even more on the meteorological conditions, wind speed, and solar radiation (Fosco and Schmeling 2006; Báez et al. 2007).

Moreover, linear regression analyses between species of greater abundance were carried out to test the existence of chemical processes in the atmosphere of Guadalajara, such as the neutralization between anions and cations. Regressions between NH_4^+ and Ca^{2+} that neutralize SO_4^{2-} and NO_3^-, expressed in micromoles per cubic meter ($\mu mol\ m^{-3}$), were done, discarding outlying data of each variable. This gave evidence of the neutralization of SO_4^{2-} and NO_3^-, both by NH_4^+ at Centro (Fig. 4a and b) and Miravalle (Fig. 4c and d). Ca^{2+} also contributed to the neutralization of NO_3^- at Miravalle (Fig. 4e) although to a lesser extent. These results confirm the role of these compounds in the formation of secondary aerosols, especially at Miravalle. At Centro, r values for regressions between NH_4^+ against SO_4^{2-} and NO_3^- were 0.49 and 0.69, respectively, while

Table 2 Spearman correlation coefficients between anions and cations associated with $PM_{2.5}$ at two sites in the City of Guadalajara during 2007

|	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Centro									
NH_4^+	1.00								
Na^+	0.07	1.00							
K^+	**0.42**	0.29	1.00						
Ca^{2+}	−0.18	**−0.28**	**−0.28**	1.00					
Mg^{2+}	−0.17	−0.03	−0.25	**0.88**	1.00				
Cl^-	0.05	−0.04	0.05	0.06	−0.10	1.00			
NO_3^-	0.48	−0.09	0.14	0.04	0.04	0.30	1.00		
HPO_4^{2-}	0.18	−0.14	−0.24	**0.70**	**0.45**	**0.39**	**0.39**	1.00	
SO_4^{2-}	0.49	−0.28	0.09	0.16	0.04	0.01	**0.42**	**0.31**	1.00
Miravalle									
NH_4^+	1.00								
Na^+	0.01	1.00							
$K+$	0.16	0.00	1.00						
Ca^{2+}	**0.24**	0.03	−0.13	1.00					
Mg^{2+}	**0.35**	0.07	0.14	**0.80**	1.00				
Cl^-	**0.27**	−0.21	0.02	**0.45**	**0.25**	1.00			
NO_3^-	**0.70**	0.19	0.07	**0.31**	**0.28**	**0.34**	1.00		
HPO_4^{2-}	0.24	0.10	−0.23	0.06	−0.25	**0.27**	**0.31**	1.00	
SO_4^{2-}	**0.76**	0.27	0.12	**0.26**	**0.34**	0.06	**0.61**	0.23	1.00

In bold, values with $p < 0.05$
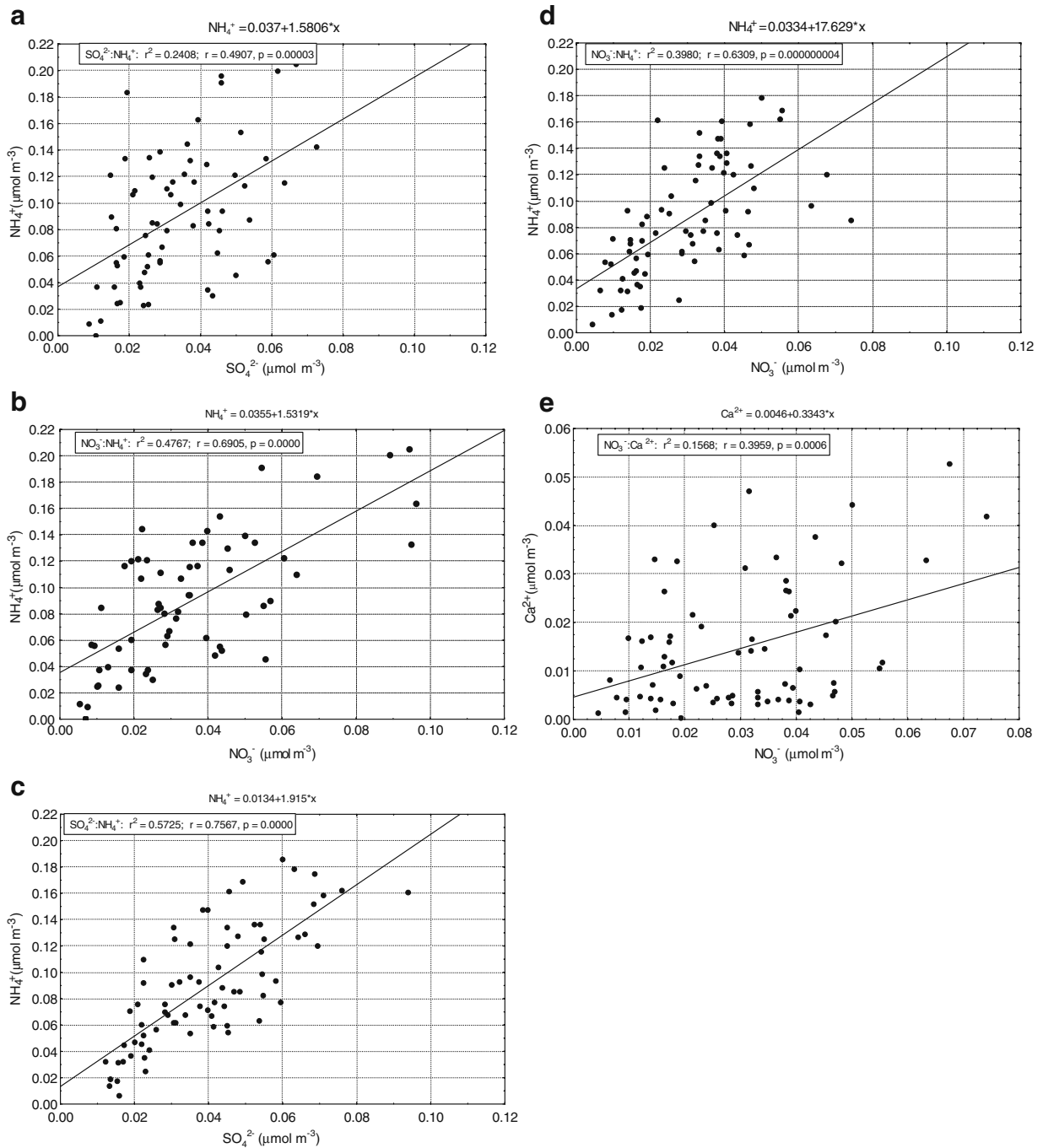
Fig. 4 Neutralization process represented by linear regressions between ammonium and sulfate (micromoles per cubic meter) at Centro (**a**, **b**) and Miravalle (**c**, **d**) and between calcium and nitrate (**e**) at Miravalle during 2007

at Miravalle, they were 0.75 and 0.63, indicating a closer relationship between SO_4^{2-} and NH_4^+ in the latter site; for NO_3^- and NH_4^+, the relationship was stronger at Centro. In addition, the positive

association between Ca^{2+} and NO_3^- at Miravalle ($r = 0.39$) also suggests a slight contribution to the formation of PM2.5 in the atmosphere of a site characterized by high industrial activity and

also implies that Ca^{2+} is probably a component of secondary fine particles (Fig. 4e). The processes of neutralization of these species in the atmosphere may be subject to environmental factors and the availability of their chemical precursors. For example, Moya et al. (2004) indicate that the low availability of precursors in the gas phase (NH_3 and HNO_3) implies a major amount of NH_4^+ in PM2.5, and the dominant mechanism for the formation of ammonium nitrate is favored by declines in temperature and high relative humidity. In addition, at high temperatures, ammo-

nium nitrate undergoes a thermal decomposition, transforming nitrate to nitric acid. In the same way, changes in the height of the mixing layer in response to fluctuations in temperature also contribute to the changes observed in the ionic species analyzed (Rattigan et al. 2006). Relationships like this could affect the outcome of neutralization between anions and cations for Guadalajara.

It is worth noting that Table 2 also includes significant correlations for some of the less abundant ions. For example, for Centro, associations were observed between HPO_4^{2-} with Ca^{2+} and Mg^{2+},

Fig. 5 Regression lines that establish the ion balance at Centro (**a**) and Miravalle (**b**) during 2007. The corresponding slopes below the unity indicate particulates with acidic properties while above the unity indicate alkalinity
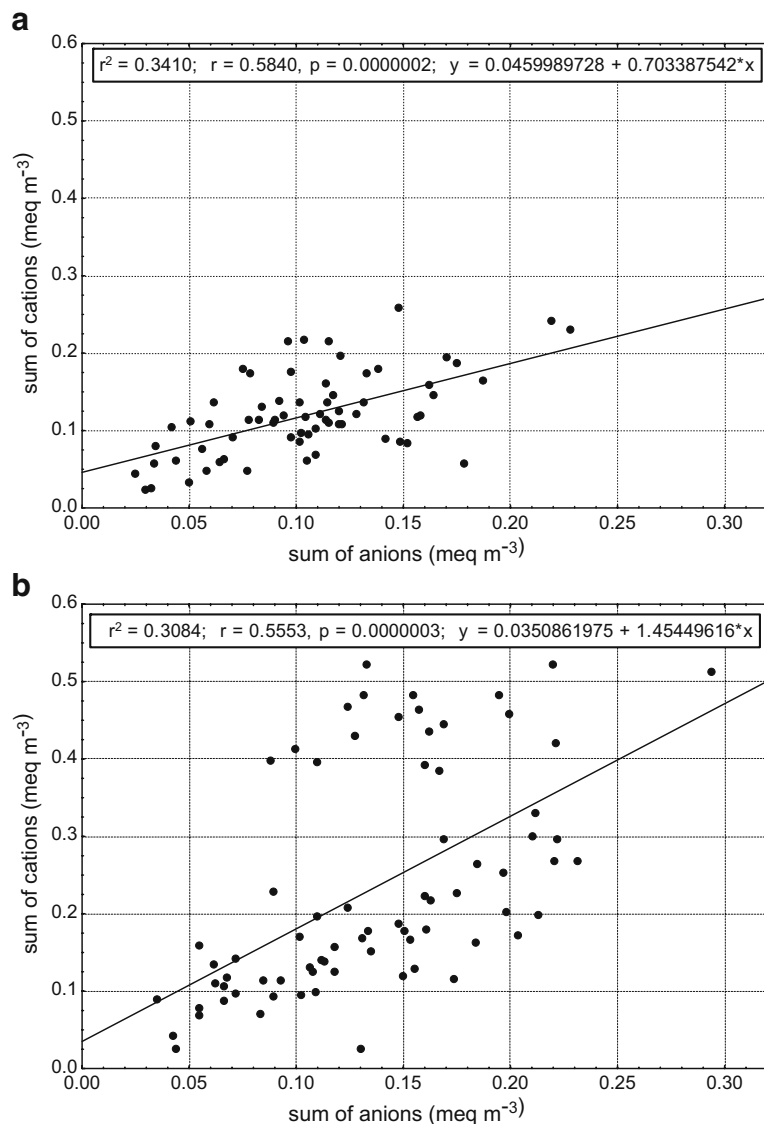
suggesting the possible presence of compounds such as calcium phosphate ($Ca_3(PO_4)_2$) and magnesium phosphate ($Mg_3(PO_4)_2$) in PM2.5. At Miravalle, the variety of possible compounds was higher due to Cl^-, NO_3^-, and SO_4^{2-} correlated with Ca^{2+} and Mg^{2+}. Thus, it is possible that the PM2.5 compound could contain calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$), calcium nitrate ($Ca (NO_3)_2$) and magnesium nitrate ($Mg(NO_3)_2$), as well as calcium sulfate ($CaSO_4$) and magnesium sulfate ($MgSO_4$). Another possible compound at this site is ammonium chloride (NH_4Cl). Levels of their respective ratios suggest a moderate role in the neutralization process between these species of anions and cations. It is possible that Ca^{2+} and Mg^{2+} come from a common source because its correlation coefficient was among the highest in the two study sites (Table 2). The concentration of Cl^- was 2.6 times higher at Miravalle than at Centro. Cl^- has been associated with burning coal (Yang et al. 2005; Aas et al. 2007), which could suggest fossil fuel consumption at Miravalle.

Ion balance associated to PM2.5

An ion balance was carried out at both sites. Figure 5a and b shows the behavior of the sum of cations against the sum of anions expressed in milliequivalents per cubic meter during the year. In both places, the slopes were significant; however, for Centro, the slope value (0.70) was lower than unity, which indicates the presence of H^+, revealing an acidic nature of the particles (Fig. 5a). It is expected that H^+ have reacted mostly with SO_4^{2-} (Koçak et al. 2007). For its part, Miravalle showed a slope greater than unity (1.45), suggesting that during most of the year at this site, the number of anions was not enough to neutralize the ammonia and other species of cations in the PM2.5, and therefore, it can be determined that the particles had an alkaline nature (Fig. 5b). Moya et al. (2003) argue that the results of ion balance will depend on the species considered. It is important to clarify that the results of the analysis of ion balance were estimated from the anions and cations present in PM2.5 in the Guadalajara atmosphere, so the results could vary if other species of ions or particles of different sizes are considered.

To complement this analysis and develop a more detailed description of the relationship between the ionic species, particles were analyzed for ammonia to determine whether the sites were rich in ammonium (non-acid environment) or poor in ammonium (acidic environment). Molar ratio was evaluated between the total ammonium and total sulfate (TA/TS) during the study period. According to theory (Seinfeld and Pandis 1998), if the molar proportion AT/ST is <2, then environmental conditions are defined as poor in ammonium. On the contrary, if it is >2, it will be abundant in this species. The molar ratio TA/TS has some characteristics according to its value:

1. Less than or equal to 0.5, the aerosol particles exist primarily as H_2SO_4 solutions.
2. Between 0.5 and 1.25, $NH_4HSO_{4(s)}$ (or an HSO_4^- and NH_4^+ solution) is the dominant component of the system.
3. Between 1.25 and 1.5, $NH_4HSO_{4(s)}$ and $(NH_4)_3H(SO_4)_2$ (letovicite) or a solution with the corresponding ions coexist in the system.
4. Equal to 1.5, the aerosol phase consists exclusively of letovicite (or a solution with the corresponding ions).
5. Equal to 2.0, all the ammonia is completely neutralized with the sulfate present and therefore the predominant component in the system is $(NH_4)_2SO_4$ or a solution with the corresponding ions.

For the TA/TS molar ratio analysis, it should be noted that the concentration of sulfuric acid in gas phase was practically negligible due to the low vapor pressure (Seinfeld and Pandis 1998). The proportions were equivalent to the slopes of the linear regressions between SO_4^{2-} and NH_4^+. We must clarify that in this study, gas-phase concentrations of NH_3 were not measured. Therefore, we are assuming that all ammonia was converted to NH_4^+ in the particulate phase. At Centro, the value of the slope to the molar proportion (TA/TS) was 1.58 (Fig. 4a), indicating that the letovicite ($(NH_4)_3H(SO_4)_2$ or their corresponding ions) was the dominant form of this sulfate (TA/TS, 1.5) at this site, while for Miravalle, the ratio was 1.91 (Fig. 4c), which means that almost all ammonium present was neutralized by sulfate so that $(NH_4)_2SO_4$ was the predominant form

of sulfate present (TA/TS, 2) or a solution with the corresponding ions. These results suggest that the ammonium was not enough to neutralize the sulfate present at Centro, whereas at Miravalle, it practically was.

The results of this study for Guadalajara acquire greater importance when one takes into account the potential indirect effects of particulates and its contents of sulfates. For example, the acid forms of sulfates can influence the bioavailability of some metals, which have been strongly involved in contributing to the toxicity of particles (Ghio et al. 1999). In addition, it has been proposed that sulfates increase the deposition of toxic compounds in the lungs and promote their absorption into particles or create a hygroscopic environment for soluble gases and help them to arrive at deep zones of the respiratory tract (Friedlander and Yeh 1998). Also, it is believed that sulfates can catalyze the formation of secondary inorganic aerosols (Jang et al. 2002). Finally, atmospheric photolysis processes can facilitate the transformation of compounds adsorbed onto particles, a process in which sulfates and nitrates may be involved (Vione et al. 2006).

Conclusions

For Centro and Miravalle in the City of Guadalajara, concentrations of the most abundant species of anions and cations associated with PM2.5 were determined. With the exception of nitrate, ammonium, calcium, sulfate, and other less abundant ions, there were little differences in their annual concentrations between sites. The differences in the concentrations of sulfates between sites corresponded well with those observed for SO_2, suggesting that this gas precursor possibly defines the concentrations of sulfates in the City of Guadalajara, with higher levels found at Miravalle. Nitrates did not have the same behavior as its precursor NO_2 between sites, which probably involves NO or both gases together in determining the level of nitrates in particles. The similar concentrations of sulfates, nitrates, and ammonium during year at Centro and sulfates and nitrates at Miravalle, the most abundant species of ions in both places, suggests the presence of sources

and atmospheric processes in common within the City of Guadalajara in the formation of these ions. Some less abundant anions and cations showed higher concentrations in seasons DS1 and DS2. In both places, it was possible to prove that neutralization of ammonium with sulfate and nitrate occurs, and in Miravalle, ammonium was neutralized with species such as calcium. These ions are derived indirectly from anthropogenic precursors or from natural sources, i.e., calcium. From the balance of anions and cations analyzed at two sites, Centro was characterized to have particles of an acidic nature, while in Miravalle, particles were alkaline. It is important to note that the results of this analysis may vary if we consider additional ions or other particle sizes. An analysis of the relationship between sulfate and nitrate, that is to say, the molar ratio TA/TS, indicated that the dominant form of sulfates in PM2.5 was letovicite at Centro and ammonium sulfate at Miravalle. The results of the ratio TA/TS at Centro suggest that the ammonium present was not enough to neutralize the sulfate, while at Miravalle, practically all the sulfate was neutralized by ammonium.

The results obtained for the composition of the ionic species that form the PM2.5 in Guadalajara, together with considerations about the effects of sulfates and nitrates, are sufficient arguments to continue with studies of chemical speciation that would not only identify (chemical species), but also try to explain their atmospheric dynamics.

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