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Presence of the Most Abundant Ionic Species and Their Contribution to PM2.5 Mass, in the City of Guadalajara, Jalisco (Mexico)

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Abstract Ambient PM2.5 samples were taken at 24 h intervals at two sites (Centro and Miravalle) in the city of Guadalajara from January to June 2008. The Centro site is located in the downtown, while the Miravalle site is located in an industrial zone south of the downtown. For both sites the higher concentrations of PM2.5 were between January and May. High correlation coefficients between sulfate, nitrate and ammonium of 0.95, 0.92 and 0.91, respectively, showed low variations in the concentrations of these species in the city. It was estimated that sulfate, nitrate and ammonium represented almost 47% of the PM2.5 mass in June at the Centro site, but in general the contributions in the other months were less than 21%, while at Miravalle this percentage was between 7.7% and 27.6%.

Keywords Ions · PM2.5 · Contribution · Ion chromatography

Anthropogenic components such as organic and elemental carbon, sulfate and nitrate are the main constituents of fine particulates (Harrison 2004). This fraction (PM2.5) has been widely investigated due to its potential health impact as shown in several epidemiological studies and the need for its control in air in order to diminish exposed populations (Pope and Dockery 2006). One of the most important constituents of these particles are the different inorganic ion species, such as sulfate, ammonium and nitrate (Walker et al. 2004; Ito et al. 2004; Reiss et al. 2007). Inorganic species generally comprise between 25 and 50% of the aerosol mass (Gray et al. 1986; USEPA 1995). Sulfate (SO_4^{2-}) and nitrate (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 2004; Báez et al. 2007). Ammonium is a component of atmospheric nitrogen and has an important role in the cycle of nitrogen in the terrestrial and aquatic ecosystems (Walker et al. 2004).

These species may determine to a large extent the acidity of particles and influence the partition of water-soluble, semi-volatile compounds between the gas phase and different size particles (Fridlind and Jacobson 2000) in addition to the rate of many important chemical reactions occurring in liquid aerosols or cloud/fog droplets (Keene and Savoie 1998; Liang and Jacobson 1999). Acidic particles contribute to the acidity of precipitation and may cause adverse health effects (Dockery et al. 1992).

The city of Guadalajara is the second most populous city in Mexico, and possesses great vehicular and industrial activity (INEGI 2005), mainly sources that produced fine particles. Because of this, it is affected by air pollution events in some periods of the year. In spite of this condition and although it is contradictory, there are at few scientific studies on the contribution of inorganic ions species to the mass of the PM2.5 for the city. Investigations of this type are very important because they permit the determination of those species of the more abundant ions, which then can be related to the acidity or alkalinity of the particles at sites where different anthropogenic activities predominate in the city of Guadalajara.

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Materials and Methods

Centro and Miravalle sites are located in the downtown and industrial zone (south), respectively, in the city of Guadalajara. Methodology for sampling, extraction and analysis has been widely described by Hernández et al. 2010. Briefly, particulate matter was collected using Partisol equipment (Rupprecht and Patashnick Co.) model 2300 with nylon filters 47 mm in diameter and pore diameter of 0.2 μm (MAGNA). Nylon filters were extracted with deionized water in an ultrasonic bath (BRANSON 5510). Ionic species were analyzed in an Ion Chromatograph (CI, Metrohm model 861 Advanced Compact with conductivity detector). The instrumental detection limits were 0.137, 0.277, 0.138, 0.255, 0.022, 0.027, 0.166 and 0.025 μg/mL for chloride, nitrate, phosphate, sulfate, sodium, ammonium, potassium and calcium, respectively. Recovery percentages were determined by spiking a standard solution into one out of every 10 samples, and they were estimated between 91.0% and 99.2% for all species.

The absence of a normal distribution of data concentration was evaluated by a Shapiro–Wilk test; while comparisons of data groups between sites and for seasons were performed using the Mann–Whitney U. The simple linear regression by least squares was used to demonstrate linear correlation. All these tests were carried out using the program STATISTICA 6.

The estimation of the contributions of each ionic species to the mass of the particles was expressed as percentages of PM2.5 for each day of sampling, and later monthly averages for each species were calculated. The same procedure was applied to the contribution of each ion species with respect to the total daily mass of ions, which were reported as monthly average proportions.

Results and Discussion

The PM2.5 mass was higher in Miravalle, with significant differences when comparing all dates for both sites (without outliers, $p < 0.0001$). For both sites the higher concentrations occurred between January and May, while the lowest was found in June (Fig. 1a). During February some of the lowest temperatures of the year were recorded (SMN-CNA, Sistema Meteorológico Nacional-Comisión Nacional del Agua 2008), which probably stopped the dispersion of contaminants and caused the conversion from the gas to the particle phase, as well as reducing the height of the mixing layer (Calvo et al. 2008; PROAIRE 1997). The levels in June can be explained by the beginning of the rainy season, when the highest precipitation of the year was recorded on the corresponding dates, according to SMN-CNA (2008). The rain works as a natural system that removes the particles from the atmosphere, perhaps with direct dragging or by causing an increase in particle size and later precipitation. The hygroscopicity of particles largely depends on chemical composition, which is

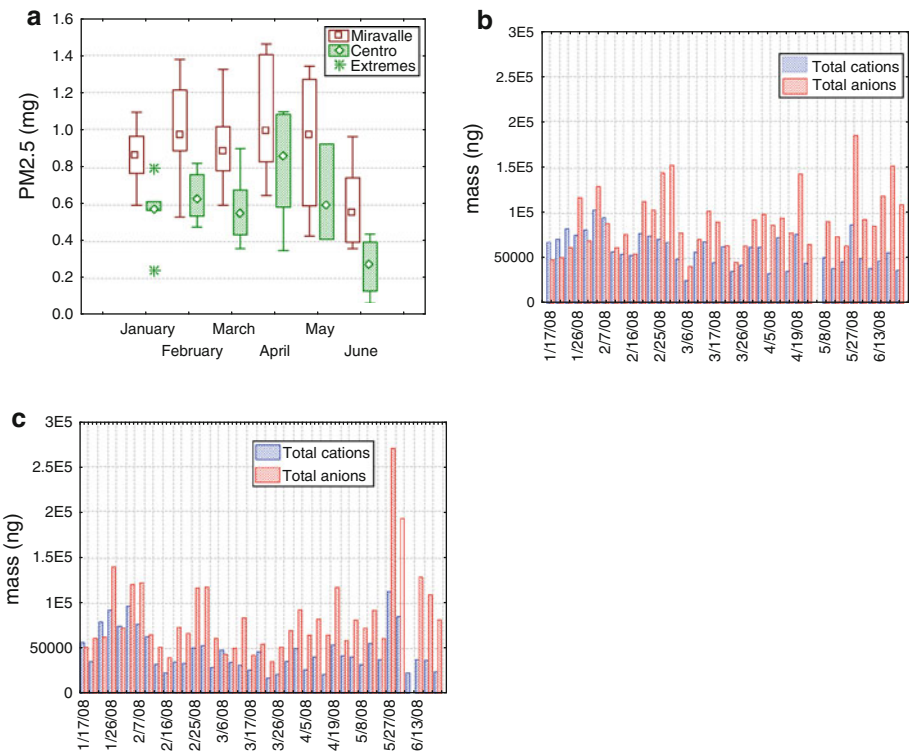

Fig. 1 **a** Monthly behaviour of PM2.5 mass during first semester 2008; **b** Daily variation for total cations and total anions at Miravalle site; **c** Daily variation for total cations and total anions at Centro site

especially true for those with high sulfate and nitrate content (McMurry 2000).

One of the meteorological parameters that has the most influence on transport of the mass of the pollutants is the wind direction and, depending on the topography of the area, will help in their dispersion or, conversely will lead to its accumulation. In the case of Guadalajara prevailing winds between February and May came from the northwest and in June from the northeast, whereas in January the winds came from the southwest (SMN-CNA 2008). In general, the predominant wind directions during almost all of the study probably contributed to the displacement of contaminants towards Miravalle. This transport from other places in the city may explain the greater mass of particles observed at this site and contributed to local levels of particles that exceeded levels found in Centro. Moreover, south and southeast of the city there are mountain ridges that form part of a natural physical barrier to wind circulation, hampering the removal of the city's polluted air (PROAIRE 1997). We consider that these conditions caused part of the differences in PM2.5 mass between the two sites, besides being sure that the high industrial activity in Miravalle also contributed to these results. The higher levels of PM2.5 at the industrial site already been reported in a previous study by Saldarriaga et al. (2009).

Table 1 shows a statistical summary of ambient ion standard concentrations (1 atm and 25°C) which includes average, standard deviation, median, maximum and minimum for the whole period for each site, including only those days where it was possible to identify this species. The comparison of the individual species concentrations between sites during 2008 indicates that only calcium and chloride had higher levels in Miravalle ($p < 0.0001$ and $p < 0.001$, respectively), with calcium being the highest of the cation concentrations, but not chloride respect to anions. Meanwhile, those anions and cations that did not have differences between sites (NH_4^+, SO_4^{2-} and NO_3^-) were very abundant, suggesting that there are common sources and formation process in the different zones of the city, especially from the central zone to the south (Miravalle). Ito et al. (2004) commented that, at established high correlations, little variation exists between atmospheric concentrations of sulfate and nitrate in different sites in the same city. We observed a similar result upon performing a linear regression for sulfate, nitrate and ammonium concentrations between Miravalle and Centro (without outliers) with correlation coefficients (r) of 0.95, 0.92 and 0.91, respectively ($p < 0.001$, in all cases) which supports the low variation in the concentrations of these species in the city of Guadalajara. It is probable that at other sites in the city with similar characteristics to the study sites, comparable concentrations could be observed for these contaminants. This can be verified when the sampling sites of PM2.5 in the city are extended.

Table 1 Descriptive statistics of anions and cations concentrations (ng m^{-3}) associated with PM2.5 at two sites, Centro and Miravalle in the City of Guadalajara during 2008 (January to June)

Species	*n*	Average (ng m^{-3})	SD	Median	Min	Max
Centro						
NH_4^+	39	1624.65	1271.94	1156.33	209.79	5290.10
Na^+	36	424.21	372.91	310.64	7.24	1471.62
K+	36	443.95	291.70	400.85	80.36	1242.51
Ca^{2+}	39	1453.90	702.71	1467.26	25.75	3403.77
Cl^-	16	226.23	114.88	220.43	68.82	445.37
$NO3^-$	38	3337.28	2159.34	2438.92	699.40	10083.61
HPO_4^{2-}	31	22.39	11.14	22.67	6.34	52.54
SO_4^{2-}	38	3711.32	2323.57	3113.65	963.41	12887.87
Miravalle						
NH_4^+	38	1514.50	860.09	1337.05	399.72	3535.51
Na^+	34	485.50	417.06	384.11	0.64	1893.26
K^+	38	523.21	323.35	596.85	10.21	1177.54
Ca^{2+}	38	2526.48	1070.15	2596.83	552.67	4746.34
Cl^-	22	565.71	446.35	461.13	36.65	1773.64
NO_3^+	38	2882.10	1277.25	2670.62	980.97	6371.17
HPO_4^{2-}	28	30.92	28.19	22.58	0.76	108.82
SO_4^{2-}	38	4211.94	1791.07	3916.74	1655.60	9295.67

n Number of dates for the average estimation during the study period, *SD* Standard deviation, *Min* Minimum, *Max* Maximum

The quantity of mass of the total anions and cations associated with collected particles during the first semester of 2008 are showed in Fig. 1b, c for Miravalle and Centro, respectively. It is observed that there is a high concentration of total anions with respect to the cations, with significant differences at both sites ($p < 0.0001$, respectively). The same difference was observed when the cations masses were compared between sites, with a higher abundance in Miravalle ($p < 0.001$), while total anions did not show the same behavior ($p > 0.05$).

Monthly average proportions of the mass of total anions and cations with respect to the PM2.5 mass (Table 2) are shown in Fig. 2a, b for Centro and Miravalle, respectively. In Centro, total ions reflected a moderate contribution in January, and diminished in March and April, and increased slightly in May. Then levels increased greatly in June, almost twice that of any previous month. In Miravalle a similar behavior was observed, although with smaller values. From January to March the contributions diminished, then increased gradually during April and May and reached the higher level for this site in June, but less than the increase observed at Centro and without significant differences between groups of monthly average proportions

Table 2 Monthly average proportions of anions and cations mass with respect to the PM2.5 mass and cumulative proportions that represents every one with respect to the total inorganic ions mass in two sites in the city of Guadalajara

	January	February	March	April	May	June
Centro						
NH_4^+	5.8	3.6	1.4	1.9	3	13.7
NO_3^-	9.5	6.9	3.9	4.7	5	17.3
SO_4^{2-}	5.9	6.2	5.7	5.9	8.7	15.8
Ca^{2+}	3.7	3.2	3.2	2.3	2	2.6
$\sum HPO_4^{2-}$, K^+, Na^+, Cl^-	3.0	2.3	1.3	1.5	3.4	3.1
Total inorganic ions	27.9	22.2	15.6	16.3	22.1	52.5
Cumulative proportions respect to the total inorganic ions						
NH_4^+	21	16	9	11	13	26
NO_3^-	55	47	34	40	36	59
SO_4^{2-}	76	75	71	76	76	89
Ca^{2+}	89	90	91	91	85	94
$\sum HPO_4^{2-}$, K^+, Na^+, Cl^-	100	100	100	100	100	100
Miravalle						
NH_4^+	3.4	2.1	1.0	1.2	2.4	5.3
NO_3^-	4.0	3.1	2.4	3.8	4.3	9.8
SO_4^{2-}	4.8	5.6	4.3	5.0	7.0	12.5
Ca^{2+}	4.0	4.0	3.3	2.9	2.0	2.3
$\sum HPO_4^{2-}$, K^+, Na^+, Cl^-	1.8	3.0	1.4	1.0	2.5	2.1
Total inorganic ions	17.9	17.8	12.4	14.0	18.1	31.9
Cumulative proportions respect to the total inorganic ions						
NH_4^+	19	12	8	9	13	17
NO_3^-	41	29	28	36	37	47
SO_4^{2-}	68	61	62	72	75	86
Ca^{2+}	90	83	89	93	86	94
$\sum HPO_4^{2-}$, K^+, Na^+, Cl^-	100	100	100	100	100	100

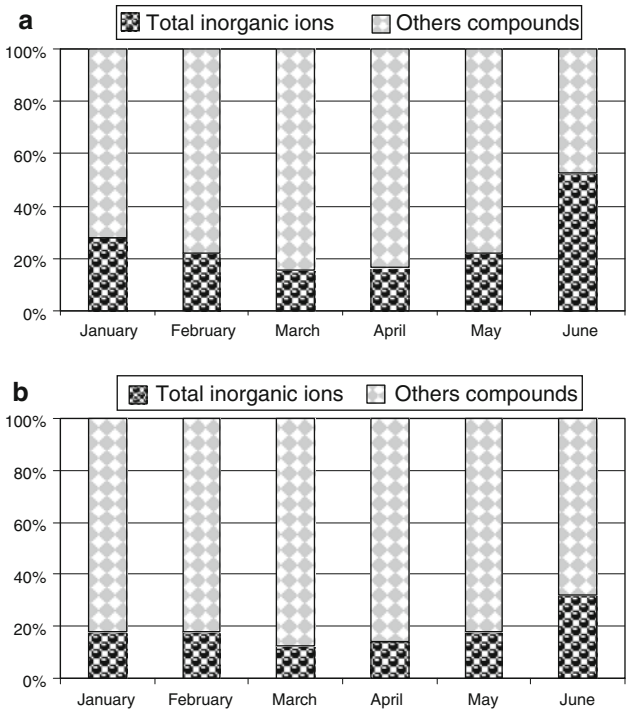

Fig. 2 Contribution of the total inorganic ions as percent of the monthly PM2.5 mass. **a** Centro; **b** Miravalle

($p > 0.05$). In addition, these results showed a high correlation when a linear regression is performed between sites with $r = 0.96$ ($p < 0.001$), suggesting a similarity in the behavior of the variation of contributions. This indicates that Centro, with respect to Miravalle, had a smaller particle amount, but the ion contributions were similar when were contrasted as monthly average proportions.

For this study, sulfate, nitrate and ammonium achieve a high contribution with respect to PM2.5 mass during June at Centro (46.8%), in the other months values were below 21%. In Miravalle these species fluctuated between 7.7% and 27.6% of the particles mass. It is worth highlighting that the sum of the contributions for phosphate, potassium, sodium and chloride was less than 3.5% in all sampling periods at both sites. In this respect Ito et al. (2004) indicated that ammonium, sulfate and nitrate explain nearly 50% of the PM2.5 mass. Meanwhile Tolocka et al. (2001), mentions that for the Eastern United States, these last species contribute between 40 and 65% of the fine particles mass. In general, the contributions of these species at both sites in Guadalajara were minor compared to that reported in previous studies, with the exception of June at the Centro site. The highest contribution for sulfate were observed between May and June when the higher temperatures were also recorded (22.3–23.5°C) (SMN-CNA 2008). The high temperatures and solar radiation allow photochemistry activity, causing an increase in the concentration of some contaminants, such as sulfate, which was reported by Calvo et al. (2008) for the city of Toulouse (France).

On the other hand, Table 2 describes in detail the average contribution of these species with respect to the monthly inorganic ions (cumulative proportions). For Centro four principal species, ammonium, nitrate, sulfate and calcium, had cumulative average contributions between 85 and 94%, while in Miravalle these values were between 83 and 94%. It stands out and is important to note that during June the lowest PM2.5 mass was measured at both sites, but at the same time the highest cumulative proportions for ammonium, sulfate and nitrate occurred. The last two ionic species are hygroscopic, which possibly

can explain the low levels of particles during intense rain in this month (McMurry 2000; SMN-CNA 2008). Likewise, calcium had more importance between February and April, principally at Miravalle. In a recent study carried out concerning the elemental composition of PM2.5 at the same sites in Guadalajara, it was observed that calcium had a geological origin due to the value based in its enrichment factor (Saldarriaga et al. 2009), indicating that natural sources at Centro and Miravalle are involved in the formation of secondary aerosols. These results demonstrate the importance of such species as ammonium, sulfate and nitrate in the contribution to total ions associated with PM2.5 in the city of Guadalajara and that they are secondary product derivates of combustion processes (Reiss et al. 2007). Rattigan et al. (2006) stated that ammonium and sulfate were dominant species and emphasized that they comprise an important fraction of the PM2.5 mass in Mexico City and the Eastern United States, respectively. This is in agreement with the results obtained for some of the most abundant ions in Guadalajara during 2007 (Hernández et al. 2010) and in this study. Considering the results obtained during the first half for 2008, it can be said that there are no concentrations gradients for the most abundant ionic species from downtown to south of the city.

In summary, higher concentrations of PM2.5 at Miravalle could be attributed in part, to the displacement of contaminants from other sites in the city, as well as topography, since to the south and southeast of the city there are mountain ridges that form part of a natural barrier to wind circulation, hindering the evacuation of contaminants and the high industrial activity in Miravalle also contributed to these results. Likewise it was estimated that sulfate, nitrate and ammonium can represent almost 47% of the PM2.5 mass in June at the Centro site, and in the other months these values were lower, about 21%. In Miravalle these species fluctuated between 7.7% and 27.6% of PM2.5 mass. These results suggest that between 53%–79% at the Centro and 72%–92% at Miravalle of PM2.5 mass are mixtures of other compounds, such as organics, metals and elemental carbon, among others. These results about the contribution of the main inorganic ions in PM2.5 will serve as a basis for establishing the connection between PM2.5 concentration and negative impacts over human health.

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