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

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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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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