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Compositional variability of the aerosols collected on Kerkennah Islands (central Tunisia)

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ABSTRACT

The aim of the present study is to investigate the seasonal variability of the aerosol concentrations and origins in central Tunisia. Four field campaigns were carried out in 2010/2011 to collect air-suspended particles on the Kerkennah Islands. The elemental composition (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, Ni, V, and As) of the particles collected in summer (June and July), autumn (September and November), winter (February and March), and spring (April and May) is determined by X-ray fluorescence analysis.

Examination of the enrichment factors (EF) of all elements indicate that Al, Fe, Si, Ca, Ti, Mn, and Cr are mainly derived from soil sources, whereas Na and Cl are mostly of marine origin. Other elements such as K and Mg or S and P have multiple origins (Marine/crustal and crustal/anthropogenic, respectively). Finally, V, Cu, Ni, As, and Pb appear to be produced by anthropogenic activities.

Based on the inter-elemental correlations, the mass concentrations of mineral dust (MD), sea-salt (SS) and anthropogenic (non-crustal and non-marine) sulfates (NSS) are quantified. MD, SS and NSS display significant inter-seasonal differences: on the one hand, MD and SS are the highest in spring and the lowest in winter, probably because of the seasonal change in meteorological conditions. On the other hand, NSS and Cu concentrations are above their autumn and winter values in spring and summer, which suggests the existence of a common source of the combustion type for these two pollutants.

1. Introduction

In recent decades, there has been a growing concern over the alarming rate at which atmospheric aerosols contaminate the ambient air environment. The assessment of the physico-chemical properties of these aerosols is crucial to apportion the role played by their sources, model their behavior in the atmosphere, and evaluate their adverse impacts on human health and the environment. Of primary importance is the chemical composition of the aerosols, which provides valuable information on the respective influence of individual sources in areas where several of them are liable to be active simultaneously (Schmeling et al., 2000). The western and eastern basins of the Mediterranean Sea are good examples of such areas. Indeed, they are under the combined influences of natural and anthropogenic sources. Mineral dust and sea salt are known to contribute largely to the overall atmospheric particle load (e.g., El Metwally and Alfaro, 2013; Marconi et al., 2014), but particles released by human activities (road and maritime traffic, industry …) are also ubiquitous as confirmed by the most recent analyses of the AERONET sunphotometer measurements (Mallet et al., 2013; Masmoudi et al., 2015). The combusted fossil fuels, automobile and industrial emissions are the principal anthropogenic sources of most toxic elements found in, or downwind of; urban areas (Pacyna, 1998; Hien et al., 2001; Zereini et al., 2005; Hao et al., 2007; Querol et al., 2007). Among these elements, the metallic constituents of atmospheric aerosols have been paid special attention due to their serious effects on human health and the environment (Nriagu and Pacyna, 1988a, b; Pirrone et al., 1995; Guoshun et al., 2001). Unfortunately, for a given location, the distribution of trace elements in airborne particulate matter is quite variable in time and hard to predict. This distribution depends on a number of factors such as the activity of the sources, the chemical reactivity of the emitted species, and the efficiency of the transport/dispersion/removal processes … In particular, meteorological conditions changing with the seasons explain a large part of the variability of the concentration fields (Statheropoulos et al., 1998; Ragosta et al., 2002; Jonsson et al., 2004; Shaheen et al., 2005). Therefore, a dense grid of stations acquiring observational data on the composition of atmospheric aerosols is highly important to achieve a comprehensive understanding of the processes that drive their properties and behavior. In spite of recent efforts made to document the aerosol characteristics in the Mediterranean area, still little research has been dedicated to the characterization of the seasonal variability of elemental composition of atmospheric aerosols along the North African coast. The present study focused on central Tunisia aims at filling this gap at least in part. More

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precisely, the study was undertaken to assess the level and characterize the variability of the concentration of various elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb, V and As) involved in atmospheric aerosols collected on Kerkennah Islands. In a second stage, this elemental composition is used for apportioning the aerosol to its mineral dust (MD), sea salt (SS), and anthropogenic sulfate (NSS) components. Finally, the seasonal averages are compared and cases corresponding to concentration peaks of either MD, SS or NSS are detailed. The data presented in this study seeks to provide new insights on an ill-explored area of research in Tunisia and contribute new information to the worldwide composition inventory.

2. Material and methods

2.1. Experimental site

The research site (latitude North 34°41′, longitude East 11°10′) is located on the archipelago of Kerkennah, at the northern end of the Gulf of Gabes and 20 km east of the industrial city of Sfax (Fig. 1). It has a population of 14,400 inhabitants distributed in a dozen of villages but this population increases during holidays and weekends and up to tenfold during the spring and summer seasons with the seasonal return of emigrants from other large Tunisian towns (especially Sfax and Tunis) and European countries (France and Italy).

From the southwest to northeast, Kerkennah stretches over a length of about 35 km with a variable width (up to 11 km). It has a moderately dry climate and a flat relief. Its maximum altitude, recorded on an area of about 157 km^2, is only 13 m.

The region is ventilated and a suitable place to monitor aerosols either generated locally or transported from more or less distant marine or continental sources.

Road traffic, transit of ships at ports such as Sidi Youssef, agriculture, and the gas production unit (Petrofac Tunisia) located NNW of the experimental site are the main sources of anthropogenic aerosols on the island. When the wind blows from the west, the city of Sfax and its industries can also be significant contributors of anthropogenic aerosols.

2.2. Meteorology

Meteorological parameters, including air temperature, wind speed and direction and relative humidity, are available from the Meteorological National Institute of Tunisia. As expected, the climate of Kerkennah Islands is influenced by the presence of the sea. As compared to more continental locations in Tunisia, daily and annual temperature variations are relatively moderate. For the four periods of study (see their details below), Table 1 reports the averages and extremes of the temperature, wind speed, and relative humidity.

The average temperature decreases from 27.13 °C in summer; to 21.46 °C in autumn, 17.9 in spring, and 12.83 °C in winter. The minimum and maximum temperatures exhibit similar variations. With a mean value of 97%, relative humidity (RH) peaks during winter, which is also the period with the largest probability of rain occurrence. RH is substantially lower in autumn and summer (60% and 62%, respectively). This can be attributed to the temperature build up in this season, leading to larger water vapor saturation pressure in the atmosphere. The largest wind velocities normally prevail in winter, whereas comparatively lower wind velocities are recorded in spring, autumn, and particularly summer.

2.3. Sampling and analysis

In the course of a one year, a total of 50 aerosol samples were collected on Nuclepore (0.4 μm porosity) membranes (dozen sample per period). The bulk total filtration unit collected the particles for a duration of 48 hours. Four sampling campaigns lasting approximately two months and covering the four seasons of the year were performed in spring (April–May, 2010), summer (June–July, 2010), autumn (September–November 2010), and winter (February–March 2011).

After collection, the aerosol samples were analyzed using an energy dispersive spectrometer (X-ray Fluorescence EDXRF, energy-dispersive) PanAnalytical-Minipal-4 (Rh anode — 30 kV) multichannel analyzer (2048 c) which is a well established technique in qualitative and quantitative elemental analysis (Quisefit et al., 1996). The method is non-destructive, multi-element, and the measurement time is short. The thin-layer calibration method of Quisefit and Randrianarivony (1998) was applied to each element under investigation and the corresponding relative sensitivity was calculated to determine the spectrometer detection limit. For each element, this detection limit is determined using the following equation:

$$\text{Detection limit} = 3 * \left(\sqrt{\text{integral of blank filter}}/\text{sensitivity(photons/ng)}\right). \quad (1)$$

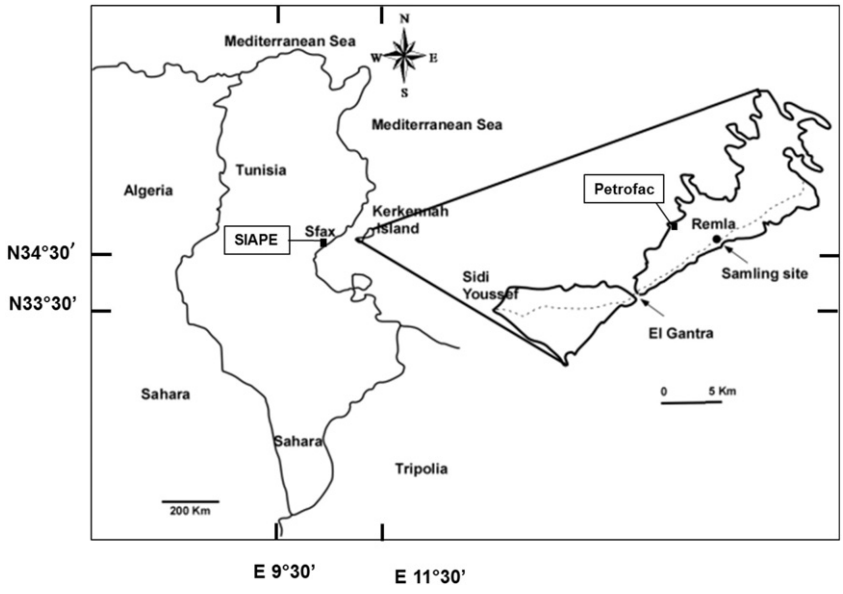

Fig. 1. Location of the sampling site.