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Assessment of fine and sub-micrometer aerosols at an urban environment of Argentina

Mariana Achad[a], María Laura López[b], Sergio Ceppi[b], Gustavo G. Palancar[a], Germán Tirao[b], Beatriz M. Toselli[a,*]

[a] Departamento de Físico Química/INFIQC/CLCM/CONICET, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Pabellón Argentina, Ciudad Universitaria, 5000 Córdoba, Argentina
[b] Facultad de Matemática, Astronomía y Física/IFEG/CONICET, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

HIGHLIGHTS

- Córdoba has particulate matter levels above WHO standards.
- Toxic metal concentrations are heavily influenced by local sources.
- Traffic and SO_4^{2-}/combustion processes are the major sources of PM2.5.

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ABSTRACT

Bulk aerosol samples collected during 2010 and 2011 at one receptor site in Córdoba City, Argentina, have been quantitatively analyzed to determine aerosol elemental composition by using SR-XRF. A receptor model analysis has been applied to ambient PM2.5 measurements. Four sources have been identified being their contributions: traffic: (13 ± 2) μg m^{-3}, SO_4^{2-}/combustion processes, including biomass burning: (15 ± 1) μg m^{-3}, mineral dust: (7 ± 2) μg m^{-3} and industry: (8 ± 1) μg m^{-3}. Source identification was carried out by inspection of key species in source profiles, seasonality of source contributions, comparison with literature data and the knowledge of the city; for the biomass burning contribution the MODIS burned area daily product was used to confirm wildfire events along the year. In addition, from May to August 2011, aerosols were collected in two additional size fractions (PM0.25–0.5, PM0.5–1) to investigate the toxic metal contributions to the finer fractions. An important result of this work is that toxic metals make an important contribution to the finest (PM0.25–0.5) size fraction. The results of the present analysis can help to demonstrate to local and national authorities the urgent need to carry out emission inventories, to implement air quality monitoring systems and to set regulations for PM2.5.

1. Introduction

Atmospheric aerosols are among the most important classes of atmospheric pollutants and many published works in the literature confirm the fact that particles with small sizes have a serious impact on human health, increasing respiratory and cardiovascular diseases and reducing life expectancy (Brugge et al., 2007). A strong association between the fine air particulate pollution and mortality rates in six U.S. cities has been also reported (Dockery, 2009). Therefore, the increasing evidence indicating that fine particulate matter in the atmosphere is responsible for adverse effects on humans led to the imposition of regulatory restrictions on PM2.5. Thus, the United States adopted the National Ambient Air Quality Standard (NAAQS), which sets the limit to 35 μg m^{-3} while the European Union legislation for air quality established a 24-h limit value of 25 μg m^{-3}. Unfortunately, for Argentina a 24-h limit value for PM2.5 has not been set.

Ambient aerosol studies have shown that there is a substantial variability in the concentration and chemical composition of the atmospheric aerosols throughout the world. It is also recognized that the composition and size of particulate matter (PM) is mostly determined by its sources. Trace metal elements are present in PM2.5 and contribute largely to the toxic properties of the fine particles (Riley et al., 2003). Beyond these properties regarding health effects, trace metals can also be used as fingerprints to

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* Corresponding author.
E-mail addresses: tosellib@fcq.unc.edu.ar, tosellib@yahoo.com.ar (B.M. Toselli).

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characterize the sources of various particle emissions. The identification of the aerosol sources and its components is critical to define source-specific health risks.

Around ten years ago the interest on PM composition shifted from PM10 to PM2.5 and PM1. Many studies of concentration components in large cities have been conducted in the Northern Hemisphere (Viana et al., 2008; Calvo et al., 2013), while only a handful of such works has been published for the Southern Hemisphere and even less for Argentina (Bogo et al., 2003; Smichowski et al., 2004, 2008; Micheletti et al., 2012). Most of the papers from Argentina report the mass concentration for the coarse size fractions. However, size distribution of aerosol particles is important not only to assess possible health impact in the respiratory human system but also they could help to understand the possible origin of these particles. From atmospheric aerosols studies carried out at urban and background sites in several places of the world based on size distribution analysis, it was concluded that there are several modes or categories in which the metals are found (Pant and Harrison, 2013, and references therein). It was found metals with most of the mass in the accumulation mode with an additional minor mode, metals with the mass distributed among fine, coarse, and intermediate mode, and metals with most of the mass in the coarse range.

Environmentally, Córdoba City is of interest because of both, its geographical location in the center of Argentina, and for being the second largest city of the country. In Córdoba there are only a few studies regarding to aerosol characterization. In one of these studies, during an air quality campaign carried out by the City government in the period 1995–2001, PM10 concentration was measured and it was the only pollutant that exceeded several times the 24-h national standard of 150 μg m^{-3}. All these episodes were during wintertime (Olcese and Toselli, 1997, 1998). The higher PM10 concentration during this period was a consequence of the lack of rain and the persistent temperature inversions (Stein and Toselli, 1996). Unfortunately, the chemical composition of these samples was not determined and PM2.5 was not measured. This is aggravated by the fact that no additional air quality monitoring is currently underway by any governmental agency. López et al. (2011) collected PM10 and PM2.5 at an urban and at a semi-urban site of Córdoba City. The results of this study suggested that the coarse fraction concentration (the difference between PM10 and PM2.5) has an important contribution from ground dust, which is composed mainly by aluminum silicates. This was in agreement with the small seasonal variability found for PM10 and PM2.5 levels. The main percentage of PM10 corresponded to the smallest particles, PM2.5 being traffic and traffic related sources the major contributors to this fraction. No clear secondary aerosol source was found in this study because it was always found mixed with other sources. Populations in the proximity of trafficked roadways are more susceptible to PM-related health effects (Tonne et al., 2007), with the most sensitive demographic being children and elderly people (Creason et al., 2001). Several studies have postulated that certain PM components, like trace metals (Verma et al., 2010), may play a role in PM toxicity. Some elements come from different anthropogenic sources. Those emitted during the burning of fossil fuels, such as V, Co, Pb, Ni, and Cr are mostly associated with particles in the PM2.5 fraction (Calvo et al., 2013), although some elements are also present in the coarse fraction. Metallurgical industries release into the atmosphere Cr, Cu, Mn, and Zn while traffic pollution involves a wide range of trace elements that include Fe, Ba, Mn, Pb, Cu, and Zn, which may be associated with the fine and coarse particles (Marcazzan et al., 2001; Smichowski et al., 2004).

To perform compositional analysis and due to the complex nature of the aerosol samples and the low concentrations involved, synchrotron radiation X-ray fluorescence (SR-XRF) analysis was utilized for this study. The technique satisfies the requirements of being sensitive, element-specific, non-destructive and accurate and has proved to be a powerful tool for the elemental analysis of ambient air samples (Bukowiecki et al., 2008). The detection limits achieved with SR-XRF experiments are in the range of ng m^{-3} of ambient air, allowing the determination of major and minor components of the filters without additional sample treatment and is becoming an important tool in atmospheric chemistry (Cliff et al., 2003).

Within the present work, bulk aerosol samples collected in Córdoba, were quantitatively analyzed by SR-XRF and their origins were identified using the multivariate factor analysis described in Ogulei et al. (2005). One of the main advantages of this technique, compared to conventional XRF, resides on the fact that the count accumulation interval per individual sample spot is substantially shorter (Bukowiecki et al., 2008).

To assess particle source contributions, receptor modeling has been widely used as a tool in air pollution source apportionment studies (Zhao and Hopke, 2006; Amato et al., 2009; Belis et al., 2013: Reff et al., 2007). Positive Matrix Factorization (PMF) modeling analysis is used to estimate the average contribution of emission sources to the PM measured at a receptor site.

This work presents the main results of a campaign carried out during specific months of the April 2010–December 2011 period conducted to characterize the mass size distribution and the elemental composition of Córdoba aerosols, and the influence of pollution sources, with the goal of addressing the contribution of the toxic metals to the fine aerosols. In order to enhance toxicological information on aerosols, in this research we included size-segregated aerosol samplings for fractions smaller than 2.5 microns. Regardless its importance, these data are relatively scant in the literature (Hays et al., 2011). Therefore, the main purposes of this work are: (1) to analyze the seasonal variability and the influence of meteorological variables in both, the PM2.5 concentration levels and in the elemental and metal concentration, (2) to present source apportionment results for PM2.5 and (3) to investigate the distributions of selected elements and metals for the different collected fractions.

2. Experimental

2.1. Study area, meteorological aspects and sampling site

The study was performed in Córdoba, the second largest city in Argentina with a population of 1.3 million inhabitants. It is located at latitude 31° 24′ S and longitude 64° 11′ W, about 470 m a.s.l. The climate is sub-humid with a mean annual precipitation of 790 mm (concentrated mainly in summer time), a mean annual temperature of 17.4 °C and prevailing winds from NE (Argentinean National Weather Service). The monthly variation of the mean wind speed, average temperature, and total precipitation for Córdoba is shown in Fig. 1 for the measurement period (2010–2011). Córdoba faces air pollution problems, especially during wintertime. This is because the longer nights, dry air and cloudless sky usually produce strong radiative inversions (Stein and Toselli, 1996). Consequently, pollutants and aerosols are trapped in a layer lower than 200 m, leading to adverse health effects (Olcese and Toselli, 2002; Amarillo and Carreras, 2012).

A variety of industrial plants are located in the suburban areas surrounding the city, including automobile factories, auto-part industries, agro industries, cement and food processing companies. The major car-manufacturing factories are located to the southeast and southwest of the town, and many small car-part factories are located around them. To the north, there is another industrial area

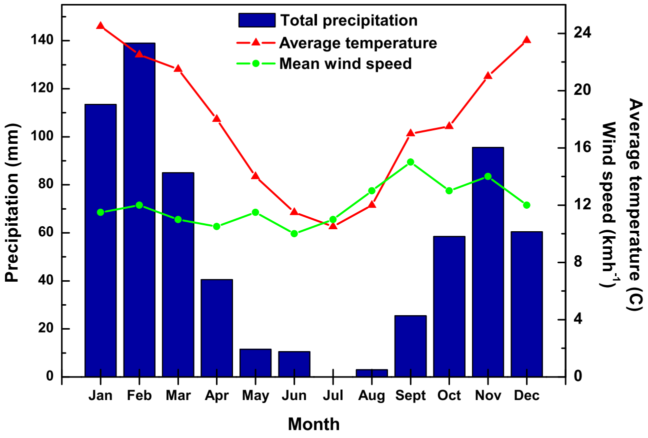

Fig. 1. Monthly values for the years 2010 and 2011 of the mean wind speed, average temperature, and total precipitation for Córdoba. Data provided by the Argentinean National Weather Service.

with many small and medium sized industries, predominantly metallurgical. The most important cement production plant is located 20 km to the West from the city core (Pignata et al., 2007). The central area is densely built-up and is located in a depression.

The fuels employed in the city for on-road transport are compressed natural gas (CNG), diesel oil and gasoline. Light-duty vehicles have mainly used unleaded gasoline since 1996 when leaded gasoline was banned from the Argentinean market. CNG has become increasingly used in the country since 1995, especially due to its lower price. Light-duty vehicles employ the three named fuels, whereas heavy-duty vehicles run only on diesel oil. Since 2010, the new Argentinean Regulations impose that the total amount of diesel sold in the country must contain at least 5% of biodiesel. In Córdoba, local sulfur dioxide emissions are low because natural gas is used, rather than coal or oil, in commercial or residential heating (D'Angiola et al., 2010). In addition, other common used fuels have low sulfur amount. In fact, SO_2 measured values for the period 1995–2001 were always below international standards at several sites of the city (Olcese and Toselli, 2002).

In the present work, the site selected for the particulate collection is located southwest of downtown, in the University Campus, a place with some trees and areas of bare soil as can be observed in Fig. 2. Due to the large increment in the construction activities in the last three years, both in the city and in the University Campus, the area can be now considered as an urban location. The impactors for the aerosols collection were placed on a balcony of a second floor building. A few low buildings that do not obstruct the air circulation surround the site. It is separated 150 m from a street that has a moderate flow of vehicles (close to 1000 vehicles per hour during daytime) and 300 m away from 2 major transportation avenues. The public transportation system (buses) makes an important contribution to traffic in the area. The sampling site is of importance because is located downwind from the downtown area.

2.2. *Aerosol sampling, X-ray fluorescence measurements and statistical analysis*

24 h samples of PM2.5 and 3 h samples of PM0.5–1 and PM0.25–0.5 were collected using two low volume impactors at one monitoring site. The Deployable Particulate Sampling system with the SKC impactor was employed for sampling PM2.5. The inertial impactor removes particles larger than the specific cut-point by capturing them on a disposable 37-mm pre-oiled porous plastic disk that reduces particle bounce. Particles smaller than the cut-point were collected on 47-mm PTFE filters. A flow rate of 10 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 with a frequency of two to three samples per month from April to December 2010, and from June to December in 2011. After collecting the material, the filters were stored in a desiccator for 24 h before weighting. PM2.5 samples were pre- and post-weighed in a temperature and relative humidity-controlled room using a microbalance (Mettler-Toledo Inc., Columbus, OH) to determine the mass concentrations. Overall, a total of 54 samples collected during week days were available for analysis.

For the size-fractionated samples, the Sioutas impactor was used. This impactor is a miniaturized cascade impactor consisting of four impaction stages and an after-filter. Particles in the aerodynamic diameter ranges of 0.25–0.5 and 0.5–1.0 microns were collected on Teflon filters. The Sioutas impactor operates at a flow rate of 9 L min^{-1}. It does not require the coating of filters to minimize particle bounce. Therefore, with this sampler, chemical

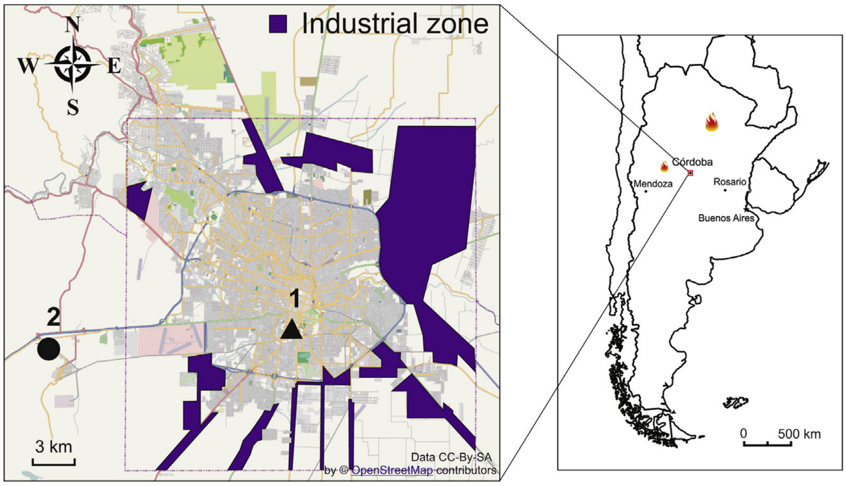

Fig. 2. A map depicting the city of Córdoba. The location of the monitoring site is indicated by a fill triangle and a major cement plant is indicated with a fill circle. The location of major industrial areas surrounded the central area of the city are painted in violet. In a larger scale is showed the map of Argentina and the most frequent locations of fires. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

species analysis can also be performed on the filter. Sixteen samples were collected from May to August 2011. The rationale for selecting these particular months of the year is related to the fact that during the dry season the highest aerosol load are usually measured.

All the collected samples were later individually analyzed by SR-XRF at the Brazilian Synchrotron Light Source Laboratory (LNLS), in Campinas City. The measurements were carried out using the D09B-XRF beamline. Aerosol samples were excited with monochromatic beams of 6 keV and 10 keV. In the case of the 6 keV monochromatic beam, the samples were measured inside a vacuum chamber at a pressure below 2×10^{-2} mbar in order to remove Ar K-shell emission lines and to improve the detection efficiency for low Z elements. The measurements using the 10 keV incident beam were obtained in air at ambient conditions of temperature and pressure. Each filter was mounted vertically in front of the side-looking detector and the beam dimensions were set to 2 mm × 4 mm, by means of vertical and horizontal slits, respectively. A Ge detector with an energy resolution of 140 eV (5.9 keV) was placed at the usual excitation geometry, i.e. at 90° respect to the incident-beam direction. The distance between the samples and the detector was about 15 mm in order to collect a large solid angle of fluorescence radiation. A multichannel analyzer (MCA) and an integration time of 500 s were used to record the XRF spectra. XRF spectra were normalized by current intensity and sampled irradiated area, and were analyzed using the well-accepted XRF AXIL code (Van Espen et al., 1977). In addition, for several samples at least three XRF spectra were recorded at different regions of the filter in order to verify the homogeneity of the aerosol deposition during the collection. Blank filters were also measured following the same procedure than the samples. Peak areas smaller than 3σ of the background noise were considered below the detection limit, and were denoted as zero. In order to perform the elemental quantification, the thin sample approximation was used (Van Grieken and Markowicz, 2001) and a NIST certified standard (SRM 2783 Air particulate on filter media) was used as a reference. The following elements were analyzed: Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.

A source apportionment analysis of the PM2.5 composition data was carried out by using the EPA PMF 3.0 software. This software allows determining the major emission sources as well as their elemental composition and the amount that they contribute to the total PM. The positive matrix factorization (PMF) model is a variant of factor analysis that constraints factor loadings and factor scores to nonnegative values, and has been described in detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997; Paatero and Hopke, 2003; Reff et al., 2007). The Polissar et al. (1998) work was followed for the treatment of uncertainties, and missing and below detection limit values in order to prepare the PMF tables. Concentration values are weighed taking into account standard deviations of measured concentrations, missing values, data below the minimum detection limit, and the outliers. All the variables were analyzed using the signal-to-noise criterion based on EPA's PMF guidelines (USEPA, 2008), to determine a species categorization. If the signal-to-noise ratio was less than 0.2, it was excluded from the analysis. If the signal-to-noise ratio was greater than 0.2 but less than 2, it was categorized as "weak" and down-weighted. The PMF model was run with a different number of factors; moreover, different pseudorandom numbers used in the iterative fitting process were examined to find the global optimal PMF solutions. For the determination of the number of factors in PMF, the primary consideration is to obtain a good fitting of the model to the original data. Given the number of samples we have available for the analysis, we obtained the calculated Q-values from trials with three to six factors and 100 model runs. The other important feature for this analysis was the desired rotation. In PMF, a key called Fpeak is used to control rotations and assist in finding a more reasonable solution. The optimal solution is determined by multiple model runs to examine the effect on the numbers of factors assigned and the different Fpeak values on the range of results that were both physically reasonable and where the objective function Q value does not change substantially. The Fpeak value was varied from −2 to +2. To assign PMF-resolved factors to aerosols sources an approach comprehending the comparison with literature data on tracer compounds and the knowledge of the site was followed.

3. Results and discussion

3.1. PM2.5

3.1.1. Average values, monthly variation and elemental mass concentrations

The results of the average elemental concentration values obtained for PM2.5 in the present work for the whole measurement period are compiled in Table 1. The elemental mass concentrations indicate that the monitoring site is affected by several sources. Geological marker elements, i.e. Al, Si, Ca, Fe, and Ti suggest that dust resuspension controls their aerosol abundance. Their presence was also verified by SEM-EDS studies (Achad et al., 2013) that were performed on the 2010–2011 campaign samples for the same site. They represent those particles originated from natural sources, and mostly include soil particles transported by the wind from the nearby rural region surrounding the city (Viana et al., 2008; Calvo et al., 2013) or resuspended soil dust. These particles contain mostly crustal elements: Si, Al, Ti, Fe and Ca. These elements appear in nature as aluminum silicates or as oxides. The major compounds in the earth's crust consist approximately of 75% of silicates and aluminum silicates in terms of weight. The aluminum silicates are characterized by high contents of Si and Al and variable content of K, Fe, Mg, and/or Ca. Titanium associated to 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 remaining elements are related to different anthropogenic sources generated by traffic, industrial activities and combustion processes and contribute to air pollution in the city. In more detail, the chemical differentiation of aerosols was made based on the chemical elements found and on the previous knowledge of the site. In addition, the abundant references in the literature referring to which elements or species can be considered as tracers of the

Table 1
Average elemental concentrations and standard deviation (ng m^{-3}) for the PM2.5 size fraction for the period April 2010–December 2011.

April 2010–Dec 2011		
Average concentration, (ng m^{-3})	Value	SD
PM2.5	50,055	29,225
Mg	73	67
Al	383	249
Si	1509	1833
S	336	172
K	628	439
Ca	308	138
Ti	22	15
V	0.5	0.7
Cr	2	1
Mn	12	6
Fe	301	182
Co	0.1	0.1
Ni	0.6	0.6
Cu	5	3
Zn	17	11

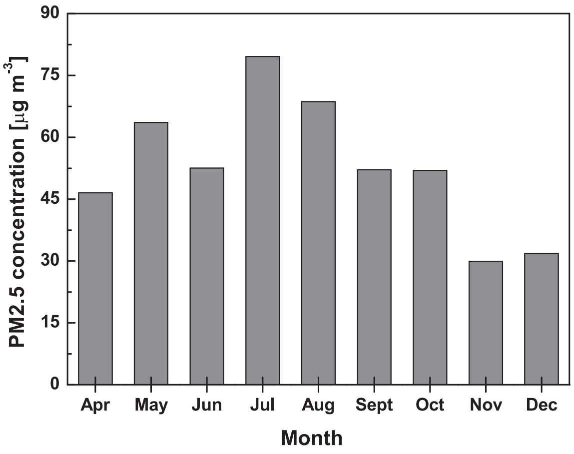

Fig. 3. Monthly average variation of ambient PM2.5 concentration measured at the monitoring site for the period (2010–2011).

different sources was used as a guidance (Viana et al., 2008; Calvo et al., 2013, and references therein). For diesel and gasoline power vehicles the main tracers are carbon in large abundance and minor contents of Fe, Cr, Ba, Zn, Ni, V and S. The occurrence of these elements is not surprising since these elements are known to be present in motor vehicle exhaust or produced through motor vehicle actions like brake wear, tire wear and road dust resuspension (Thorpe and Harrison, 2008; Viana et al., 2008). Mg and Ca are representative of construction activities, which were very abundant in the city. Some metal elements, Cr, Cu, Zn, are associated to metallurgical activities that are the main industries located within the urban perimeter and along the direction of the dominant winds (from NE).

Fig. 3 shows the average monthly evolution of PM2.5 for the period April to December (2010–2011). From the figure, it is possible to observe that the total PM2.5 mass concentration increases from April to July where it reaches the maximum value, after that month there is a gradual decrease in the PM levels until the minimum value is reached in the period November–December. This behavior can be explained mainly by the meteorology of the city. As mentioned above, Córdoba faces severe pollution effects during wintertime. In June and July Córdoba can be viewed as a large size chemical reactor stirred by weak winds with a dominant NE–SW direction. Rain is almost absent, so there is not removal of pollutants by wet precipitation. Radiative temperature inversions lasting until noontime are frequent and pollutants are trapped in a layer not higher than 200 m. In August and September, the situation changes, due to stronger winds blowing during most of the day. The NE–SW direction is still very important, but the N–S direction has also relevance. The morning temperature inversion now last for a short time and radiation levels starts to increase. In early October, spring time in the southern hemisphere, some days with rain and strong turbulence quickly dilute pollutants producing a gradual decrease in the levels of particulate matter. This picture continues during most of the summer. Fig. 4a–d show the monthly dependence of the concentration of some elements (K, S, Cu, and Ca), considered as possible source tracers. Hence, their monthly variations will be analyzed in the following section to understand the temporal dependence of the assigned sources.

3.1.2. *Receptor model and source apportionment*

In this section, we present the results obtained by applying the PMF model to PM2.5. PMF receptor model was run for different number of factors and the source profiles (factors) were examined looking for specific tracer contributions. Their average seasonal dependence was investigated to confirm the assigned sources.

We have found that a 4 factor solution explains well the measured PM2.5 concentrations. Sensitivity analyses of this 4 factor solution were performed by varying the Fpeak parameter. As recommended by Paatero et al. (2005), we look for solutions that produce 'edges' in G-space scatter plots. We have found that a solution with Fpeak = −0.30 is the most plausible one. The statistical results for the 14 species fitted are shown in Table 2. Most fitted elements have regression coefficients (R^2) greater than 0.8, except

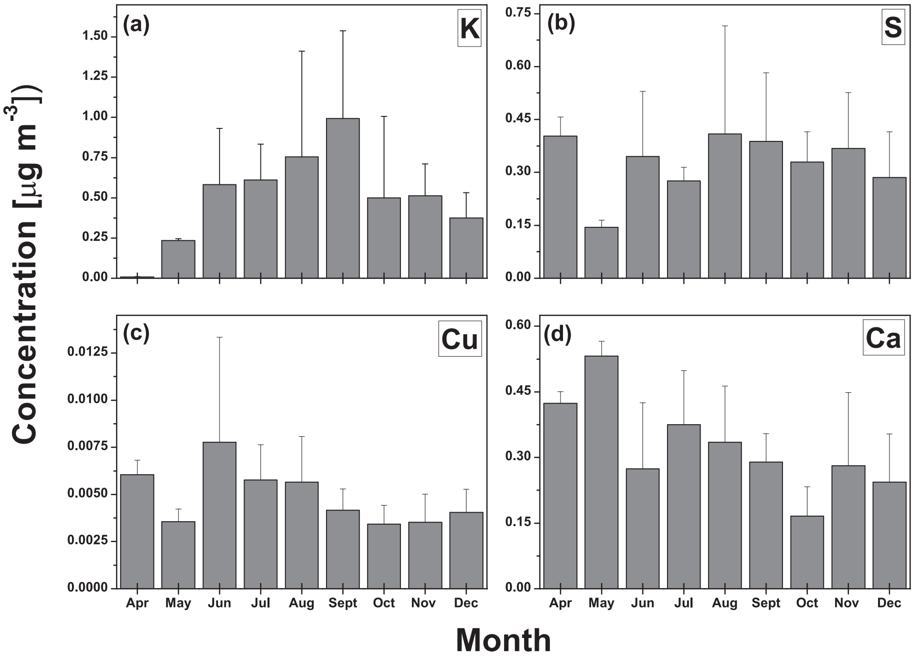

Fig. 4. Monthly average variation of the elemental concentrations for (a) K, (b) S, (c) Cu and (d) Ca measured at the monitoring site for the period (2010–2011).

Table 2
Regression diagnostics for a 4 factor solution, PM2.5 data.

Species	Intercept	Slope	Std. error	R^2
Al	0.01	0.95	0.08	0.89
Si	0.30	0.68	0.31	0.84
S	0.05	0.67	0.10	0.57
K	0.01	0.97	0.05	0.99
Ca	0.03	0.84	0.08	0.69
Ti	0.00	0.82	0.00	0.94
V	0.00	0.90	0.00	0.98
Cr	0.00	0.51	0.00	0.39
Mn	0.00	0.86	0.00	0.89
Fe	0.06	0.77	0.05	0.90
Co	0.00	0.67	0.00	0.79
Ni	0.00	0.58	0.00	0.37
Cu	0.00	0.73	0.00	0.84
Zn	0.01	0.59	0.00	0.80

Ca, S, Cr and Ni that were kept because they are tracers of different sources.

Table 3 shows the source profiles in units of concentration (ng m^{-3}) and in percentage for a 4 factor solution using an Fpeak of −0.30.

To account for many of the sources of error in the PMF model, the technique of bootstrapping was used (Paatero et al., 2014). Bootstrapping is available for use in EPA-PMF and involves randomly selecting a certain number of samples with replacement from a dataset to create a new dataset, executing PMF on this bootstrapped sample, and estimating factor profiles. Two hundred bootstrapped datasets are modeled and summary statistics calculated. Bootstrapping can be used to determine the precision of PMF profiles by calculating the standard deviation (assuming normality) or various percentiles of factor profiles (F matrix values) from numerous bootstrap runs. For PM2.5, two factors account for most of the mass concentration. One of them with (15 ± 1) μg m^{-3} has the highest S and K contribution. This source is attributed to a combination of sulfate and combustion processes, including biomass burning. S is indicative of combustion from fossil fuels as well as secondary aerosols if appears associated with ammonia, while K is a marker of combustion, including biomass burning. There are two facts that led us to infer that part of the S could have secondary origin being its content directly related to the level of sulphates present in the airborne particulate matter that is formed by photochemical reactions (Reich et al., 2009). First of all, the low emission of sulfur from combustion activities as a consequence of the massive usage of CNG and second the fact that the Argentinean oil products have low percentages of sulfur (D'Angiola et al., 2010). As it was mentioned above, K makes an important contribution to this factor and is an indicator of combustion, including biomass burning. During the dry season (from May to September), air masses are mostly arriving to the site from the northeast region of Argentina. Fire density begins to increase in this region from June to September due to the onset of several meteorological conditions, such as dryness of the soil, winds with a NNE direction and low relative humidity (Di Bella et al., 2011). Therefore, the site receives emissions from the surrounding fires being K its typical tracer.

The other important factor in terms of mass contribution (13 ± 2) μg m^{-3} presents high contributions of metals like Cu, Zn, Ni and V and is attributed to a traffic related source since these elements are found in abrasion processes, lubricants and additives (Thorpe and Harrison, 2008). In Argentina, these elements have been found in abundance in cities like Buenos Aires (Fujiwara et al., 2011). Zn is an oil additive and all engine oils contain a compound called ZDDP (Zn dialkyldithiophosphate) for wear protection. In general, heavy-duty engine oils have a higher level of this compound. Automotive engine oils generally have a lower level of ZDDP to protect catalytic systems. Mn is being used as an antiknock agent in motor vehicle fuel additives. Cu and Zn are reported as typical traffic related elements. Increasing traffic densities and the development of more powerful and faster vehicles have led to a substantial and continuous increase of these metals emission. Different additives, parts of vehicles or oils contain those elements that are released to the environment through different mechanisms (Fujiwara et al., 2011).

The third and fourth factors contribute similar amounts in terms of mass concentration (7 ± 2) μg m^{-3} and (8 ± 1) μg m^{-3} respectively. The first of them presents a high loading of Al, Si, Ti, Ca and Fe, identifying a source characterized by crustal elements, and it was attributed to mineral dust. The other one presents a high loading of Cr together with of Cu and Zn. This profile was assigned to an industrial source, mostly metal mechanics.

In Fig. 5, the monthly variation of the 4 factors is presented and the mean value for the seven months period is indicated. The temporal evolution of the SO_4^{2-}/combustion, including biomass-burning factor shows a maximum in September, coinciding with the monthly evolution of K (Fig. 4a). In September, the low relative humidity and the severe dryness of the soil favor conditions for the production of wild fires in the neighboring regions. In fact, it is the month where the surface burned is larger than in any other of the previous months. Important fires in the North–Northeast of the country are detected by MODIS every year (Justice et al., 2002). On

Table 3
Source profiles for a 4 factor solution, PM2.5 data (Fpeak = −0.3).

Species	Concentration [ng m^{-3}]				Percentage [%]			
	Industrial	Traffic	SO_4^{2-}/combustion	Mineral	Industrial	Traffic	SO_4^{2-}/combustion	Mineral
PM2.5	7612.90	12,747.00	14,567.00	7045.60	18.1	30.4	34.7	16.8
Al	50.87	35.85	69.78	221.64	13.5	9.5	18.5	58.6
Si	156.33	122.67	214.26	685.97	13.3	10.4	18.2	58.2
S	71.62	67.71	115.39	28.57	25.3	23.9	40.7	10.1
K	46.85	143.40	331.69	122.80	7.3	22.2	51.4	19.0
Ca	50.72	76.79	46.04	102.33	18.4	27.8	16.7	37.1
Ti	3.03	3.65	3.77	11.42	13.8	16.7	17.2	52.2
V	0.02	0.43	0.01	0.01	3.5	90.6	3.2	2.7
Cr	0.47	0.26	0.42	0.30	32.3	18.1	29.0	20.6
Mn	1.87	2.34	2.11	4.88	16.7	20.9	18.8	43.6
Fe	45.63	64.74	53.57	130.54	15.5	22.0	18.2	44.3
Co	0.01	0.02	0.02	0.04	8.3	22.3	22.6	46.9
Ni	0.09	0.17	0.12	0.01	22.5	43.6	31.2	2.8
Cu	1.35	1.53	0.87	0.75	30.0	34.1	19.3	16.6
Zn	4.55	5.11	2.82	2.46	30.5	34.2	18.9	16.5

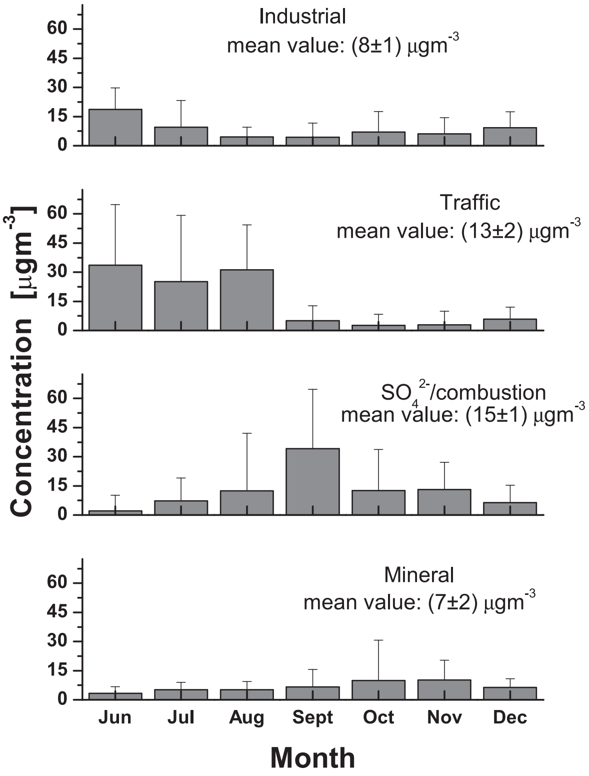

Fig. 5. Monthly bar plots of the PMF factors determined in this study for PM2.5 fraction.

the other hand, if S is coming from regional transport, no variation is expected due to local sources. Moreover, the expected increase due to the intense photochemical activity in summer time is moderated by the greater dispersion capability of the atmosphere. The balance of these factors can explain the substantial stability of sulfur concentrations from June to December (see Fig. 4b).

As expected, the traffic factor has a larger contribution during the cold months (June to August) compared to the spring–summer months (September to December); the same monthly variation is observed in Fig. 4c for Cu concentration. The negative correlation of temperature with traffic is explained because lower surface air temperatures are correlated with ground level atmospheric stability (Stein and Toselli, 1996). The industrial factor, shows a similar profile to the traffic factor. The dust factor shows a temporal trend showing a slight increase from June to September/October (dry season). This behavior can be understood considering the meteorology in the area. September and October can be considered as transition months between the dry winter and the rainy summer. Both, the lack of precipitation and the high wind speed are factors that favor aerosol loading enriched in soil particles. After these months wind speed is in its maximum but precipitations show a significant increase (reaching a maximum in December) having the effect of moderating the load of soil particles. This factor makes only a small contribution in terms of mass concentration to PM2.5 (7 ± 2) µg m^{-3}. There are some constraints on the inter-elemental ratios in crustal material; for Si/Al, a ratio of 3.8 in the upper continental crust was reported by Rudnick and Gao (2006). The Si/Al mass ratio reported in this work for the dust factor of 3.1 is in good agreement and reinforces the assignment of this source.

The results of the PMF analysis pointing to only four factors for this fraction are not surprising. Geographically the city is located at the central region of the country far away from the Atlantic or Pacific oceans to receive apportionment from marine aerosols as happen in Santiago de Chile and Buenos Aires (Jorquera and Barraza, 2012; Artaxo et al., 1999; Reich et al., 2009).

The sources found in the present work seem, a priori, different from the work of López et al., (2011) carried out for the city of Córdoba. However, in that work the profiles were a combination of two or three sources. For example, the urban dust factor was a combination of traffic, oil combustion and crustal elements. In addition, no secondary aerosol factor was resolved in the study. It was concluded that secondary aerosols were present in the area even though the model was unable to resolve them as a single source because they were mixed with other sources. We consider that the modification in the experimental setup to carry out the SR-XRF measurements for the low Z elements, i.e. under vacuum, improved the quantification of S and K resulting in cleaner profiles determination, mainly for SO_4^{2-}. Taking into account these considerations we can reconcile these differences. The traffic factor is similar (28% compared to 30.4% in this work), the industrial factor is almost the same (16 and 18%, respectively), and the previously called urban dust factor with 50% contribution could be understood as the sum of the remaining two factors in the present work: 16.8% attributed to mineral dust because it has only crustal elements in the profile and 34.7% attributed to combustion, including biomass burning with S and K signature (combustion from traffic and from biomass burning). The sulfate contribution to PM2.5 in Córdoba includes emissions from thermal power plants and several industries located nearby to the South of the city. However, the receptor model results cannot discriminate more than one sulfate source. Thus, we acknowledge that our estimates of the SO_4^{2-}/combustion contributions are upper bounds of the total contributions to ambient PM2.5 at Córdoba. Besides, it should be noticed that the most subjective and least quantifiable step in applying PMF for PM source apportionment is the assignment of identities to the factors (Reff et al., 2007). A common strategy is to search the literature for measured PM source profiles with characteristics similar to factor profiles in the F matrix. Databases of source profiles are available for such analyses, although their use for this purpose is not documented very often. A more precise identification of the sources can be performed by comparing certain species ratios in PMF profiles to the same ratios in measured PM source profiles. Some researchers perform local and/or regional source sampling along with the ambient PM sampling to identify PMF profiles, which helps minimize uncertainty in the identification process, because the sampled sources should resemble PMF profiles more strongly than source profiles collected in other locations. Some recent PMF publications have made comparisons to factor profiles from previously published PMF studies to aid in source identification (Reff et al., 2007).

Trajectory analysis can be used to help and/or to confirm source identification. Recently an analysis of the dynamics of the air masses arriving to the region has been presented (Olcese et al., 2014). In this work, back trajectories were calculated for this period by using the HYSPLIT 4 model (Draxler and Hess, 1998, 2004) and clustered to show the climatology of the air masses arriving to the region according to both position and frequency. It was concluded that air masses arrive to Córdoba region from the Northeast direction although specific remote sources which could contribute to observed profiles could no be determined. One of the main drawbacks for carrying out trajectory analysis in our region is the lack of highly resolved meteorological fields in both space and time. An improvement in the availability of these resources would lead to a better resolution of the atmospheric physics and to the ability of better infer the movement, mixing and transport of atmospheric constituents.

Table 4
Average elemental concentrations and standard deviation (ng m^{-3}) for PM0.25–0.5 and PM0.5–1 size fractions for the period May–August 2011.

Average concentration [ng m^{-3}]				
Species	PM0.25–0.5		PM0.5–1	
	Value	SD	Value	SD
Mg	10	17	25	35
Al	49	60	75	116
Si	170	197	229	353
S	41	31	8	10
K	58	36	31	31
Ca	58	37	68	96
Ti	5	3	8	9
V	0.2	0.5	0.3	0.5
Cr	0.3	0.4	0.02	0.03
Mn	1	1	0.9	0.8
Fe	23	15	35	29
Co	0.02	0.01	0.02	0.01
Ni	0.07	0.09	0.06	0.02
Cu	1.0	0.5	0.5	0.3
Zn	2	3	0.8	0.7

3.2. Size selective mass distribution

From May to August 2011, an additional campaign has been carried out to measure PM0.5–1 and PM0.25–0.5 size fractions. Table 4 shows the average elemental concentrations and standard deviation (ng m^{-3}) for PM0.25–0.5 and PM0.5–1 size fractions for the period May–August 2011. The obtained average elemental concentrations are presented in Fig. 6 together with the results for the PM2.5 average values for these four months. Direct observation of the PM2.5 concentrations in the figure permits to differentiate elements that are mainly emitted from mechanical processes from those that are emitted through the engine exhaust. The former have their origins in road resuspension (Al, Fe, Si, Ca, Ti) and are concentrated in the coarse size range (larger than 1 μm). The latter are mainly formed inside the engine and are concentrated in the finest fraction. However, there are some elements, such as Mn, Cr, Zn, Ni, and Cu, that by the size distribution, seems to have a double origin, i.e. in the interior of the engine and in mechanical wearing. Unfortunately, due to the way the Sioutas impactor collects the sample and the need to have an optically thin sample to perform SR-XRF measurements prevent us to collect enough mass on the filters so that the total PM mass can be accurately measured for these fractions. This drawback and the fact that we have 16 samples in total prevent us to perform a reliable source apportionment analysis for these fractions. Fig. 7 shows the average elemental concentration for the size fractions measured in our work, PM0.25–0.5 and PM0.5–1 for some selected metals. It is important to note that the most toxic metals (i.e. Cr, Zn, Ni, Cu, and Mn) tend to have an important contribution in the finest size fraction of the particulate matter. As it was mentioned above, the government of Córdoba city is not currently making any air quality control on the levels of toxic metals in the air. However, it is important to note that the reported concentration values for Ni, V, and Mn are much lower than the limits established by the World Health Organization (WHO, 2000). For the case of Cr, it is worth to clarify that atmospheric Cr exists in two forms: Cr (III) and Cr (VI). Of them, Cr (VI) can have a carcinogenic effect and can be harmful to the kidneys and heart. The WHO only sets a limit concentration value for Cr (VI), while the data reported in this work are for total Cr.

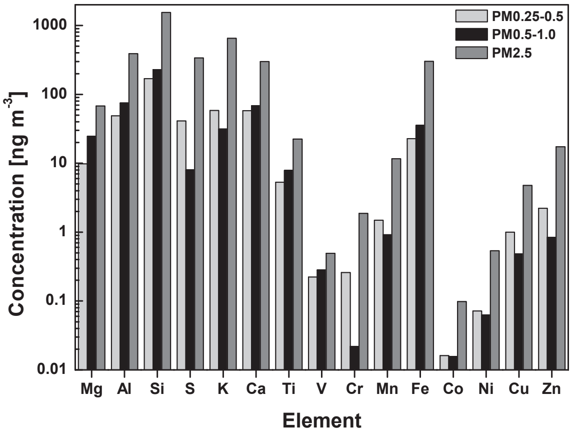

Fig. 6. Elemental concentration levels of PM0.25–0.5, PM0.5–1 and PM2.5 for the study site for the period May–August 2011.

3.3. Comparison with literature values for selected elements

Table 5 shows the values of elemental concentration for transition metals measured in this work, in comparison to the reported ones for other cities. As can be seen, the reported concentration values for PM2.5 are comparable to those previously found by López et al. (2011). The comparison with the values reported by Dos Santos et al. (2009) for Buenos Aires city, shows considerably higher values than the informed in this work for Cr, Cu and Zn. The concentration values measured in Santiago de Chile (Jorquera and Barraza, 2012 and by Artaxo et al., 1999) are very similar to the values observed in Córdoba, whereas those measured for Antofagasta (Jorquera and Barraza, 2013) are clearly higher. The authors explained these results considering that mining activities have been increasing, leading the economic growth in that area. Finally, the works of Castanho and Artaxo (2001) for Sao Paulo, and Miranda et al. (2012) for six cities in Brazil, reports similar concentration values for the toxic elements.

Regarding to the finer two fractions measured in this work (PM0.5–1 and PM0.25–0.5) there are no reported values for Argentinean and other South American cities therefore, the average concentration values for the transition metals in the PM0.25–1 fraction, obtained by adding the two finer fractions measured in this work, were compared with those reported for some European sites for PM1. Three sites were selected: a small industrial site (Perrone et al., 2013), a highly polluted city (Ariola et al., 2006) and an urban and background site in Switzerland (Minguillón et al., 2012). The fact that the results found in Córdoba are comparable with those found in Zurich and in a central Mediterranean site in Italy (Salento) show how complex the system (city) is regarding to meteorological variables, air mass dynamics, geographical location, and local and regional sources.

Although PM1 content has not been regulated so far, it represents a significant fraction of PM10 and PM2.5 in urban and industrial areas (Ariola et al., 2006). Moreover, several elements are mainly concentrated in the finer fraction of particulate matter (<1 μm) making it potentially more hazardous to human health and favoring long-distance transport processes (Moreno et al., 2011).

4. Conclusion

We have applied a receptor model analysis to integrated 24 h ambient PM2.5 concentrations taken in 2010–2011 at one site in Córdoba. The elemental concentration values obtained in this work are comparable to those found in 2009 for the same site and were also similar to the levels found in Buenos Aires City, Argentina. Four sources were identified being their mass contributions: traffic:

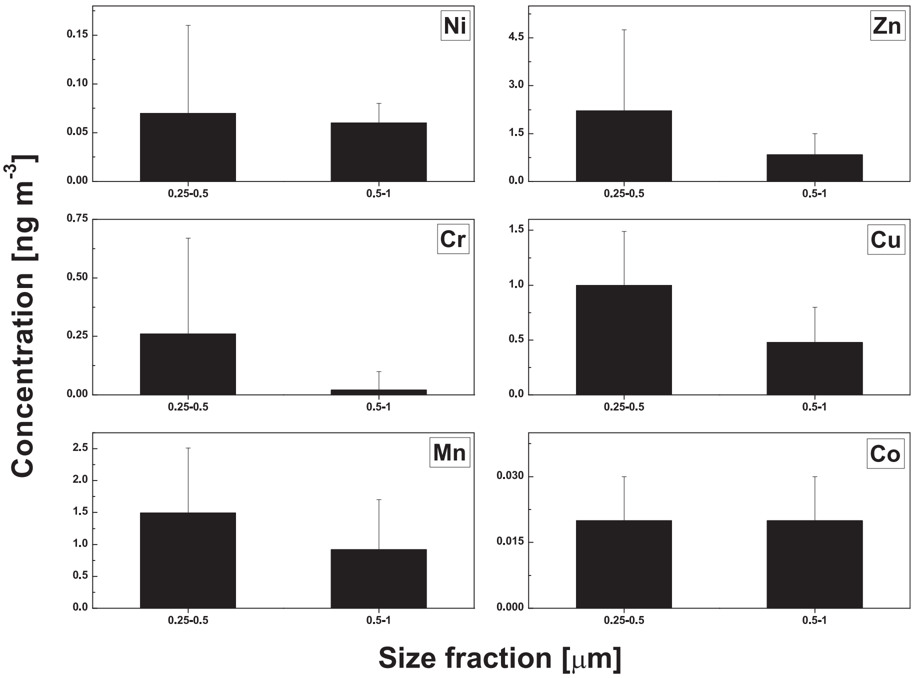

Fig. 7. Elemental concentration levels of selected toxic metals for the PM0.25–0.5 and PM0.5–1 fractions for the study site measured from May to August 2011.

Table 5
Average elemental concentration values for the PM2.5 and PM0.25–1, evaluated as (PM0.25–0.5 + PM0.5–1) size fractions, for this study compared with the PM2.5 and PM1 reported in other studies. Values between parentheses correspond to standard deviation values.

Elemental concentration (ng m^{-3})				V	Cr	Mn	Fe	Co	Ni	Cu	Zn
PM2.5											
This study	Córdoba, Argentina	SR-XRF	EPA PMF 3.0	0.5 (0.8)	2 (1)	11 (6)	299 (171)	0.1 (0.1)	0.6 (0.6)	5 (3)	18 (12)
López et al., 2011	Córdoba, Argentina	SR-XRF	EPA PMF 3.0	7 (2)	3.5 (0.8)	13 (9)	345 (211)	0.6 (0.2)	2.8 (0.7)	9 (5)	28 (22)
Dos Santos et al., 2009	Buenos Aires, Argentina	HPLC – ICP OES	–	–	10.5	9.9	305.2	–	–	36.2	163.7
Jorquera and Barraza, 2013	Antofagasta, Chile	XRF	EPA PMF 3.0	7 (3)	–	10 (4)	354 (173)	–	2 (1)	68 (43)	60 (41)
Jorquera and Barraza, 2012	Santiago de Chile, Chile	XRF	EPA PMF 3.0	0.5 (0.3)	1.7 (1.2)	11.9 (7)	244 (90)	–	0.4 (0.3)	19.3 (9)	46 (26)
Castanho and Artaxo, 2001	San Pablo, Brazil (w)	PIXE	APFA	11.7 (6.5)	9.6 (3.7)	12.6 (8.1)	532 (273)	–	3.9 (2.8)	19 (11)	126 (107)
	San Pablo, Brazil (s)			8.9 (3.3)	–	6.7 (4.7)	179 (79)	–	3.1 (1.5)	5.4 (4.2)	51 (32)
Miranda et al., 2012	Sao Paulo, Brazil (s)	EDXRF	–	1.3 (0.9)	1 (1)	6.6 (21.2)	128.3 (57.2)	–	0.9 (1.5)	8.1 (13.8)	53.6 (41.1)
	Sao Paulo, Brazil (w)			2 (1.5)	2.1 (1.8)	8.2 (5)	247.9 (142.6)	–	1.2 (1.1)	13.1 (9.8)	99 (96.1)
	Río de Janeiro, Brazil (s)			4.9 (2.9)	1.8 (0.7)	3.7 (1.9)	56.3 (26.4)	–	3.6 (1.5)	7.7 (4.8)	18.1 (15.9)
	Río de Janeiro, Brazil (w)			3.8 (2.2)	1.8 (0.7)	5 (3.4)	89.5 (65.9)	–	2.2 (1.4)	9.9 (10.7)	30.9 (26.5)
	Belo Horizonte, Brazil (s)			1.5 (0.8)	0.7 (0.9)	25.2 (60.5)	107.9 (80.6)	–	0.8 (0.5)	4.1 (6.4)	12.6 (12.3)
	Belo Horizonte, Brazil (w)			1.6 (0.8)	0.6 (0.6)	49.2 (44.9)	142.6 (77.7)	–	0.8 (0.6)	2.5 (3.8)	16.1 (13.5)
	Porto Alegre, Brazil (s)			0.9 (0.5)	1.3 (0.7)	2.8 (2.8)	60.2 (44.9)	–	0.7 (0.2)	1.9 (1.8)	12.4 (18.9)
	Porto Alegre, Brazil (w)			1.5 (1)	12.1 (69.1)	6.2 (19.7)	90.7 (134.3)	–	4.7 (13.9)	5.2 (7.5)	18.7 (20.2)
	Curitiba, Brazil (s)			0.7 (0.6)	0.7 (0.6)	2.1 (4.4)	57.3 (31.7)	–	0.4 (0.5)	2.6 (4.2)	9 (10.6)
	Curitiba, Brazil (w)			0.7 (0.9)	0.8 (0.8)	2.5 (2.2)	82.9 (59.9)	–	0.9 (0.8)	3.8 (4.8)	25.8 (46.1)
	Recife, Brazil (s)			0.4 (0.3)	0.4 (0.4)	1.3 (1.3)	50.7 (46.7)	–	0.3 (0.3)	0.9 (0.9)	8.9 (10.9)
	Recife, Brazil (w)			0.3 (0.2)	0.5 (0.5)	2.9 (3.4)	74.4 (52.4)	–	0.4 (0.5)	1.8 (1.8)	24.9 (28.9)
Perrone et al., 2013	Salento, Italy	ICP AES	PMF2	4 (4)	4 (3)	2 (1)	100 (100)	–	5 (2)	4 (7)	–
PM1											
This Study	Córdoba, Argentina	SR-XRF	EPA PMF 3.0	0.5 (0.9)	0.3 (0.4)	2 (2)	58 (44)	0.03 (0.03)	0.1 (0.1)	1.5 (0.8)	3 (3)
Perrone et al., 2013	Salento, Italy	ICP AES	PMF2	3 (3)	4 (3)	1 (3)	60 (30)	–	3 (3)	2 (5)	–
Minguillón et al., 2012	Zürich, Switzerland	ICP MS	EPA PMF 3.0	~0.6	~0.8	~0.9		~0.05		~1	~10
Ariola et al., 2006	Genoa, Italy	PIXE – EDXRF	–	~10	~6	~5	~50		~7	~4	~20

(13 ± 2) μg m^{-3}, SO_4^{2-}/combustion processes, including biomass burning: (15 ± 1) μg m^{-3}, mineral dust: (7 ± 2) μg m^{-3} and industry: (8 ± 1) μg m^{-3}. It is important to note that the source apportionment was partially limited by the lack of carbon measurements. Additional measurements would be very useful in order to perform a mass closure calculation. Carbon measurements will be performed in the future by the Soft X-ray Absorption technique using synchrotron radiation.

By comparing the elemental concentrations found in the two sub-micrometer PM fractions for the toxic metals, we concluded that they make an important contribution to the finest one. This result is relevant considering the increasing evidence indicating that fine particulate matter in the atmosphere is responsible for adverse health effects on humans. Therefore, the identification of the aerosol sources and its components is critical to define source-specific health risks.

The results of the present analysis can help demonstrate to local and national authorities the urgent need to carry out emission inventories, to implement air quality monitoring systems and to set regulations for PM2.5 following what has being done for other countries of the World. These policies will be useful to both, local and regional scales. For the mixed sources found, such as sulfates/combustion, further source apportionment may be accomplished by conducting dispersion modeling of the participating sources.

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