



# Analysis of PM<sub>2.5</sub> in Córdoba, Argentina under the effects of the El Niño Southern Oscillation



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## HIGHLIGHTS

- Córdoba has PM<sub>2.5</sub> levels well above WHO standards for the (2014–2016) period.
- Heavy levels of toxic metal concentrations are found in the City.
- Combustion and traffic-related emission processes are the major sources of PM<sub>2.5</sub>.
- The effect of ENSO on PM<sub>2.5</sub> speciation data was analyzed.

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## ABSTRACT

In this work, PM<sub>2.5</sub> samples were collected in the winter-spring months of 2014–2016 at an urban site in Córdoba. Córdoba is the second largest city in Argentina and is an important industrial and touristic center. The collected samples were individually analyzed for chemical composition using different techniques. The soluble inorganic ions and carbonaceous particles were determined from bulk aerosol samples for the first time in the city. The mass concentrations of PM<sub>2.5</sub>, organic carbon, elemental carbon, inorganic ions and metals were determined according to the mass balance. The dominant mass components were organic matter and elemental carbon (54.8%), mineral dust (6.1%), secondary inorganic aerosols (3.0%), and salt (1.2%). A principal component analysis was applied to the samples and resulted in five major factors that explained 79% of the variance in PM<sub>2.5</sub>. These factors represented combustion, industrial sources, soil dust, secondary inorganic aerosol, and salt, and each explained between 11% and 20% of the variance. A comparison with the results from a previous campaign (2010–2011) revealed appreciable changes in the PM<sub>2.5</sub> chemical composition. These changes were attributed to the two extreme meteorological conditions that prevailed in the region. The years 2014–2016 were largely dominated by the warm phase of the El Niño–Southern Oscillation, which leads to humid and cold weather in the Córdoba region, while the samples from 2010 to 2011 were collected during the dry and hot years resulting from the La Niña regime.

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## 1. Introduction

Ambient aerosols have received much attention due to their potential influences on air quality, climate change, and human health. According to the World Health Organization (WHO, 2013), urban air pollution can be blamed for several health issues such as pulmonary and respiratory diseases as well as certain types of

human cancer. High levels of particulate matter increase the number of deaths from cardiovascular events (Pope, 2000; Seaton et al., 1995). Air pollution from fine atmospheric particulate matter (PM<sub>2.5</sub> or particulate matter finer than 2.5 μm) has accounted for 3.1 million deaths worldwide (Apte et al., 2015), and the resulting costs have reached 5% of the GBP (World Bank, 2016). Thus, each 10 μg m<sup>-3</sup> increase in PM<sub>2.5</sub> concentration is linked to a 10% increase in overall mortality and a 3–7% increase in cardiovascular disease mortality (Brook et al., 2010).

One of the main components of fine particles (PM<sub>2.5</sub>) is water-soluble inorganic ions, accounting for a large fraction of the PM<sub>2.5</sub>

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mass concentration. In addition, the mass contribution of the carbonaceous fraction is also important. According to their thermal and optical properties, carbonaceous particles are classified as elemental carbon (EC) and organic carbon (OC). EC is usually emitted as a primary pollutant into the atmosphere due to the incomplete combustion of fuels. On the other hand, although a fraction of OC can also arise from combustion sources, an important fraction is generated by complex secondary aerosol formation processes (Jimenez et al., 2009).

To assess the contributions of different particle sources, receptor modeling has been a widely used tool in studies of air pollution source apportionment (Belis et al., 2013). Receptor tools analyze the matrixes of experimental particulate matter (PM) chemical speciation data, identify the major factors or sources, and subsequently obtain the quantitative estimations of their specific contributions to the ambient PM mass concentrations.

There are limited studies on air pollution in Córdoba, Argentina, and studies have only been performed during the last few decades (Stein and Toselli, 1996; Olcese and Toselli, 2002). The results of these studies have revealed the frequent occurrence of thermal inversions during the winter due to the topography of Córdoba. Stable atmospheric conditions that are due to strong radiative temperature inversions prevent the vertical diffusion of air pollutants, while calm winds prevent the horizontal transport. Therefore, air pollutants remain near the surface in the city. Particulate matter is the pollutant of primary concern, and PM<sub>10</sub> values have been measured to be much higher than  $150 \mu\text{g m}^{-3}$  on several days during the year (Olcese and Toselli, 2002). More recently, studies on the compositions of PM<sub>10</sub> and PM<sub>2.5</sub> have been performed (López et al., 2011; Achad et al., 2014). These studies have measured the elemental aerosol composition using synchrotron radiation X-ray fluorescence. Due to the nature of this technique, neither carbonaceous species nor water-soluble inorganic ions were determined in these studies.

The present study aims to increase the knowledge of PM<sub>2.5</sub> composition by quantifying species that were not determined before for the city, and to assess the effects of the meteorology on the collected aerosol samples. To achieve that, PM<sub>2.5</sub> samples were collected at one representative monitoring site of Córdoba, Argentina in 2014–2016. The bulk aerosol samples were quantitatively analyzed using a variety of techniques (Querol et al., 2001) to determine inorganic ions, carbonaceous particles, and metals. The chemical composition of PM<sub>2.5</sub>, the site-specific characteristics, and the meteorology were examined to determine the formation and sources of PM<sub>2.5</sub> in the city. A principal component analysis (PCA) was used to estimate the contribution of the different emission sources to the PM measured at the study site. To the best of our knowledge, this is the first time that soluble inorganic ions and carbonaceous particles (EC and OC) were determined from bulk aerosol samples in the city. A comparison with the results of a previous campaign (2010–2011) is also presented. The samples for both campaigns were collected at the same monitoring site but under opposite El Niño–Southern Oscillation (ENSO) conditions. It has been demonstrated that meteorology plays an important role on air pollution at a given site (Fleming et al., 2012; Olcese and Toselli, 1997; Wie and Moon, 2017; Singh and Palazoglu, 2011, 2012).

In relation to that, the ENSO is a phenomenon that is considered the strongest natural climate fluctuation on the global timescale. The ENSO has two phases: warm (El Niño) and cold (La Niña), which are characterized by positive and negative sea surface temperature anomalies, respectively. These oscillations occur every three to seven years and produce worldwide weather perturbations with strong effects on the environment (Kogan and Guo, 2017). Following the ENSO, some regions experience hot and dry weather, while others experience wet and cool weather. There is evidence

that the effects of El Niño are stronger and more direct in South America than in North America (Meerhoff, 2008). In periods associated with La Niña, central Argentina is characterized by drought and an abundance of fires in the Córdoba region (Achad et al., 2014) whereas the opposite is found during El Niño regimes.

The knowledge gained from this study can provide a scientific basis for emission control policies used for the remediation of local air pollution when El Niño and La Niña regimes influence the air quality in the study region.

## 2. Methodology

### 2.1. Study area and sampling site

The study was performed in Córdoba, the second largest city in Argentina, with a population of 1.3 million people. It is located at  $31^\circ 24' \text{ S}$  and  $64^\circ 11' \text{ W}$  at approximately 470 m.a.s.l. The climate is subhumid with a mean annual precipitation of 790 mm (mainly concentrated in the summer), a mean annual temperature of  $17.4^\circ \text{C}$  and winds prevailing from the NE (Argentinean National Weather Service, [www.smn.gov.ar](http://www.smn.gov.ar)). The 2014–2016 sampling campaign was carried out during the El Niño Southern Oscillation, which was one of the strongest events of the past 36 years. The ENSO started to form during late 2014, and it developed until 2016. As previously stated, El Niño years in northern-central Argentina are characterized by wet and cool weather (Kogan and Guo, 2017).

Several industrial plants are located in the suburban areas surrounding the city, including automobile factories, auto part industries, agro-industries, cement, and food processing companies (Fig. 1). The major car manufacturing factories are located in the southeast and southwest parts of the town and many small auto part factories are located in the same area. There is another industrial area to the north with many small and medium-sized industries, predominantly metallurgical. The central area is densely built-up and is located in a depression (Achad et al., 2014).

In the present study, the site selected for PM<sub>2.5</sub> sampling and characterization is located 2.5 km south of downtown (Fig. 1) on a university campus where there are some trees and bare soil areas. The PM<sub>2.5</sub> sampler was placed on a balcony on the second floor of a building. A few low buildings that do not block the air circulation surround the site. The sampling site is 150 m from a street with a moderate flow of vehicles (close to 1000 vehicles per hour during the daytime) and 300 m away from 2 major transportation avenues with high traffic densities during most of the day. The public transportation system (buses) makes an important contribution to the traffic in the area. The sampling site is located downwind from the downtown area (Figs. 1 and 2).

### 2.2. Experimental setup

A total of 21 24-h samples of PM<sub>2.5</sub> were collected using a low-volume impactor at one monitoring site. The SKC Deployable Particulate Sampling System was employed to sample PM<sub>2.5</sub>. Particles smaller than the cut-point were collected on 47-mm quartz filters (Pall Corporation). A flow rate of  $10 \text{ L min}^{-1}$  was maintained to ensure the maximum efficiency of the instrument, and the total sampling volume was registered for each measurement. The samples were collected at a frequency of two to three samples per month from August to November of 2014 and 2015, and additional measurements were collected in May 2016. It is important to point out that although the number of samples seems to be low, the results that will be presented here were not obtained from filters collected by an automatic air monitoring station, because unfortunately none is available in Córdoba city (not even in Argentina). In this work, the filters were collected each day that it was possible to

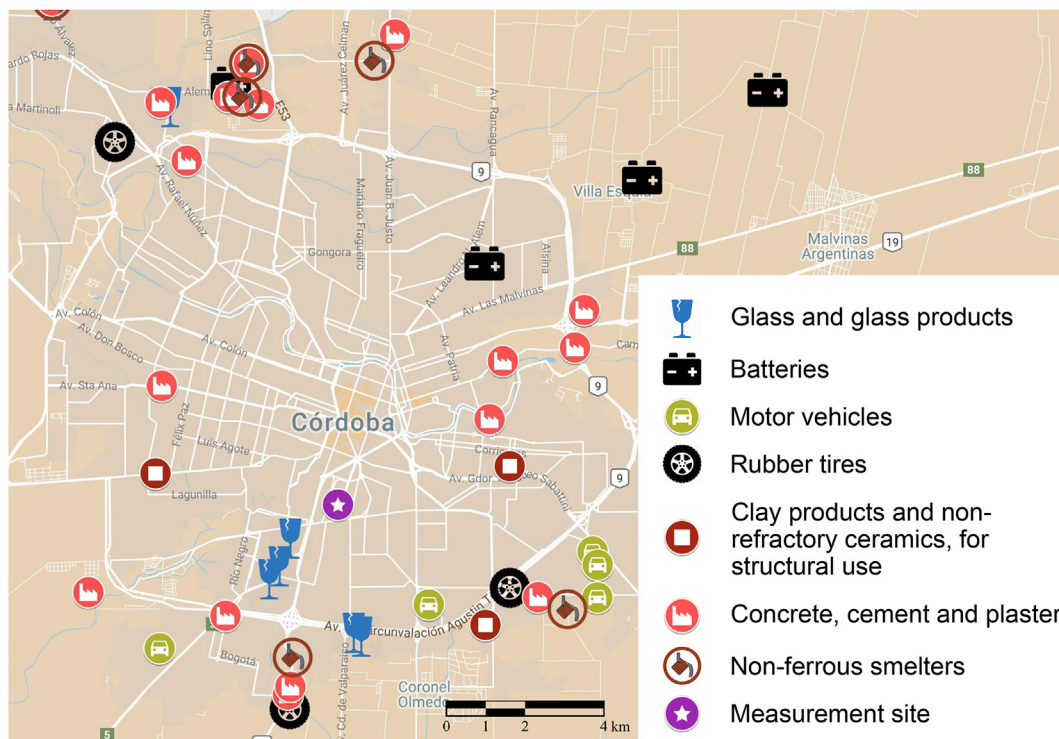


Fig. 1. A map depicting the city of Córdoba together with the location of the monitoring site and the major industrial types that surround the central area of the city.

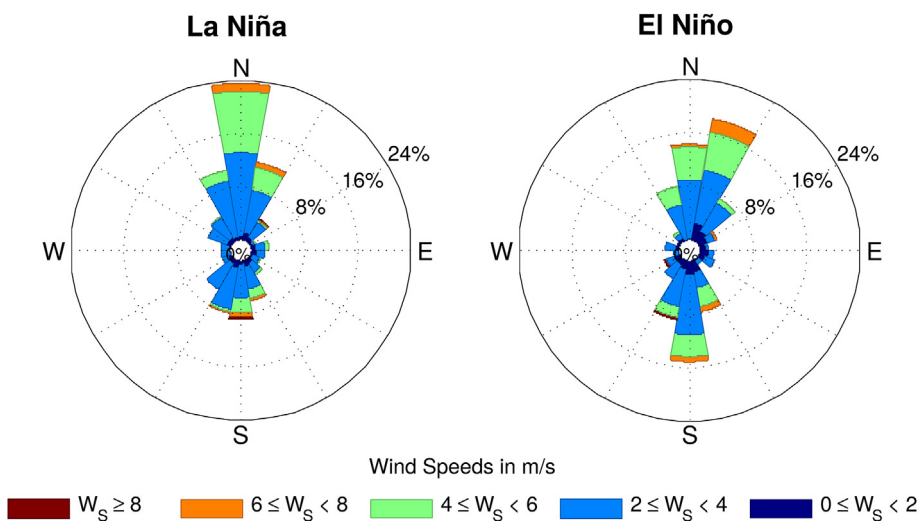


Fig. 2. Wind rose for the months when the PM<sub>2.5</sub> data were collected during the La Niña (2010–2011) and El Niño (2014–2016) conditions. The data were provided by the Argentinean National Weather Service.

perform the sampling and after that, the composition analysis was carried out. Unfortunately, during the months of the campaign abundant days of heavy rains and some experimental problems prevented us to carry out the measurements for PM<sub>2.5</sub> in a more continuous way. Gravimetric determinations of the quartz micro-fiber filters were performed following standard procedures. The filters were pretreated at 205 °C, conditioned at 20 ± 2 °C and 50 ± 5% RH, and weighed before and after sampling until constant values were obtained. Subsequently, the filters were treated and analyzed using a variety of techniques to determine the concentrations of the carbonaceous fraction (OC and EC), soluble ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>), and major and trace elements (Al, Fe, Ca, Na, K,

Mg, P, Ti, Mn, Sr, Rb, Zn, Cu, Sb, Sn, Pb, V, Ni, Co, among others) according to the methodology by Querol et al. (2001) and Cavalli et al. (2010). Blank filters were analyzed with each batch, and the corresponding values were subtracted from each sample.

An acid (HF:HClO<sub>4</sub>:HNO<sub>3</sub>) digestion of half of each filter was carried out for each sample to yield the solutions for the subsequent analysis of the major and trace elements using inductively coupled atomic emission spectrometry (ICP-AES)(iCAP 6500 Radial, THERMO), and inductively coupled plasma mass spectrometry (ICP-MS)(X Series II, THERMO), respectively. The low volume samples coupled with the analytical methodology allowed for ICP-AES detection limits below 0.1 µg m<sup>-3</sup> for most major elements,

with the exception of K ( $0.5 \mu\text{g m}^{-3}$ ). The detection limits for all trace elements with ICP-MS were  $0.6 \text{ ng m}^{-3}$ , although many of the detection limits were close to  $0.1 \text{ ng m}^{-3}$ . The estimated relative analytical errors were lower than 10% for most elements, except for P and K (15%). The concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were determined from the water leachates of the half fraction of each filter using ion chromatography HPLC (high-performance liquid chromatography) using a Waters IC-Pak Anion HR column, a DIO-NEX BioLC ED50 electrochemical detector and a JASCO UV 2075 Plus detector ( $\text{NO}_3^-$ ). The  $\text{NH}_4^+$  concentrations were determined from the same leachates using an ion selective electrode (THERMO Orion High-Performance Ammonia Electrode). The detection limits were 0.2, 0.09, 0.2 and  $0.1 \mu\text{g m}^{-3}$  for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NH}_4^+$ , respectively. Finally, the OC and EC levels were determined directly from the  $1.5 \text{ cm}^2$  filter sections using a thermal/optical carbon analyzer (SUNSET, EUSAAR2 protocol, Cavalli et al., 2010). The detection limits of this method were below  $0.2 \mu\text{g m}^{-3}$  for both OC and EC.

The  $\text{SiO}_2$  was determined indirectly depending on Al ( $\text{SiO}_2 = 2.5 \text{ Al}_2\text{O}_3$ ) using prior experimental equations (Querol et al., 2001). The OM (organic matter) was determined from the OC ( $\text{OM} = 2.1 \text{ OC}$ , Turpin and Lim, 2001). The crustal components were grouped as mineral matter (sum of  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and  $\text{P}_2\text{O}_5$ ). This methodology allowed us to determine from 65% of the PM mass. The unaccounted mass is generally attributed to the particle-bound or particle adsorbed water that is not eliminated during the filter conditioning or to the measurement artifacts (Perrino et al., 2013).

### 2.3. Source apportionment and trajectory analysis

Principal component analysis (PCA) is a method of source apportionment approved and recommended by the US Environmental Protection Agency (EPA). PCA was used in the present study to correlate the measured variables with the possible sources without any specific assumptions about the number or nature of the sources (Pitchford et al., 1967). PCA is useful for reducing the dimensions of large datasets containing a large number of variables and for retaining as much of the variation in the original data as possible. In this study, PCA was employed to investigate the statistically significant relationships between the variables using the orthogonal transformation of the raw datasets. PCA was performed using the “psych” package (version 1.7.5, Revelle, 2017) in R (version 3.4.0, R Core Team, 2017).

The hybrid single particle Lagrangian integrated trajectory (HYSPLIT; Stein et al., 2015; Rolph, 2017) model was used to compute the 48-h backward trajectories starting at 10 m above the surface. A new trajectory began each hour during each of the 24-h PM2.5 collection when high aerosol loads were recorded. Additionally, the same kind of trajectories were computed up to 12-h before the start of sampling to account for the previous loading of the atmosphere. Overall, 36 48-h backward trajectories were computed for each of those days. The NCEP GDAS meteorological fields with a horizontal resolution of  $0.5 \times 0.5^\circ$  and 47 vertical levels were used.

## 3. Results and discussion

### 3.1. Meteorological differences between the 2014–2016 El Niño and the 2010–2011 La Niña

As previously stated, 2010–2011 were dry and hot years due to the La Niña regime, which is characterized by drought and an abundance of forest fires in the Córdoba region (Achad et al., 2014). In late 2014, El Niño conditions began to develop, leading to humid

and cold weather.

In this campaign (2014–2016), more than 50% of the sky was covered with clouds for 46% of the year, compared to 27% of the year observed in the 2010–2011 campaign. It rained an average of 124 days per year in 2014–2016, opposed to only 83 days per year in 2010–2011. The influence of El Niño was observed not only in changes in the wet/dry, cold/hot conditions (El Niño/La Niña) but also in changes in the wind patterns between the two periods. Fig. 2 shows the wind rose for the months where PM2.5 was collected during the La Niña and El Niño conditions. The percentage of the winds originating from the south doubled, and the southern part of the city is where the largest cement and motor vehicle industries are located (Fig. 1).

### 3.2. PM2.5 ambient concentrations

Table 1 shows that very high mean PM2.5 concentrations were recorded during the 2014–2016 campaign, with 48, 28, 17 and  $164 \mu\text{g m}^{-3}$  as the mean, median, min, and max values, respectively. Fig. 3 shows the average monthly evolution of PM2.5 from August to November (2014–2015) together with measurements obtained in a previous study (2010–2011) at the same site (Achad et al., 2014). The concentrations measured in May were not included in this figure because they are only from 2016.

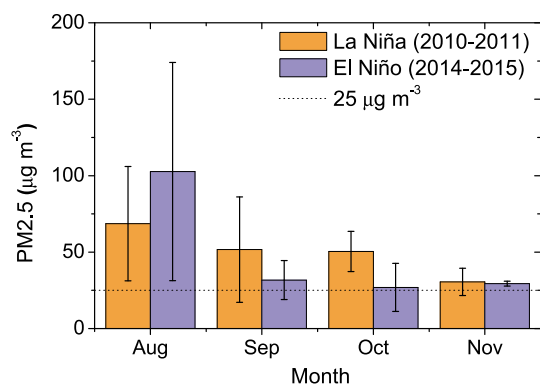
The average monthly concentrations exceeded the daily PM2.5 guideline recommended by the WHO ( $25 \mu\text{g m}^{-3}$ ) in both

**Table 1**

Average elemental concentrations, standard deviations, minimum values, medians, and maximum values ( $\text{ng m}^{-3}$ ) for the PM2.5 size fractions for May–November (2014–2016).

| Species ( $\text{ng} \cdot \text{m}^{-3}$ ) | Average | SD      | Minimum | Median  | Maximum  |
|---|---------|---------|---------|---------|----------|
| PM2.5                                       | 48111.3 | 44553.9 | 16583.9 | 28240.4 | 163669.7 |
| OC  | 11306.3 | 13398.9 | 2580.4  | 4290.9  | 45817.7  |
| EC  | 2664.2  | 1054.0  | 790.2   | 2665.0  | 4696.9   |
| $\text{SO}_4^{2-}$                          | 862.2   | 354.7   | 210.4   | 813.4   | 1670.2   |
| $\text{NH}_4^+$                             | 217.5   | 213.1   | 68.0    | 144.5   | 797.9    |
| $\text{Cl}^-$                               | 440.0   | 242.2   | 281.6   | 356.4   | 1128.5   |
| $\text{NO}_3^-$                             | 343.6   | 219.5   | 146.3   | 260.9   | 1009.8   |
| Al  | 208.8   | 125.1   | 14.6    | 184.0   | 458.0    |
| Ca  | 364.6   | 371.9   | 5.2     | 286.1   | 1306.7   |
| Fe  | 156.8   | 80.4    | 20.0    | 151.0   | 280.9    |
| K   | 134.6   | 188.9   | 4.2     | 62.5    | 861.5    |
| Mg  | 72.0    | 34.8    | 20.0    | 70.3    | 162.2    |
| Na  | 173.3   | 194.6   | 6.6     | 109.0   | 838.3    |
| P   | 31.7    | 48.0    | 0.7     | 20.0    | 225.3    |
| S   | 215.3   | 132.2   | 60.4    | 194.3   | 541.0    |
| Ti  | 14.4    | 6.9     | 3.2     | 15.1    | 30.3     |
| V   | 5.9     | 5.2     | 0.3     | 4.3     | 20.2     |
| Cr  | 7.9     | 9.1     | 1.7     | 2.3     | 27.3     |
| Mn  | 4.4     | 1.5     | 1.3     | 4.8     | 7.0      |
| Co  | 5.9     | 5.4     | 0.4     | 4.7     | 14.9     |
| Ni  | 12.3    | 13.4    | 1.6     | 7.2     | 35.5     |
| Cu  | 7.1     | 12.8    | 0.5     | 2.8     | 46.6     |
| Zn  | 17.0    | 12.6    | 4.5     | 14.0    | 55.1     |
| Ge  | 0.4     | 0.2     | 0.1     | 0.4     | 0.9      |
| As  | 2.7     | 2.1     | 0.4     | 2.3     | 8.4      |
| Rb  | 0.6     | 0.1     | 0.4     | 0.6     | 0.8      |
| Sr  | 1.5     | 0.7     | 0.5     | 1.5     | 3.0      |
| Y   | 0.2     | 0.2     | 0.0     | 0.2     | 0.5      |
| Zr  | 3.3     | 2.4     | 0.1     | 3.1     | 8.6      |
| Mo  | 3.5     | 1.6     | 1.1     | 3.4     | 6.0      |
| Cd  | 12.0    | 14.8    | 1.0     | 6.1     | 28.9     |
| Sn  | 0.5     | 0.5     | 0.0     | 0.4     | 1.6      |
| Sb  | 1.4     | 0.9     | 0.5     | 1.1     | 3.5      |
| Ba  | 6.0     | 3.7     | 1.9     | 4.9     | 15.5     |
| La  | 0.2     | 0.2     | 0.0     | 0.1     | 0.8      |
| Ce  | 0.3     | 0.3     | 0.1     | 0.3     | 1.3      |
| Nd  | 0.1     | 0.0     | 0.0     | 0.1     | 0.2      |
| Pb  | 8.6     | 9.3     | 1.1     | 6.1     | 40.4     |





**Fig. 3.** Average monthly concentrations of PM<sub>2.5</sub> for August to November (2014–2015) together with the measurements obtained in a previous study (2010–2011).

campaigns. In addition, 67% of the daily concentrations exceeded this guideline in 2014–2016, and 88% exceeded the guideline in the 2010–2011 campaign. The similar proportion of exceeding days indicated that despite the extreme differences in the meteorology between the two campaigns, no major changes in PM<sub>2.5</sub> loads were evident between the two evaluated periods.

Fig. 3 also indicates that the mean August PM<sub>2.5</sub> mass concentrations were much higher in the present campaign than the equivalent values obtained during the 2010–2011 period. This increase in PM<sub>2.5</sub> concentration was mainly attributed to the presence of fires in the northeast and southwest regions of the country, which are clearly evident in the fires and biomass burning product (MOD14) from MODIS (Fig. 4). The HYSPLIT backward trajectory analysis of all trajectories with high aerosol loads showed that from all intermediate points, in only 4% of them the air mass was located more than 200 m above the surface. This result indicated that there was no vertical dispersion of air pollutants over the whole trajectory that went from the air mass origin to the monitoring site.

For example, Fig. 4 shows the backward trajectories and the forest fires that occurred on August 19, 2014, which is one of the days with the highest PM<sub>2.5</sub> concentrations. According to the backward trajectory analysis, the forest fire emissions could have influenced the monitoring site on all days when high aerosol loads were measured (both August 2014 and 2015). This influence was also supported by the maximum OC and EC levels in PM<sub>2.5</sub> during these days.

### 3.3. Mass concentrations of chemical species

The average, median, min and max data on the PM<sub>2.5</sub> chemical composition in the present work for the whole measurement period are compiled in Table 1. As expected, the PM<sub>2.5</sub> speciation data reflected the influence of several relevant emission sources. Mineral/crustal elements (i.e., Al, Si, Ca, Fe, and Ti) occurred in relatively high concentrations. Considering the fact that we analyzed PM<sub>2.5</sub> and the mineral fraction is a coarse dominated one, these results suggest that dust resuspension was a very relevant source in the area. Thus, the dust load was estimated using the algorithm to determine the crustal fraction from the elemental analysis by Querol et al. (2001), and an average of 2.9 µg m<sup>-3</sup> (6.0% of the mass) in PM<sub>2.5</sub> was estimated. The crustal fraction was derived from aluminum silicate and carbonate rich material, which are the major components of Earth's crust. These aluminum silicates were characterized by high contents of Si and Al and variable contents of K, Fe, Mg, and/or Ca. Titanium that was associated with these particles was also found, and the same natural source was

assumed for this element because it is one of the most abundant in the terrestrial core (Achad et al., 2013).

The potential maximum sea salt contribution reached a very small load (0.6 µg m<sup>-3</sup>, 1.2% on average), both because PM<sub>2.5</sub> was sampled (and the mass size distribution of sea salt has a major coarse mode) and because of the continental situation of the sampling area.

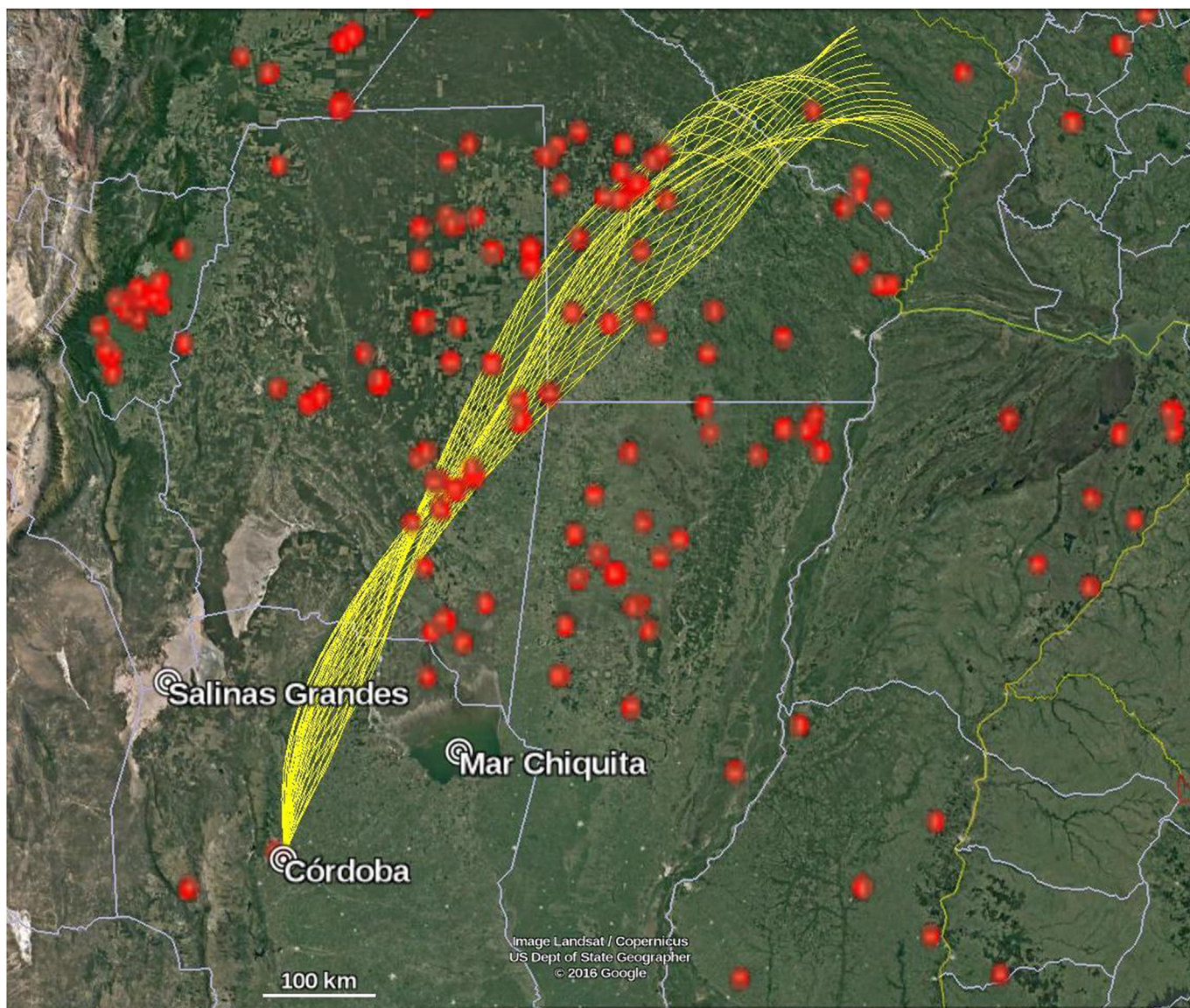
The rest of the species were emitted by different anthropogenic sources such as roads, traffic, industrial activities and other combustion processes. These elements are significant to the air pollution in cities and have a great contribution to the PM<sub>2.5</sub> mass. The elements found in the emissions from motor vehicles are also released by other sources, such as industrial processes, electric power generation, and heating. The contributions of motor vehicle emissions to ambient levels of PM<sub>2.5</sub> vary between 25 and 40% (Kheirbek et al., 2016), although these values are noticeably higher in a few cases, especially for ultrafine particles. Therefore, the site location and season of the year are important factors that can influence the contributions of motor vehicle emissions to ambient levels of PM<sub>2.5</sub>.

A comparison of the selected elements measured in the current study and the work by Achad et al. (2014) is presented in Fig. 5. The concentrations of most crustal elements (Al, K, Fe, Ti, Mn) were lower in the present campaign compared to the previous one. However, the reverse situation was found for specific metals such as V, Cr, Co, and Ni. The difference in the lower concentration of crustal elements can be explained by the number of rainy days during 2014–2016, which was higher than in the previous years. The increase in the concentrations of the above metals could also be influenced by the changes in the wind pattern (Fig. 2) that led to a greater contribution of emissions from large cement industries and motor vehicle factories. As previously stated, even when the PM<sub>2.5</sub> total concentration did not strongly vary between the two campaigns, the effect of the opposite El Niño/La Niña conditions were observed in the chemical compositions.

The average concentrations of OC and EC observed in Córdoba reached 11 ± 13 and 3 ± 1 µg m<sup>-3</sup>, respectively (Table 1). Both carbon fractions exhibited high concentrations in the winter, reflecting an input of emissions from wildfire biomass burning in the NE region of the country combined with unfavorable dispersion conditions (Fig. 3).

The OC/EC ratio has been used as an indicator of carbonaceous aerosol sources, mainly to distinguish between primary sources and secondary atmospheric processes. Ratios ranging from 2 to 5 are commonly observed in urban background atmospheres and are assumed to indicate a significant contribution of secondary aerosol sources (Querol et al., 2013). Ratios lower than 1 usually describe the composition of fresh traffic emissions (Pio et al., 2011). The average OC/EC ratio for the entire sampling period in Córdoba reached 4 ± 3. If the OC/EC ratios are plotted against the PM<sub>2.5</sub> concentrations, there is an R<sup>2</sup> value of 0.71 in the linear correlation. When the OC is compared to the PM<sub>2.5</sub>, the R<sup>2</sup> is equal to 0.99. During the campaign, there were six days when the PM<sub>2.5</sub> concentrations exceeded 50 µg m<sup>-3</sup>. During those days, the ratios OC/EC ranged from 3.9 to 13, and these ratios increased with the increase in the PM<sub>2.5</sub> concentration. These values and correlations indicated that OC was not the only contributor to PM<sub>2.5</sub> mass, but there was also a significant contribution of secondary aged carbon during the abnormally polluted episodes. This reinforced the previous explanation that aged biomass burning emissions transported from regional sources were the principal cause of extreme PM<sub>2.5</sub> concentrations in August.

It should be mentioned that the chemical speciation values presented in Table 1 were similar, regarding to K, Fe, Ti, Mn, Ni, As and Pb concentration, to those reported by Tavera Busso et al.



**Fig. 4.** HYSPLIT trajectories (yellow lines) and fires (red dots) that occurred on August 19, 2014. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(2017) also for Córdoba city, while V and Cd were almost an order of magnitude higher. Although in general the results of both works are in good agreement, the differences found for some specific elements might be attributed to the variability of daily data, meteorological conditions, sampling site characteristics and to the fact that Tavera Busso et al. (2017) only collected samples from August to October 2014.

Table 2 shows the values of the sulfate, nitrate, chloride, ammonium, organic and elemental carbon concentrations measured in this work in comparison to the concentrations reported for other cities in South America. The values of EC and OC are similar to other cities in South America, and the OC/EC ratio ranges from 2.3 (São Paulo) to 3.9 (Córdoba), which reflects the similar aging processes of the carbonaceous aerosols. The  $\text{NH}_4^+$  values are similar to most of the other reported cities in South America except for Santiago de Chile, where much higher values have been recorded. The atmosphere of Santiago de Chile has been reported to be rich in ammonia (Toro et al., 2014).

### 3.4. PCA

For this analysis, 18 of the species determined in the samples were selected according to the previous analysis of the correlations between the elements, signal/noise ratio, and the amount of missing values. These species were used to determine which could contribute information to differentiate the sources. The included species were Al, Ca, Na, Mg, Fe, Ti, Mn, V, K, Zn, As, Sb,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , EC, and OC.

A total of 79% of the variance was explained by five factors. A total of 43% of the residuals were larger than 0.05, and their distribution was normalized. The root mean squared residual was equal to 0.066, and the fit based on the off-diagonal values was equal to 0.96.

Finally, to assign the PCA-resolved factors to the aerosol sources, an approach that utilized a comparison with the literature on the tracer compounds and the knowledge of the site was followed. The results of PCA that explain the variance of each factor is given in



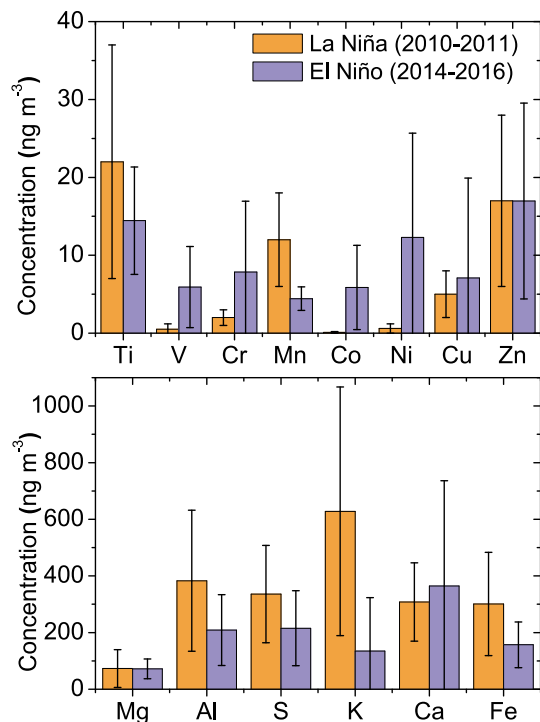


Fig. 5. Comparison of the selected elements measured in this work and the work of Achad et al. (2014).

Table 3. A brief explanation of the determining species for each factor is given below.

#### 3.4.1. Factor 1: combustion and traffic-related emission processes

The most important factor identified by the model was characterized by OC, EC, K, and Sb as the major components, which explained 20% of the variance. It can be associated with the organic matter and EC components in the mass chemical balance, which accounted for an average of 54.8% of the PM<sub>2.5</sub> mass concentration.

The factor was considered to be a mixture of different combustion sources including vehicle engines. Motor vehicles are important sources of carbonaceous aerosols, particularly for PM<sub>2.5</sub> (Pant and Harrison, 2013). PM emissions from vehicles depend on the engine type, age and maintenance and contain carbon in the forms of OC and EC (lower OC/EC in diesel cars) with smaller amounts of trace metals (Brook et al., 2007; Robert et al., 2007). OC and EC are also enriched in soot from biomass burning (Andreae and Merlet, 2001). The PM emissions from diesel vehicles are much higher than the emissions from gasoline or CNG. Light-duty vehicles employ CNG, unleaded gasoline and diesel oil, whereas heavy-duty vehicles run almost only on diesel oil. According to the data provided by the local authorities (private communication), 51% of the local fleet runs on gasoline, 35% on diesel, and 14% on CNG. The fleet consists of 480,000 passenger cars, 74,000 pickups, 11,000 light duty vehicles and heavy-duty trucks, 30,000 buses and other similar vehicles, and 237,000 motorcycles. According to COPERT v.4 (Ntziachristos et al., 2009), old motorcycles, like 2-stroke motor bikes, emit large amounts of soot. Pre-Euro to Euro2 2-stroke motorcycles emit 26–200 mg PM/km, and the newest models emit 12–18 mg PM/km, whereas current diesel and gasoline passenger cars emit 5 mg PM/km. The fleet is increasing at a rate of 16% per year; therefore, air pollution from traffic is a major concern for the city.

In addition to traffic emissions, biomass burning could make a significant contribution to the ambient concentrations of carbonaceous matter (OC and EC) together with K. To distinguish

between the two sources, the ratios  $K^+/OC$  or  $K^+/EC$  are usually employed. In this study, the  $K/OC$  ratio had an average value of 0.021, while the  $K/EC$  ratio had an average value of 0.061. These values should be considered the upper limits, because, in this work, the total K was determined and not the  $K^+$ . In addition, the ratios reported here are lower than the ones found from biomass burning conditions in other regions. For instance, Lin et al. (2010) reported values of 0.08–0.11 for  $K^+/OC$  in ambient samples influenced by biomass burning whereas Andreae and Merlet (2001) found ratios of 0.04–0.13 in agricultural waste burning emissions. A lower  $K^+/OC$  ratio is obtained from traffic emissions. Therefore, from this analysis, it is possible to conclude that the main source of carbonaceous particles was combustion from traffic emissions, although some samples had a contribution from biomass burning (Fig. 4).

Antimony is a potentially toxic trace element that may produce adverse effects to humans and the environment (Fujiwara et al., 2011). The presence of Sb in the atmosphere is associated with brake pad wear. Percentages up to 7% of Sb in the form of  $Sb_2S_3$  are used in brake pads (or linings) as a lubricant to reduce vibrations and improve friction stability (Thorpe and Harrison, 2008).

#### 3.4.2. Factor 2: salt from medium range transport

This factor was characterized by high percentages of Na and  $Cl^-$  and a fraction of As. It explained 17% of the variance, and it was associated with the salt component in the chemical mass balance and contributed 1.2% of the average PM<sub>2.5</sub> levels. The presence of this factor is interesting since Córdoba is located far away from any sea. However, the shallow lake Mar Chiquita is located approximately 150 km northeast of Córdoba, (30°45'S and 62° 30'W) (Fig. 4). This saline lake is endorheic and is the largest water body in Argentina (its area ranges from 2000 to 6000 km<sup>2</sup>). Currently, the waters in Mar Chiquita are strongly saline (sodium chloride-sulfate; Martinez, 1995). The Salinas Grandes are located at approximately the same distance away but in the northwest direction (Fig. 4). The Salinas Grandes are salt flats with an area of 6000 km<sup>2</sup> and the same geological origin as Mar Chiquita.

Arsenic is emitted by nonferrous metal smelters (gold, copper, lead, and zinc) and mining-related industries (Martin et al., 2014), and in general, is found as part of the industrial factor. However, this kind of industry is not found near Córdoba, given that the local non-ferrous smelters work mainly with aluminum. Instead, the soils in Córdoba province are loess with anomalously high contents of As, especially in the regions to the east and the south. This results in groundwater that is highly contaminated with As (Nicolli et al., 1989), which is a problem found in the whole province.

Thus, it has been concluded that this factor was characterized by the medium-range transport of elements from natural sources, which are not elements that dominate the fine fraction of particulate matter, and hence do not contribute significantly to the PM<sub>2.5</sub> mass concentration.

#### 3.4.3. Factor 3: soil dust

The urban dust factor was characterized mainly by Al, Fe, Ti, and Mn and explained 15% of the variance. This source may represent a mixture of resuspended road dust, non-exhaust vehicle emissions, and natural mineral sources. In the chemical mass balance, the mineral component of soil dust contributed 6.1% to the averaged PM<sub>2.5</sub> levels. Iron in urban areas is usually associated with brake discs (Thorpe and Harrison, 2008; Amato et al., 2009). In addition, Al, Ti, Mn and other crustal elements in urban areas are found to be associated with road dust, desert dust and other types of mineral dust (Amato et al., 2009).

#### 3.4.4. Factor 4: secondary inorganic aerosols

This factor was characterized by nitrate, ammonium and sulfate,

**Table 2**  
Average elemental concentration values for the PM<sub>2.5</sub> in this study compared with the values reported in other studies from South America. The values between parentheses correspond to the standard deviation values.

| Reference                  | Techniques                        | Sampling period | Sampling site            | Concentration ( $\mu\text{g}\cdot\text{m}^{-3}$ ) |                              |                               |                 |               |              | Ratio        |
|----------------------------|-----------------------------------|-----------------|--------------------------|---|------------------------------|-------------------------------|-----------------|---------------|--------------|--------------|
|                            |                                   |                 |                          | NO <sub>3</sub> <sup>-</sup>                      | NH <sub>4</sub> <sup>+</sup> | SO <sub>4</sub> <sup>2-</sup> | Cl <sup>-</sup> | EC            | OC           | OC/EC        |
| This Work                  | ICP MS - ICP OES - IC - TOA EC/OC | 2014–2016       | Córdoba, Argentina       | 0.34<br>(0.22)                                    | 0.22<br>(0.21)               | 0.86<br>(0.35)                | 0.44<br>(0.24)  | 2.7 (1.1)     | 11 (13)      | 3.9<br>(3.4) |
| Dos Santos et al., 2009    | ICP OES - HPLC                    | 2006–2007       | Buenos Aires, Argentina  |   | 0.13<br>(0.05)               | 0.77<br>(0.14)                | 0.22<br>(0.10)  |               |              |              |
| Villalobos et al., 2015    | IC - TOA EC/OC                    | 2013            | Santiago de Chile, Chile | 7.1 (5.5)   | 3.3 (1.8)                    | 2.0 (0.9)                     |                 | 4.3 (2.2)     | 12 (6.3)     | 2.8<br>(0.4) |
| Prieto-Parra et al., 2017  | XRF - TOA EC/OC                   | 2010–2011       | Santiago de Chile, Chile |   |                              |                               |                 | 4.5 (1.8)     | 12 (5.4)     |              |
| Jorquera and Barraza, 2013 | XRF - IC - TOA EC/OC              | 2007–2008       | Antofagasta, Chile       | 0.35<br>(0.13)                                    |                              | 12 (4)                        |                 | 1.1 (0.4)     | 2.6<br>(0.8) |              |
| Souza et al., 2014         | IC - TOA EC/OC                    | 2008            | Piracicaba, Brazil       | 0.50  | 0.65                         | 1.8                           | 0.05            | 1.7           | 4.4          | 2.7<br>(0.4) |
|                            |                                   |                 | São Paulo, Brazil        | 2.1   | 1.5                          | 3.4                           | 0.27            | 6.6           | 10           | 2.3<br>(2.1) |
| Gonçalves et al., 2016     | IC - TOA EC/OC - ICP MS           | 2014            | Araraquara, Brazil       | 1.6 (0.50)  | 0.40<br>(0.22)               | 1.5 (0.52)                    | 0.14<br>(0.08)  | 1.7<br>(0.90) | 7.3<br>(5.3) |              |
| Mateus et al., 2013        | ICP MS - ICP OES - IC             | 2010–2011       | Rio de Janeiro, Brazil   | 1.3 (1.0)   |                              | 2.9 (2.3)                     | 0.90<br>(0.81)  |               |              |              |
| Miranda, 2012              | ED XRF - IC                       | 2007–2008       | São Paulo, Brazil        | 1.2 (1.1)   | 1.3 (0.89)                   | 3.1 (2.0)                     | 0.24<br>(0.29)  |               |              |              |
|                            |                                   |                 | Rio de Janeiro, Brazil   | 0.56<br>(0.80)                                    | 0.80<br>(0.78)               | 1.9 (1.4)                     | 0.11<br>(0.25)  |               |              |              |
|                            |                                   |                 | Belo Horizonte, Brazil   | 0.19<br>(0.13)                                    | 0.34<br>(0.19)               | 1.2 (0.51)                    | 0.04<br>(0.03)  |               |              |              |
|                            |                                   |                 | Porto Alegre, Brazil     | 0.43<br>(0.43)                                    | 0.35<br>(0.36)               | 1.2 (0.91)                    | 0.15<br>(0.17)  |               |              |              |
|                            |                                   |                 | Curitiba, Brazil         | 0.16<br>(0.13)                                    | 0.37<br>(0.27)               | 1.1 (0.68)                    | 0.07<br>(0.15)  |               |              |              |
|                            |                                   |                 | Recife, Brazil           | 0.11<br>(0.06)                                    | 0.18<br>(0.13)               | 0.61<br>(0.33)                | 0.15<br>(0.16)  |               |              |              |

**Table 3**  
Determining species for each factor in PCA of the PM<sub>2.5</sub> data. The values in bold correspond to the determining species for each factor.

|                               | Factor 1    | Factor 2    | Factor 3    | Factor 4    | Factor 5    |
|-------------------------------|-------------|-------------|-------------|-------------|-------------|
| NH <sub>4</sub> <sup>+</sup>  | 0.02        | -0.09       | 0.11        | <b>0.94</b> | 0.02        |
| Cl <sup>-</sup>               | -0.13       | <b>0.88</b> | 0.13        | -0.17       | -0.11       |
| NO <sub>3</sub> <sup>-</sup>  | -0.01       | 0.53        | 0.04        | <b>0.8</b>  | -0.08       |
| SO <sub>4</sub> <sup>2-</sup> | -0.06       | 0.19        | 0.03        | <b>0.7</b>  | 0.25        |
| OC                            | <b>0.91</b> | -0.06       | -0.03       | -0.19       | -0.08       |
| EC                            | <b>0.84</b> | -0.03       | -0.11       | 0.28        | -0.07       |
| Al                            | 0.01        | 0.01        | <b>0.68</b> | -0.09       | 0.09        |
| Ca                            | -0.02       | -0.08       | 0.02        | 0.15        | <b>0.83</b> |
| Fe                            | 0.26        | 0.12        | <b>0.82</b> | 0.34        | 0.04        |
| K                             | <b>0.8</b>  | -0.02       | 0.08        | -0.02       | 0.14        |
| Mg                            | 0.63        | 0.59        | 0.2         | 0.29        | 0.11        |
| Na                            | -0.01       | <b>0.91</b> | 0           | 0.15        | -0.04       |
| Ti                            | -0.11       | 0.11        | <b>0.81</b> | 0.03        | 0.11        |
| V                             | -0.1        | 0.35        | 0.51        | -0.26       | <b>0.56</b> |
| Mn                            | 0.53        | 0.06        | <b>0.73</b> | 0.36        | 0.08        |
| Zn                            | -0.04       | -0.05       | 0.2         | 0.08        | <b>0.85</b> |
| As                            | 0.03        | <b>0.84</b> | 0.14        | 0.34        | 0.09        |
| Sb                            | <b>0.79</b> | -0.05       | 0.21        | -0.2        | -0.25       |
| % var.                        | 20          | 17          | 15          | 15          | 11          |

and it explained 15% of the variance. The sum of nitrate, sulfate and ammonium contributed 3.0% to the average PM<sub>2.5</sub> levels. These secondary aerosols could be largely from coal and biomass combustion. The precursor of nitrate, NO<sub>x</sub>, is largely emitted by diesel engines and stationary sources such as plants generating thermal electricity. In Córdoba, one power plant is located southwest of the city, and seven more are located at distances between 20 and 200 km from the city in the Córdoba province.

#### 3.4.5. Factor 5: industrial

Factor 5, which contains a high percentage of V, Zn, and Ca, refers to a mixed urban source of oil burning probably in industries, cement, and thermal power plants, and explained 11% of the variance. This factor could not be associated with a component of the chemical mass balance, so how much it contributed to the average PM<sub>2.5</sub> levels could not be estimated.

V is present in relatively high concentrations in petcoke and heavy fuel oil. The use of petcoke by the nearby cement industries has increased in the last several years (101,309 tons in 2015, private communication) due to the restriction of natural gas use imposed on the industries in recent years. The cement industries also burn tires as alternative fuel, which is an additional source of Zn in PM<sub>2.5</sub> (Thorpe and Harrison, 2008; Amato et al., 2009). Ca is the main component of limestone, which is the raw material used in cement plant.

## 4. Summary and conclusion

A receptor model analysis was applied to integrated 24-h ambient PM<sub>2.5</sub> concentrations collected in 2014–2016 at one site in Córdoba. This study improved upon the previous campaign that was carried out in the city due to the determination of the soluble inorganic ions and carbonaceous particles (EC and OC) of the bulk aerosol samples. These new results provide additional knowledge of the sources that contribute to the PM<sub>2.5</sub> mass and the effects of meteorology, which provides a scientific basis for emission control policies used for the remediation of local air pollution under particular situations.

The chemical composition values obtained in this work presented important differences with respect to a former campaign



from 2010 to 2011. The comparison of this campaign (2014–2016) with the results from the previous campaign (2010–2011) allowed for an understanding of the effects of two extreme meteorological conditions on the PM<sub>2.5</sub> composition. The years of 2010–2011 were dry and hot due to a La Niña regime, which is characterized by drought and an abundance of fires. Conversely, the years of 2014–2016 were humid and cold (Kogan and Guo, 2017). The average PM<sub>2.5</sub> values did not present strong differences between the two campaigns. However, the chemical composition of the PM<sub>2.5</sub> reflected the differences between the opposite ENSO regimes, with lower concentrations of crustal elements and higher values of some anthropogenic metals measured in the current study.

In the analysis presented here and because the sampling was carried out during a 24 h period is likely that some details about the aerosol formation and aging could have been missed. However, most of the regulatory air quality monitoring as well as measurements performed for epidemiological studies, derives from chemical composition of atmospheric PM from 24-h average data. Daily-averaged concentrations of PM<sub>2.5</sub>, as well as meteorological parameters, tend to reduce data variability and can, therefore, limit our ability to detect the associations between emission sources/components and other parameters. This is particularly apparent in studies performed in large urban areas, such as Cordoba, where the impacts of emissions from local point and mobile sources are rapidly changing, and PM is added to the complex mixture of regional source emissions transported into the region that varies on longer time scales. Daily and weekly measurements hinder the statistical decoupling of PM emission sources and their contributions to space and time. However, there was no way to confront our measurement with other studies on PM composition resolved in time along 24 h period.

In the present campaign, the mass contributions to the PM<sub>2.5</sub> levels according to the chemical mass closure were 54.8% organic matter and EC, 6.1% mineral, 3.0% secondary inorganic aerosol, and 1.2% salt. PCA was performed, and five factors explained 79% of the variance. The determining elements of each factor were associated with the contributions calculated in the chemical mass closure, with the addition of a fifth component representing industrial sources. Each of the factors explained between 11% and 20% of the variance. The PCA performed in this work was not intended as a modeling/predictive tool, rather as an exploratory data analysis tool. This sampling period cannot be considered as representative of the whole year, neither to a typical average year, because of El Niño influence. For these reasons, PCA was used as a descriptive method, valid only for the measurement period and conditions. The factors found here should not be considered valid to other times of the year or representative of every El Niño hitting the region. To obtain more conclusive results additional periods affected by El Niño should be analyzed.

Given that an air quality monitoring network does not exist in either Córdoba or Argentina, the results of this work are relevant to raise the awareness of the government agencies, as the measured PM<sub>2.5</sub> values are routinely above the international air quality standards.

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