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TECHNICAL PAPER

Source apportionment of PM_{2.5} for supporting control strategies in the Monterrey Metropolitan Area, Mexico

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ABSTRACT

The Monterrey Metropolitan Area (MMA) in Northeast Mexico has shown high PM_{2.5} concentrations since 2003. The data shows that the annual average concentration exceeds from 2 to 3 times the Mexican PM_{2.5} annual air quality standard of 12 µg/m³. In a previous work we studied the chemical characterization of PM_{2.5} in two sites of the MMA during the winter season. Among the most important components we found ammonium sulfate and nitrate, elemental and organic carbon, and crustal matter. In this work we present the results of a second chemical characterization study performed during the summer time and the application of the chemical mass balance (CMB) model to determine the source apportionment of air pollutants in the region. The chemical analysis results show that the chemical composition of PM_{2.5} is similar in both sites and periods of the year. The results of the chemical analysis and the CMB model show that industrial, traffic, and combustion activities in the area are the major sources of primary PM_{2.5} and precursor gases of secondary inorganic and organic aerosol (SO₂, NO_x, NH₃, and volatile organic compounds [VOCs]). We also found that black carbon and organic carbon are important components of PM_{2.5} in the MMA. These results are consistent with the MMA emission inventory that reports as major sources of particles and SO₂ a refinery and fuel combustion, as well as nitrogen oxides and ammonium from transportation and industrial activities in the MMA and ammonium from agricultural activities in the state. The results of this work are important to identify and support effective actions to reduce direct emissions of PM_{2.5} and its precursor gases to improve air quality in the MMA.

Implications: The Monterrey Metropolitan Area (MMA) has been classified as the most air-polluted area in Mexico by the World Health Organization (WHO). Effective actions need to be taken to control primary sources of PM_{2.5} and its precursors, reducing health risks on the population exposed and their associated costs. The results of this study identify the main sources and their estimated contribution to PM_{2.5} mass concentration, providing valuable information to the local environmental authorities to take decisions on PM_{2.5} control strategies in the MMA.

PAPER HISTORY

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Introduction

The Monterrey Metropolitan Area (MMA) is located in the northeast of Mexico, in the state of Nuevo Leon, and comprises 12 municipalities. The MMA is the third largest city in the country, with an estimated population of 4.3 million inhabitants in the year 2014. Industrial activities are intense in the area, with a fleet of more than 2 million vehicles in 2013. The MMA has an automatic air quality monitoring system known as SIMA (Integral System for Environmental Monitoring) that started with 5 monitoring stations in 1993 and has grown to 10 monitoring stations in the last 5 years. Historical data of SIMA indicate that the most important pollutants in the MMA are PM_{2.5}, PM₁₀, and ozone (SIMA, 2015). Figure 1 shows

the PM_{2.5} annual average concentration reported by SIMA in five monitoring stations that measure this pollutant in the MMA since 2003. In the figure we observe that the most polluted region is located southwest (SW) of the MMA, followed by the northeast (NE) and northwest (NW) regions. The data shows that all regions in the MMA have exceeded the PM_{2.5} annual air quality standard of 12 µg/m³, reaching values between 20 to 35 µg/m³. We also observe variations in the concentrations along the different years. This might be caused by variations in rain and humidity and construction activities near the monitoring stations (SIMA, 2015).

Figure 2 shows the PM₁₀ annual average concentration data reported by SIMA since 1993. It can be

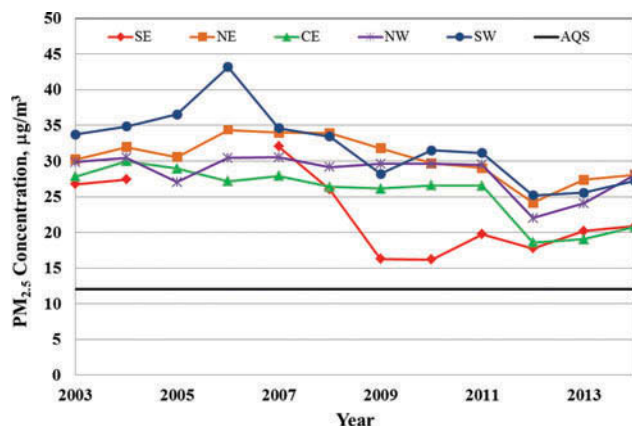


Figure 1. Annual average concentration of $PM_{2.5}$ in the Monterrey Metropolitan Area (MMA).

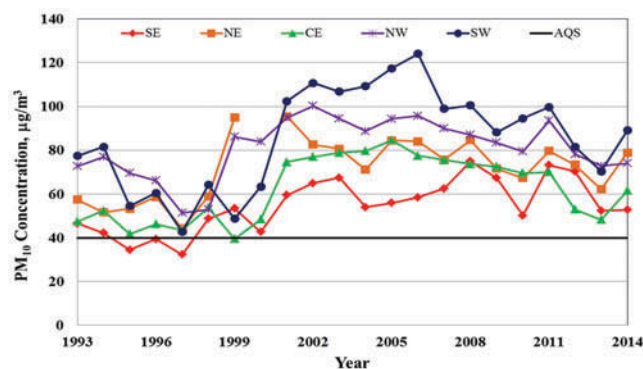


Figure 2. Annual average concentration of PM_{10} in the Monterrey Metropolitan Area (MMA).

observed that the most polluted region is located SW of the MMA, followed by the NW and NE regions. The data show that all regions in the MMA have exceeded the PM_{10} annual air quality standard of $40 \mu\text{g}/\text{m}^3$ since 1993 (SIMA, 2015). In the figure we observe an increase in concentration in the years 2000 to 2002. This may have been caused by an increase in the capacity of a refinery upwind of the MMA and by the introduction of approximately 300,000 used vehicles from the United States. We also observe a decrease and then an increase in concentrations of PM_{10} from 2005 to 2014; this might be caused by variations in rain and humidity through the different years (SIMA, 2015).

Air suspended particles impose a significant health risk and their impact on human health is well documented in the literature. In particular, $PM_{2.5}$ causes cardiovascular diseases and respiratory disorders (Dockery et al., 1993; Pope et al., 1995; Schwartz et al., 1996). Because of the size of these particles they can penetrate the respiratory system. A healthy human can retain most of the PM_{10} in the nose, or trap it in the mucous secretion, and limit them to the initial segments of the upper respiratory system. However, $PM_{2.5}$ can travel virtually unstopped to the

inner part of the respiratory system. Particulate matter has also the ability to transport several chemicals to the respiratory system, rendering them available for absorption. Nose exposure to $PM_{2.5}$ can produce inflammation with rising levels of eosinophils and $\alpha 1$ -antitrypsin (Nikasinovic et al., 2006). Both PM_{10} and $PM_{2.5}$ are associated with more emergency departments visits or hospital admissions (Norris et al., 1999; Lokman et al., 2008), and their effects vary from local irritation with cough triggering, to bronchospasm, lung tissue inflammation, lung remodeling, lung fibrosis, and lung metaplasia or neoplasia (Pope, 2000). In a national study of 3109 U.S. counties the association between long-term exposure to air pollution and death/chronic lower respiratory disease was established (Yongping et al., 2015). It has also been shown that when a child moves to another less polluted city that child's lung development and functioning improve (Avol et al., 2001). Gauderman demonstrated that when air quality improvement programs for nitrogen dioxide and $PM_{2.5}$ were implemented in polluted cities of California, the lung-growing capacity of children improved (Gauderman et al., 2015). Effective air quality improvement programs are necessary in the MMA. The rising levels of $PM_{2.5}$ in the MMA have been associated with increased asthma prevalence. This early health indicator points out the pernicious health effects of $PM_{2.5}$, and it also predicts other chronic health outcomes (Canseco et al., 1993; Vargas, 2009; Nathan et al., 2015).

The high levels of $PM_{2.5}$ concentration represent a serious health risk to the MMA population. In order to provide decision makers with technical and scientific information that allows them to implement strategies to control emissions of $PM_{2.5}$ and its precursors, we performed a source apportionment study using data from samples collected at two sites in two 15-day field campaigns, one in the autumn of 2007 and other in the summer of 2008. The samples were analyzed to obtain data about their chemical composition. In a previous work we analyzed the data of the autumn 2007 to identify main sources of pollutants using a factor analysis technique (Martinez et al., 2012). The sources identified included geological components (Al and Si); products of fuel combustion (elemental carbon, EC, and organic carbon, OC); biomass burning (K^+); and fuel burning emissions from electric power plants, industries, and refinery activities (V, S, and SO_4^{2-}). An important finding was that chlorine and chromium were associated with industrial activities rather than sea salt, due to the distance of the MMA of the ocean. The enrichment factor found of greater than 1000 for chlorine confirmed this hypothesis (Martinez et al., 2012). The results found were consistent with major sources of primary $PM_{2.5}$ and the precursor gases reported in emission inventories of the MMA

(SEMARNAT, 2015). However, the contribution of the different sources on $PM_{2.5}$ concentration levels in the atmosphere was not determined. The main objective of our study was to perform a source apportionment using the chemical mass balance (CMB) receptor model. Receptor models have been developed to identify and estimate the contributions of different sources in concentrations of airborne particulate matter. Receptor models oriented to source distributions infer the contribution of emission sources and atmospheric processes from measurements of air quality (Watson et al., 2008). Although we had a limited set of data to use the CMB at the time we performed this study, there is no other information to obtain a source apportionment of $PM_{2.5}$ in the MMA. Furthermore, the amount of secondary aerosol components in $PM_{2.5}$ was unknown. Despite this limitation, the results of this study are a basis to take better decisions on future air quality studies and to design basic strategies to improve the air quality in the MMA. In general, the results show that organic material and secondary inorganic aerosol (in the form of ammonium sulfate and ammonium nitrate) were the major mass components of $PM_{2.5}$. The principal sources identified were vehicle and refinery emissions of EC and precursor gases of secondary inorganic and organic aerosol. It was also found that the secondary organic aerosol (SOA) formation is most important during the summer than in the autumn, accounting for 69% of the organic carbon measured.

Methodology

We selected two sites in the NW and SW of the MMA to collect $PM_{2.5}$ samples. These sites are downwind of predominant winds in the MMA and are located approximately 21 km apart one from each other. The sites were identified as Escobedo (ESC) and Santa Catarina (SC), respectively. We collected 24-hr samples during two field campaigns. One was carried out in autumn 2007, from November 21 to December 10, and the other in summer 2008, from July 12 to 31. The ESC site was an area surrounded by warehouses and the samplers were located in the yard of a municipal office. Heavy-duty and light-duty vehicles circulate in a highway approximately 1 km north from the sampling site. Industrial activities are scarce near this site. This road connects the eastern area with the western area of the MMA, forming an arc north of the MMA. The SC site is an area surrounded by manufacturing industries and some chemical industries. The samplers were located in an area of administrative municipal offices. The two sites selected report the highest $PM_{2.5}$ concentrations measured in the MMA by the SIMA monitoring stations.

Experimental methods

Collection of $PM_{2.5}$ samples

We used Teflon and quartz filters to collect pairs of $PM_{2.5}$ samples at each site during autumn 2007 and summer 2008. We collected a total of 29 pairs of samples, 14 pairs at the SC site and 15 pairs at the ESC site, during autumn 2007, and a total of 30 pairs of samples, 15 pairs at the SC and 15 pairs at the ESC site, during summer 2008. Two pairs of low-volume sampling devices by Minivol Airmetrics were used to collect 24-hr samples of $PM_{2.5}$ at each site for both campaigns. These samplers (5 L/min) have been used before to address mass and chemical composition of fine PM (Chow and Watson, 2002; Vega et al., 2007). These samplers are reliable and have yielded similar concentration levels when they are located with another Minivol or other reference particulate sampler device (Baldof et al., 2001; Chow et al., 2008; Hill et al., 1999). A precalibrated digital manometer (Dwyer) was used to calibrate the inlet flow every day during the sampling period.

Analysis of $PM_{2.5}$ samples

The mass and trace elements were analyzed using the samples collected in the 47-mm Teflon filters. Anions, cations, elemental carbon (EC), and organic carbon (OC) were analyzed in the samples collected in the 47-mm quartz filters. The filters were prepared and analyzed by Chester LabNet in Tigard, OR. The filters were conditioned 48 hr at $20 \pm 1^\circ\text{C}$ and with a relative humidity of 30 to $40 \pm 5\%$, according to the method of reference for gravimetric use. The field blank filters (Teflon and quartz) were conditioned under the same conditions. All quartz filters were pre-fired to eliminate residues that could bias the chemical analysis. The filters were analyzed and the mass of the chemicals was subtracted from those measured in the filters used for sampling. Trace elements were analyzed using x-ray fluorescence (XRF) (Watson et al., 1999). After subtracting the elemental concentrations found in the blank filter, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb were detected with significant concentrations. Ion chromatography (IC) was used to analyze ions. The anions analyzed were Cl^- , nonvolatilized NO_3^- , and SO_4^{2-} . The cations analyzed were NH_4^+ , K^+ , and Na^+ . Organic carbon (OC) and elemental carbon (EC) were analyzed by thermal-optical transmittance (TOT).

Chemical composition

Correlation analysis was performed to evaluate the quality of the data (Chow et al., 1996; Vega et al.,

2004). We assumed that aerosol samples were formed by seven components: crustal matter, salts, ammonium sulfate, ammonium nitrate, EC, organic matter (OM), and trace elements not included in crustal matter. Ammonium nitrate and ammonium sulfate are an estimation of inorganic secondary aerosol. This classification has been used in other studies and is based on the mass balance and typical PM_{2.5} sources (Chan et al., 1997; Kovouras and Koutrakis, 2001; Zhang et al., 2002). The concentration of ammonium nitrate was estimated as $1.29 \times \text{NO}_3^-$ concentration and the concentration of sulfate salts was estimated as ammonium sulfate as $1.374 \times \text{SO}_4^{2-}$ concentration. Other sulfate and nitrate salts may be present in the PM_{2.5} samples, for example, NaNO₃. Then the mass of nitrate or sulfate salts may be higher than the mass estimated as ammonium salts and the latter would be a lower estimated value of nitrate and sulfate salts. We refer to the lower value as an estimate of the mass of sulfate and nitrate salts. Organic matter was obtained as $1.2 \times \text{OC}$ concentration in order to compensate for the mass of elements like oxygen, nitrogen, and hydrogen. Some authors suggest a value of 1.4 or even 1.6 (El-Zanan et al., 2009; Turpin and Lim, 2001). In this work we used a factor of 1.2 because it presented a better adjustment to the total daily mass concentrations obtained from the SIMA monitoring stations nearby the sampling sites. Crustal material was estimated as $1.89 \times \text{Al} + 2.14 \times \text{Si} + 1.4 \times \text{Ca} + 1.43 \times \text{Fe}$ concentrations. Trace elements were obtained adding all the elements from Na to Pb except Al, Si, Ca, Fe, Cl, K, Na, and S. As mentioned before, chlorine was associated to industrial sources rather than to sea spray and may be in the form of CaCl₂ and MgCl₂. We decided to confirm this hypothesis, including the marine salt profile in the CMB model analysis. The mass of marine salt was estimated as a function of the ion Cl⁻ multiplied by a factor of 1.65 (Vega et al., 2004). We refer to this estimated mass as chloride salts.

CMB model

The CMB model solves a set of linear equations using least squares. The equations express the relationship of ambient concentrations of chemical species with the sum of the product of the composition and contribution of emission sources. These equations are a direct consequence of the conservation of mass law and the ambient concentration of a species is expressed by eq 1 (Watson et al., 1998):

$$C_i = \sum_{j=1}^J F_{ij} \cdot S_j \quad (1)$$

In this equation, C_i is the ambient concentration of the species i measured at the receptor site; J is the number of sources that contribute; F_{ij} is the emissions fraction of the species i from the source j or emission profiles; and S_j is the impact of source j to the receptor (calculated source contribution). The equation is solved for each individual sample. If the measurement error is considered in eq 1, the ambient concentration is expressed by eq 2:

$$C_i = \sum_{j=1}^J F_{ij} \cdot S_j + e_i \quad (2)$$

In eq 2, e_i is the random error of measurement for the species i . The concentration of the species i in the receptor C_i may be measured at the receptor site. The emission profiles F_{ij} can be obtained from previous studies in the study site or similar sites. Thus, the CMB receptor model expresses concentrations of different chemical species (C_i) measured at a monitoring site (or "receptor") as a linear sum of products of source profile abundances (F_{ij}) and source contribution estimates (S_j). Source profiles are the mass fraction of a chemical or other property in the emissions from each source type that might contribute in the ambient concentration. Profiles are measured on samples from these sources at times and places believed to represent the composition of emissions when receptor measurements are made. The assignment of a specific source to the total mass of the PM_{2.5} depends of the emission profiles used. In this study we used the emission profiles for fugitive dust (paved and unpaved roads, agricultural soil, landfill, asphalt, cement, and gravel) reported by Watson and Chow (2001) for Mexicali, B. C., and for Mexico City (light and heavy gasoline and diesel vehicles and cooking processes) reported by Vega et al. (2001, 2009). We also used the emission profiles for secondary nitrate and sulfate reported by Watson et al. (1994). The U.S. Environmental Protection Agency (EPA) CMB model, version 8, was used for the analysis of the data (Watson et al., 1998; Watson et al., 1997).

Results and discussion

Figure 3 shows the average PM_{2.5} concentration values (μg/m³) for the Santa Catarina and Escobedo sites for both field campaigns. For comparison, the ambient 24-hr average air quality standard of 45 μg/m³ for PM_{2.5} is displayed in the figure. We observe that PM_{2.5} concentrations were higher during November–December than in July. The highest values were reached on November 29, 2007, with 51.7 μg/m³ for the SC site and December 4, 2007, with 59.3 μg/m³ for the ESC site. We observe

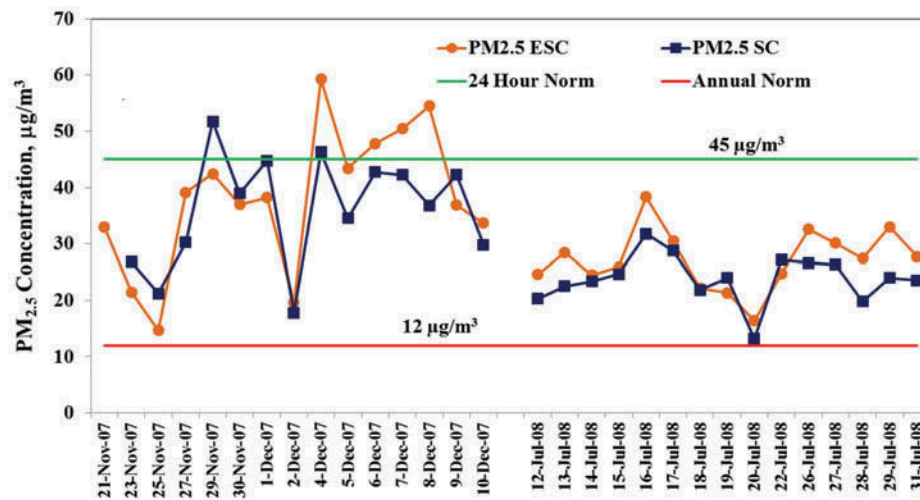


Figure 3. Mass concentration of PM_{2.5} obtained from gravimetric analysis in Escobedo (ESC) and Santa Catarina (SC) during the autumn 2007 and summer 2008 campaigns.

that the 24-hr standard for PM_{2.5} was exceeded twice in SC and four times in ESC. In the summer season campaign the concentration values were lower than in the autumn and reached maximum values on July 16, 2008, and July 29, 2008, with concentrations of 38.3 µg/m³ and 32.98 µg/m³, respectively. The 24-hr average was not exceeded in this campaign. It is important to note that the annual PM_{2.5} average norm of 12 µg/m³ was exceeded all days in both sides during the two campaigns. These concentrations are typical in these sites and represent a serious threat to the population's health. Lower values, but still well above the annual PM_{2.5} air quality standard, are found in other sites of the MMA. The associated health care and productivity costs are important, and actions need to be taken to reduce PM_{2.5} concentration in the MMA.

To confirm the homogeneity (or heterogeneity) of PM_{2.5} concentrations between the two sites, we calculated the divergence coefficient (DC), defined by eq 3, for each of the campaigns:

$$DC = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (3)$$

In eq 3 x_{ij} and x_{ik} represent the daily average PM_{2.5} concentrations at sites j and k , p is the number of observations, and i is the observation, in this case the daily data (Wongphatarakul et al., 1998). Values less than 0.2 indicate a good homogeneity between the two sites (Wilson et al., 2005). Such is the case of Escobedo and Santa Catarina for both campaigns. Table 1 shows the descriptive statistics of PM_{2.5} concentrations (µg/m³) in the ESC and SC sites for the two campaigns. The results indicate that the volume of air is well mixed at ground level on the west side of MMA, where the two sampling campaigns were performed. Regarding the variability of daily measurements, there is greater variability in autumn 2007 (average standard deviation of 11.45) than in summer 2008 (average standard deviation of 4.85). The high variability in the autumn can be due to accumulation of particles because of the low wind speed and the lower mixing height. These conditions may cause that some days present high PM_{2.5} concentration levels.

Chemical analysis of the samples

Table 2 shows the mean concentrations and standard deviations of 16 elements, three anions, three cations,

Table 1. Descriptive statistics of gravimetric analysis data of PM_{2.5} (µg/m³) for both sites (ESC and SC), in autumn 2007 and summer 2008 field campaigns.

Variable	Autumn 2007		Summer 2008	
	ESC	SC	ESC	SC
Number of samples	15	14	15	15
Mean concentration (µg/m ³)	38.09	36.15	27.18	23.86
Std. Dev. (µg/m ³)	13.01	9.88	5.38	4.32
R ²	0.586		0.591	
Linear Regression	PM _{2.5} (SC) = 0.582*PM _{2.5} (ESC) + 13.772		PM _{2.5} (SC) = 0.957*PM _{2.5} (ESC) + 4.335	
Divergence Coefficient (DC)	0.108		0.087	

Note: ESC (Escobedo) and SC (Santa Catarina). One sample was eliminated due to a failure of the sampling equipment in SC in the autumn 2007 campaign.

Table 2. Mean concentration and elemental analysis of 16 components of PM_{2.5}, in $\mu\text{g}/\text{m}^3 \pm$ standard deviation.

Component	Autumn 2007				Summer 2008			
	ESC		SC		ESC		SC	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
PM _{2.5}	38.0903	12.6138	36.1532	9.8809	23.8647	4.3171	27.1872	5.3829
Al	0.2512	0.2227	0.1243	0.0857	0.5633	0.3540	0.4604	0.3053
Si	0.5204	0.3738	0.4429	0.2748	1.0818	0.6260	0.9345	0.5958
S	1.5075	0.8368	1.6744	0.9398	2.3425	0.7680	2.4284	0.8963
Cl	0.2693	0.1640	0.3903	0.2970	0.0216	0.0455	0.0045	0.0124
K	0.3794	0.2226	0.3172	0.1336	0.1746	0.0803	0.1904	0.0888
Ca	1.6965	1.1561	1.5424	1.1789	0.6529	0.2526	0.4460	0.1900
Ti	0.0218	0.0149	0.0175	0.0085	0.0332	0.0189	0.0316	0.0168
V	0.0060	0.0075	0.0050	0.0039	0.0027	0.0031	0.0049	0.0055
Cr	0.0023	0.0031	0.0038	0.0029	0.0018	0.0018	0.0020	0.0021
Mn	0.0359	0.0305	0.0270	0.0204	0.0108	0.0056	0.0175	0.0101
Fe	0.4936	0.3586	0.4655	0.2657	0.3730	0.1850	0.4211	0.1836
Ni	0.0015	0.0018	0.0012	0.0015	0.0022	0.0034	0.0021	0.0028
Cu	0.0134	0.0097	0.0161	0.0204	0.0049	0.0036	0.0040	0.0046
Zn	0.1897	0.1065	0.1299	0.0529	0.0457	0.0231	0.0870	0.0355
Br	0.0259	0.0177	0.0093	0.0045	0.0030	0.0022	0.0059	0.0019
Pb	0.0719	0.0642	0.0835	0.0582	0.0299	0.0131	0.0288	0.0160
Cl ⁻	0.8530	0.4799	1.1173	0.4923	0.0743	0.1077	0.2847	0.1668
NO ₃ ⁻	3.6189	2.2190	3.8553	2.5280	0.8978	0.2318	1.3476	0.4080
SO ₄ ⁼	6.3952	3.2076	5.8829	2.8421	8.1376	2.8361	8.5597	2.3975
NH ₄ ⁺	0.9871	0.8405	1.0229	0.8921	1.8953	0.8240	2.0103	0.7691
K ⁺	0.3223	0.2053	0.2310	0.1179	0.0309	0.0819	0.0674	0.1186
Na ⁺	0.0	0.0	0.0	0.0	0.2182	0.1816	0.9759	1.7020
OC	13.5992	6.6581	12.0805	4.6298	6.5626	1.2993	7.9060	1.6775
EC	2.7352	0.9751	2.6227	1.3982	1.4230	0.5551	1.6284	0.4829
TC	16.3440	7.4524	14.6949	5.9470	7.9844	1.7108	9.5338	2.0505

Note: ESC (Escobedo) and SC (Santa Catarina).

and EC, OC, and total carbon (TC) analyzed in the filter samples for the two field campaigns. The data of the autumn 2007 campaign was published in a previous paper where the chemical composition of PM_{2.5} was discussed and a factor analysis technique was used to identify sources of PM_{2.5} (Martínez et al., 2012). In that campaign, values of Na⁺ concentration were not obtained and they were not included in the analysis of samples after subtracting the concentration of the blank filter. In Table 2 we observe that the major components in PM_{2.5} mass during the autumn 2007 campaign were organic carbon and elemental carbon, with concentrations of 13.6 $\mu\text{g}/\text{m}^3$ and 2.7 $\mu\text{g}/\text{m}^3$, respectively. Ions with higher contribution to PM_{2.5} mass were SO₄²⁻ with 6.4 $\mu\text{g}/\text{m}^3$ and NO₃⁻ with 3.6 $\mu\text{g}/\text{m}^3$. The chemical elements with the highest contribution to the mass were calcium with 1.7 $\mu\text{g}/\text{m}^3$, sulfur with 1.5 $\mu\text{g}/\text{m}^3$, and iron with 0.5 $\mu\text{g}/\text{m}^3$. During the summer campaign of 2008, the daily average PM_{2.5} concentration was lower than in the autumn campaign. The major contributors to PM_{2.5} mass were organic carbon and elemental carbon. The chemical elements with the highest mass contribution were sulfur with 2.34 $\mu\text{g}/\text{m}^3$, Si with 1.08 $\mu\text{g}/\text{m}^3$, and calcium with 0.65 $\mu\text{g}/\text{m}^3$. We observe that in many cases the calculated standard deviation of each chemical species is large compared with the calculated mean. This indicates variations in the chemical composition of the different daily samples of PM_{2.5}. Therefore, if we compare the mean concentrations of some species, like Cl and Cl⁻, we can infer inconsistencies

in the calculated concentrations; however, the estimated standard deviations compensate the difference and may lead to a different conclusion. More PM_{2.5} samples need to be analyzed in a future work to have a better understanding and conclusions about the chemical characterization of this pollutant in the MMA.

The data show that the amount of ammonium is not sufficient to neutralize all sulfate and nitrate; hence we expect that other sulfate and nitrate salts must be present. As we commented in the Experimental methods section, we estimated the mass of sulfate and nitrates as ammonium salts, considering the values obtained as lower estimates of the mass of these anions, and we refer to them as sulfate salts and nitrate salts. Although the chemical analysis does not report Na⁺ in the autumn 2007 samples, the low ratio Cl⁻/Na⁺ of the summer 2008 samples indicates the possible formation of NaNO₃ and gaseous HCl (Pio et al., 1996; Contini et al., 2014). In the work developed by Martínez et al. (2012) it was found that chloride in the MMA may come mostly from industrial process. We may expect that other insoluble forms of chloride salts like CaCl₂ and MgCl₂ may be present, as well as carbonate salts, like CaCO₃ and MgCO₃ (Contini et al., 2014; Perrino et al., 2014).

The results show that the concentrations of the chemical elements in the ESC and SC sites in each campaign are very similar in terms of their contribution to the mass. This can be seen in Figures 4 and 5, which show, respectively, the percentages of the main element and ion

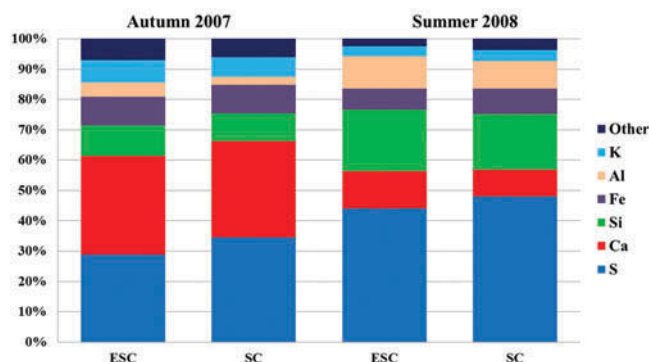


Figure 4. Percentage contribution of chemical elements in the autumn and summer campaigns.

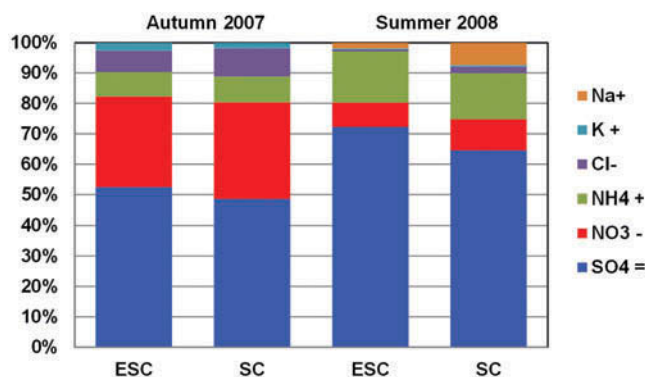


Figure 5. Percentage contribution of anions and cations in the autumn and summer campaigns.

components for the autumn 2007 and the summer 2008. The main element components in $PM_{2.5}$ are S, Ca, Si, Fe, Al, and K. We observe in Figure 4 that the percentage contents of Ca, Fe, and K associated with mineral dust in the autumn is higher than in the summer, perhaps associated with an increase of $CaCO_3$ (Perrino et al., 2014), while the percentages of S, Si, and Al are higher in the summer. In Figure 5 we observe that the main ion component is sulfate, representing 52% in ESC and 49% in SC of the ion mass in the autumn. These percentages increase in the summer to 72% of the total ion mass in ESC and 69% in SC. This increment might happen because the main route of inorganic secondary aerosol formation of ammonium sulfate is the reaction of sulfur dioxide with the radical $OH\cdot$ (which depends on solar radiation), forming sulfuric acid, the main precursor of $(NH_4)_2SO_4$. Other main ion components in $PM_{2.5}$ are nitrate and ammonium.

Correlation among chemical elements

We calculated correlation coefficients (r^2) between chemical species to verify the quality assurance–quality

control of the chemical analysis data for both $PM_{2.5}$ Teflon filters (metals) and quartz filters (anions, cations, organic carbon, and elemental carbon) (Watson and Chow, 2001; Chow et al., 1994). Figure 6 shows the correlation between the mass measured by gravimetry and the sum of the mass of 38 metals measured by XRF. The correlation for the autumn 2007 campaign was $r^2 = 0.827$ while for the summer campaign it was $r^2 = 0.684$. The correlation between anions and cations for the autumn 2007 campaign was $r^2 = 0.932$ and 0.785 for summer 2008, as shown in Figure 7. These correlation coefficients indicate that the chemical analyses of samples were consistent in the quantification of ions for the two seasons. We observe an outlier in the summer data corresponding to a higher concentration of cations than anions. If this datum is neglected, the coefficient of correlation would be closer to 1.0. The atmosphere should be neutral if the relation of cations and anions were 1:1. As commented in the previous section, since some

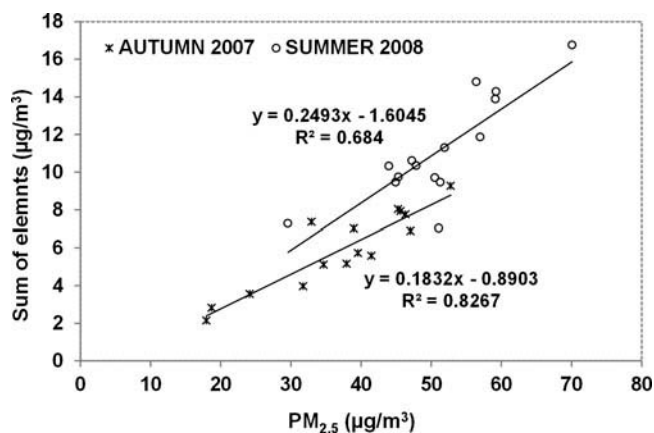


Figure 6. Correlation between $PM_{2.5}$ mass and the sum of elements measured by XRF.

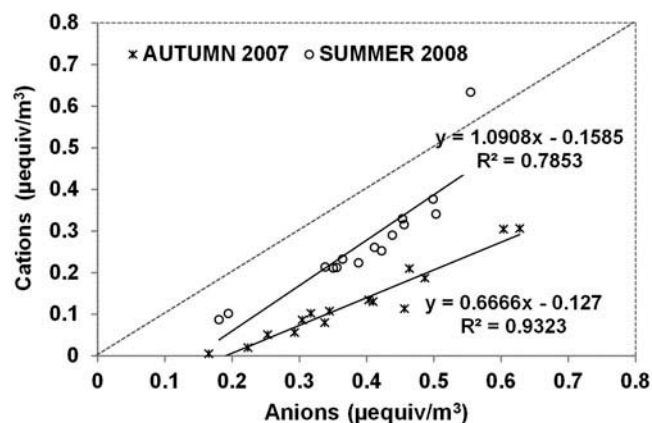


Figure 7. Correlation between anions and cations ($\mu\text{equiv}/\text{m}^3$). The dotted line represents 1:1 ratio of cations and anions.

cations may not be measured, specifically Ca^{2+} , Mg^{2+} , and Na^+ ions, we expect that the sum of anions is higher than the sum of cations.

Chemical components quantified in both monitoring campaigns in the ESC and SC sites were grouped and classified as organic matter (OM), crustal material (CM), trace elements not included in the geological material (TE), nitrate salts, sulfate salts, chloride salts (Salts) and elemental carbon (EC). Figure 8 shows the contributions of each component as a percentage. In this figure we observe that the chemical composition of $\text{PM}_{2.5}$ at both sites is similar. In autumn 2007 the OM contribution in Escobedo was 43%, and 40% in Santa Catarina. In summer 2008, the OM contribution in Escobedo was 29.4%, and 32% in Santa Catarina. The same behavior was observed for the contributions of ammonium sulfate in the 2007 autumn campaign, being 23.10% in Escobedo and 22.41% in Santa Catarina. During the summer these percentages were 41.83% and 39.90% in Escobedo in Santa Catarina, respectively. In the autumn, OM is the predominant component, while in the summer, ammonium sulfate is the predominant component. We also observe that the amount of chloride salts (Salts) is about five times higher in SC than in ESC. This may be due to the presence of manufacturing and chemical industries in SC that may be an important source of chloride emissions.

Primary organic aerosol (POA) and secondary organic carbon (SOC)

The EC tracer method was used to estimate the fraction of secondary organic carbon (SOC) in $\text{PM}_{2.5}$ (Turpin and Huntzicker, 1995). In this study the lowest 20% OC/EC ratios were used in a Deming regression to estimate the primary organic carbon (POC). We obtained eqs 4 and 5 applying Deming regression:

$$\text{Autumn 2007 POC} = - (1.07 \pm 3.13) + (3.88 \pm 1) \text{ EC} \quad (4)$$

$$\text{Summer 2008 POC} = - (1.78 \pm 2.6) + (4.36 \pm 1.38) \text{ EC} \quad (5)$$

The average intercept (b) in both campaigns was negative, but it can be positive in one of its limits. A negative value of b represents a correction of primary organic carbon that comes from the combustion or biogenic sources, such as industrial processes from grinding of abrasive minerals containing carbon (Baumann et al., 2008; Cabada et al., 2004). The uncertainties in the estimated value of this parameter suggest that there may be elemental carbon that comes from combustion processes. Some studies did not include the parameter b in estimating POC, which means that the OC sources, other than combustion, are ignored. Table 3 shows the percentage contribution of SOC ($\text{SOC}/\text{OC}_{\text{measured}} \times 100\%$) estimated in the campaigns of autumn 2007 and summer 2008 with and without considering the intercept b .

Source apportionment using CMB

In this study we applied the CMB model to analyze the data obtained in each sampling site and then to the whole data. We used this procedure for the autumn 2007 and summer 2008 campaigns. Figure 9 shows the average percent source apportionment obtained for each

Table 3. Estimated secondary organic carbon (SOC) for autumn 2007 and summer 2008 field campaigns (95% confidence interval).

Campaign	Average %SOC	
	POC = (OC/EC)*a+b	POC = (OC/EC)*a
Autumn 2007	34% (0 – 67%)	24% (17 – 39%)
Summer 2008	69% (–)	40% (23 – 39%)

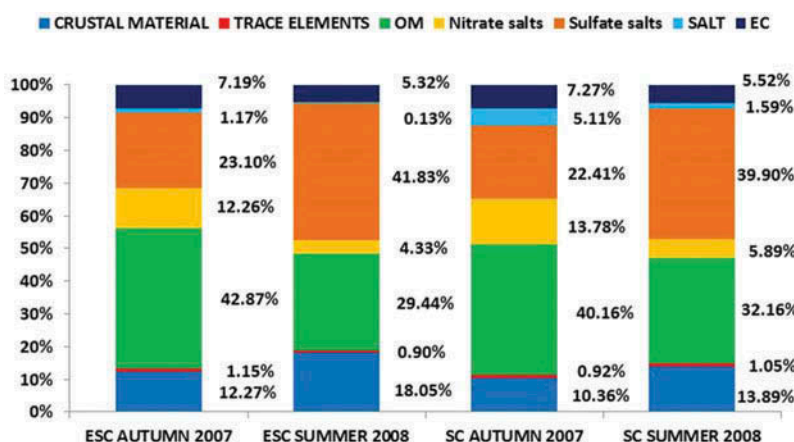


Figure 8. Percentage mass contribution of $\text{PM}_{2.5}$ components at the (Escobedo) ESC and Santa Catarina (SC) sites.

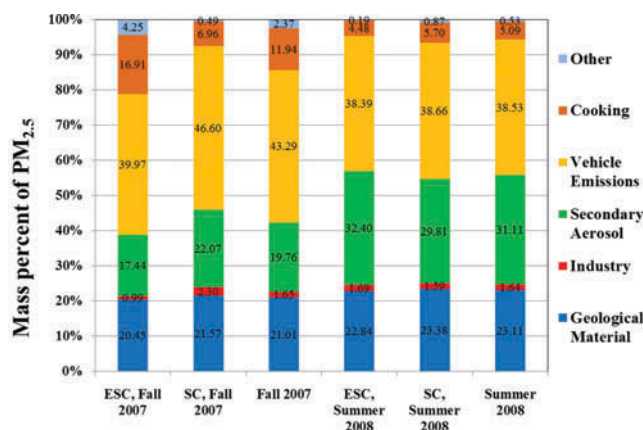


Figure 9. Estimated source contribution in percent to PM_{2.5} concentration using the CMB model in the autumn 2007 and summer 2008 campaigns.

sampling season and for all the samples resulting in an estimated seasonal average apportionment of the different sources. We observe that the source apportionment is similar for both sites in each campaign. For the autumn campaign of 2007, we found that the largest contribution to the total mass of PM_{2.5} was vehicle emissions with 43% and a concentration of $16.04 \pm 17.56 \mu\text{g}/\text{m}^3$. Secondary aerosol was the second highest contribution with approximately 20% and a concentration of $7.31 \pm 7.39 \mu\text{g}/\text{m}^3$. The industrial sources contributed with approximately 2% of the total mass and a concentration of $0.60 \pm 0.79 \mu\text{g}/\text{m}^3$. Cooking food, that is, emissions from food cooking processes like tortillas or corn-patty production, meat frying, and charbroiling (Vega et al., 2009), accounted for 12% ($4.48 \pm 8.63 \mu\text{g}/\text{m}^3$), while crustal material contributed with 21% and a concentration of $7.79 \pm 6.98 \mu\text{g}/\text{m}^3$. The results of the CMB model for the summer 2008 campaign show that the major sources of PM_{2.5} were mobile sources and secondary inorganic aerosol. The contribution of vehicle emissions was 38% ($9.19 \pm 6.77 \mu\text{g}/\text{m}^3$). The contribution of inorganic aerosol was 31% and a concentration of $7.42 \pm 5.61 \mu\text{g}/\text{m}^3$. The industrial sources contributed with approximately 2% ($0.39 \pm 0.29 \mu\text{g}/\text{m}^3$). Cooking contributed 5% to the total mass of PM_{2.5} ($1.21 \pm 0.85 \mu\text{g}/\text{m}^3$) and crustal material had a contribution of 23% ($5.52 \pm 4.01 \mu\text{g}/\text{m}^3$). The CMB model did not select the marine salt profile, confirming the hypothesis that industries are the main sources of chloride, rather than marine salt form the ocean spray.

Important uncertainties exist in the estimated average contributions of the different sources to the PM_{2.5} mass shown in Figure 9. These uncertainties are inherent to the sampling process, chemical analysis techniques, and emission profiles used in the CMB model. Moreover, the

model adjusts the profiles to the actual composition data, minimizing the difference of the actual concentrations of chemical species and the calculated concentrations with the model. Then we may expect an error in the approximation of the actual contribution of the source and the estimated contribution of the source included in the analysis. These facts and the lack of data of some chemical species explain differences in the mass closure if we compare Figures 8 and 9. For example, calcium and magnesium carbonates not considered in the crustal material may cause a lower estimate in the amount of geological material than that estimated from the CMB model. On the contrary, secondary aerosol is larger than the amount calculated with the CMB model because measured ammonium is not sufficient to neutralize the sulfate and the nitrate and there may be sodium nitrate present. Despite these differences, the results of this study are consistent in general with the sources reported in the emission inventory and are valuable for designing strategies to control emissions sources of PM_{2.5} and its precursor gases.

We also observe in Figure 9 that vehicle emissions were more important in autumn 2007, while the contribution of secondary aerosol was more significant in summer 2008. One possible explanation for the seasonal variation is the largest impact on gasoline engines in particulate emissions during cold starts at low temperatures (Ke et al., 2008). The production of secondary sulfate in the summer is partially due to the higher solar radiation and high temperatures, which favor the photochemical conversion of sulfur dioxide to sulfate (Kasibhatla et al., 1997; Querol et al., 1998; Vecchi et al., 2004). Table 4 shows a summary of the estimated average contribution in percentage by source category and location using the CMB model. We observe that the major sources of primary and secondary PM_{2.5} include mobile sources, secondary inorganic and organic aerosol formation, geological material, cooking, and industrial sources. We also observe that the source apportionment on PM_{2.5} concentration in the ESC and SC sites is very similar except for the case of cooking, where its contribution in ESC is around 68% higher than in SC.

Table 4. Estimated source contribution on PM_{2.5} concentration at the Escobedo (ESC) and Santa Catarina (SC) sites.

Source	ESC	SC
Vehicle Emissions	39.18	42.63
Secondary Aerosol	24.92	25.94
Geological Material	21.645	22.475
Cooking	10.695	6.33
Industry	1.34	1.945
Other	2.22	0.68
Total	100%	100%

There is a strong need for air quality improvement programs for the MMA. We have an urgent need to lower PMs, nitrous oxides, sulfur oxides, ozone, VOCs, and other air pollutants. With an increasing and heavily polluted city we are generating weaker individuals, with increased susceptibility to several acute and chronic diseases and with limited life span, limited quality of life, and increased costs for their medical care. This study provides information to take better decisions on air pollution control in the MMA. The results show that vehicle emission and secondary inorganic and organic aerosol are the major contributors to the mass of PM_{2.5} in the MMA. To reduce PM_{2.5} concentration it is necessary to focus on strategies for reducing the use of cars and on establishing programs of inspection and maintenance for motor vehicles. An integrated transportation system that substitutes for the use of cars can be an efficient strategy to reduce emissions of ammonium, nitrogen oxides, and VOCs, all of them precursor gases of secondary aerosol and components of PM_{2.5} in the atmosphere of the MMA. An important component of the inorganic secondary aerosol is sulfate. Hence, it is necessary to reduce SO₂ emissions from the oil refinery located in Cadereyta, east and upwind of the MMA, as well as sulfur content in fuels, another important source of SO₂ in the MMA.

Summary

In this work we present the results of a chemical characterization and source apportionment study of PM_{2.5} in the MMA. Samples were taken in two different seasons, autumn 2007 and summer 2008, at two sites, Escobedo (ESC) and Santa Catarina (SC). The chemical analysis of the samples shows that the composition of PM_{2.5} is similar in both sites in each campaign, with predominance of organic and elemental carbon in the autumn and of ammonium sulfate during the summer. These results indicate that both sites, located west of the MMA, receive a similar mixture of aerosol resulting from the sources of primary PM_{2.5} and its precursors located upwind, at the center and east of the MMA. The control and reduction of NO_x, VOCs, NH₃, and SO₂ emissions seems to be a good strategy to reduce PM_{2.5} concentration in the MMA. The main sources of sulfur are an oil refinery east of the MMA and the sulfur content in fuels. A good strategy would be the reduction of direct emissions and the sulfur content in fuels. The results obtained with the CMB model show that mobile sources are an important source of primary PM_{2.5} and its precursors, NO_x, VOCs, and NH₃. Emissions from mobile sources may be reduced through an integrated transportation system and

improving the mechanical and operation conditions of the vehicle fleet.

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