Regional and long-range transport of aerosols at Mt. Aitana, Southeastern Spain

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HIGHLIGHTS

- PM_1 was mainly composed of organic carbon and ammonium sulfate
- Concentrations of PM_{10} and crustal elements were highly correlated
- The lowest PM levels were associated to air masses coming from the Atlantic
- PM_{10}, Ti and Fe concentrations were significantly enhanced during Saharan events
- Ca/Ti and Ca/Fe ratios can be used as sensitive indicators of Saharan events

GRAPHICAL ABSTRACT
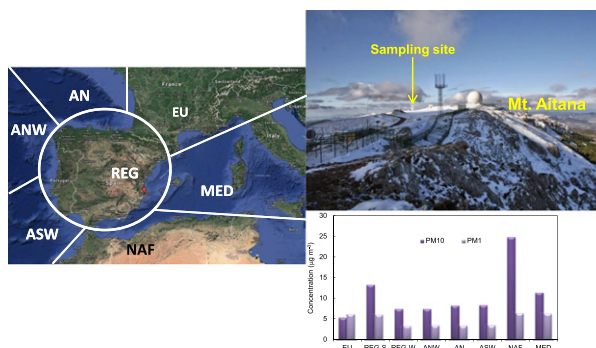
ABSTRACT

More than 150 particulate matter (PM) samples with aerodynamic diameters smaller than 1 and 10 μm (PM_1 and PM_{10}, respectively) were collected during an 18-month sampling campaign at Mt. Aitana (1558 m a.s.l.), located in the western Mediterranean basin. PM samples were analyzed for water-soluble ions, carbonaceous species and trace metals using standard procedures. Average mass concentrations of PM_1 and PM_{10} were, respectively, 5.0 and 13.3 μg m^{-3}. PM_1 was composed mostly of organic carbon and ammonium sulfate, while nitrate and crustal elements were major components of the PM_{10} fraction. A significant positive correlation was determined between PM_{10} and mineral elements such as Ca or Fe. The study of the influence of air mass origin upon PM mass concentrations and composition showed that Saharan dust outbreaks were associated with the highest PM_{10} levels (24.9 μg m^{-3} average during African events). Nitrate and crustal components were also considerably increased during these episodes, especially Ti and Fe (~190% higher compared with the average value for the whole study period). The results indicate that Ca/Ti and Ca/Fe ratios can be considered reliable indicators of Saharan dust intrusions.

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1. Introduction

Aerosols can be released into the atmosphere by a wide variety of local sources, both natural and anthropogenic, or come from remote areas transported over long distances by strong winds. Alternatively, some inorganic and organic gaseous pollutants can be converted into secondary aerosols by chemical reactions induced by sun light. All these processes determine the physico-chemical characteristics of

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aerosols and therefore their impacts on human health and the climate system (Raes et al., 2000). Among the natural sources of aerosols, mineral dust from the Sahara desert is one of the most important on a global scale. Dust plumes often enter the atmosphere and can travel up to thousands of kilometers before settling back to earth (Engelstaedter et al., 2006). During transport, dust particles tend to adsorb acidic gases such as SO_2 or NO_x, facilitating their transformation into sulfates and nitrates (Abdelkader et al., 2015). The western Mediterranean basin is especially sensitive to Saharan dust events due to its proximity to Northern Africa (Galindo et al., 2008; De la Paz et al., 2013). Additionally, the region's typical climate, characterized by low precipitations and summer droughts, favors soil dust resuspension and contributes to increase background levels of mineral matter. The relative input of local versus Saharan dust is rather difficult to estimate due to a similar chemical composition (Nicolás et al., 2008). Other important processes associated with high aerosol levels in this area are the typical recirculation patterns of air masses and the intense solar radiation that promote the formation of secondary compounds through photochemical reactions (Millán et al., 2002; Rodríguez et al., 2002).

Stations located at high mountain sites are particularly suitable to study regional processes and long range transport of pollutants since the interference of anthropogenic local sources is often extremely low (Ripoll et al., 2014; Moroni et al., 2015). With this aim, at the end of 2010 we established a monitoring station at Mt. Aitana (1558 m), the highest peak of the Betic Cordillera located in southeastern Spain. The present study is focused on the influence of air mass origins on the levels and composition of PM_1 and PM_{10} at this site, with special attention to Saharan dust outbreaks.

2. Experimental

2.1. Sampling site

The sampling station is located at Mt. Aitana (38°38′56.8″N 0°15′55.2″W; 1558 m a.s.l.), in southeastern Spain. It is situated 16 km from the nearest Mediterranean coast and <40 km from the city of Alicante (Fig. 1). Since the surrounding area is sparsely populated, pollutant emissions from human activities are very low. Vegetation is scarce and large areas of soil are exposed to wind erosion. Average temperatures vary between 3 °C in winter and 20 °C in summer. Prevailing winds blow mainly from the coast during summer and from the NNW direction during the winter season. Annual precipitation at Mt. Aitana usually ranges from 600 to 800 mm, while coastal areas receive a rainfall of <300 mm. More details of this site can be found in Nicolás et al. (2015) and Galindo et al. (2016).

2.2. Sampling and analysis

The sampling campaign was carried out between 17th March 2014 and 4th September 2015. Twenty-four-hour PM_1 and PM_{10} samples were collected with an approximate frequency of three times a week starting at 00:00 UTC each day. The collection of PM_1 samples was simultaneously performed by means of high-volume (MCV, 720 m^3 day^{-1}) and low-volume samplers (LVS 3.1, 55 m^3 day^{-1}) using quartz fiber (Whatman QM-H, 150 mm) and Teflon (Whatman 2 µm PTFE 46.2 mm PP ring supported) filters, respectively, as substrates. PM_{10} particles were sampled onto quartz fiber filters (150 mm) using a Digitel high-volume sampler (820 m^3 day^{-1}). During the measurement period, about 180 and 160 PM_1 samples were collected with the low- volume and high-volume samplers, respectively. In the case of PM_{10}, a total of 162 valid samples were collected and analyzed. It is important to mention that the fraction of samples gathered during the summer season was significantly higher than in winter since (1) the measurement period does not cover two complete years and (2) samplers failure is more frequent during winter due to adverse ambient conditions.
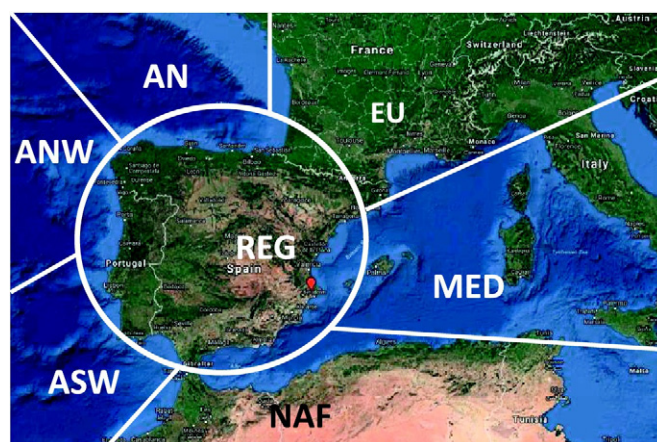

Fig. 1. Location of the sampling site in the southeast of the Iberian Peninsula. EU: European, MED: Mediterranean, NAF: North Africa, ASW: Atlantic South West, ANW: Atlantic North West, AN: Atlantic North, REG: Regional.

All filters were conditioned for at least 24 h at a relative humidity of 50 ± 5% and temperature of 20 ± 1 °C and weighted using electronic balances (Ohaus AP250D and Mettler-Toledo XP105) with 10-µg sensitivity. Concentrations were then calculated by dividing PM masses by the sampled air volume. After weighting, the filters were stored in the fridge at 4 °C until chemical analysis.

PM_1 samples on Teflon filters and a punch of 47 mm diameter of each PM_{10} sample were extracted ultrasonically with 15 mL of ultra-pure water and heated at 60 °C for about 6 h. The aqueous extracts were then analyzed by ion chromatography (IC) for the determination of ion concentrations (Cl^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). Anions were analyzed by means of a Dionex DX-120 ion chromatograph with an IonPac AS11-HC separation column using KOH 15 mM as eluent. The analysis of cations was performed using a Dionex ICS-1100 ion chromatograph equipped with a CS12A analytical column and 20 mM methane sulfonic acid as eluent. To determine organic and elemental carbon concentrations punches of 1.5 cm^2 area from PM_1 and PM_{10} samples collected onto quartz fiber filters were analyzed with a Thermal-Optical Carbon Aerosol Analyser by Sunset Laboratory using the NIOSH 5040 protocol to quantify the elemental and organic carbon fractions (Birch and Cary, 1996). A detailed description of the analytical procedures can be found in Yubero et al. (2015). The elemental composition of PM was determined by means of Energy Dispersive X-Ray Fluorescence (ED-XRF) using an ARL Quant'x Spectrometer (Thermo Fisher Scientific, UK). The excitation X-rays were obtained with an X-ray tube with an Rh anode ($I_{max} = 1.98$ A, $V_{max} = 50$ kV). The fluoresced X-ray photons are detected and converted to an electrical signal by means of a Si(Li) detector. The instrument was calibrated using different standards (Micromatter). The accuracy of the quantitative method was checked by analyzing the SRM NIST2783 standard ($PM_{2.5}$ on polycarbonate membrane). Detection limits ranged from 0.1 to 60 µg cm^{-2} depending on the element. In the case of PM_1, these analyses were performed on samples collected on Teflon filters since the use of quartz fiber filters as substrates only enables the reliable determination of elements from Ca due to the presence of silicon in the filter.

2.3. Meteorological data and back-trajectory analysis

Temperature, solar radiation, relative humidity, rainfall, wind speed and wind direction were continuously monitored by a meteorological station located at the sampling site.

Back trajectories of air masses arriving at Mt. Aitana were calculated using the HYSPLIT model developed by the National Oceanic and Atmospheric Administration (NOAA) (Draxler and Rolph, 2013). Ninety-six hour backward trajectories (for 12 a.m. modelling vertical velocity and for 3 different heights, 500, 1500 and 2500 m above ground level,