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Compositional variability of the aerosols collected in Sfax (Central Tunisia)

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ABSTRACT

In order to assess the variability of the chemical composition of atmospheric aerosols in Central Tunisia and determine their origin, 140 aerosols samples were collected from March 2015 to April 2016 in the industrial city of Sfax. The particles collected on membranes were submitted to X-ray Fluorescence analysis and the concentrations of sixteen elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn and Pb) quantified. According to the values of their enrichment factors (EF) relative to the composition of the Earth crust and of sea-salt, these elements can be classified in three main categories: 1) crustal (Al, Si, Fe, Ca, Ti, Ni, P, and Mn), 2) marine (Na, Cl), and 3) anthropogenic (S, Zn, Cu, and Pb). Then, we apply the Positive Matrix Factorization (PMF) to the dataset in order to assess the profiles and contributions of the main sources of the aerosol. Beside the marine and anthropogenic factors, 3 other factors are necessary to represent the mineral dust component, which emphasizes the diversity of its sources. In usual conditions, the dominating factor (Ca-Dust) is enriched in both Ca and Mg, and is most probably emitted from regional sources. Its contribution to the atmospheric aerosol loading usually lies between 0.75 and 6.37μg/m^3(10th and 90th percentiles, respectively) but can peak at 9.28μg/m^3. The second factor, simply referred to as the Dust factor, corresponds to dust emitted by, and transported from, more distant desert sources. During the massive advection events, its contribution to the aerosol loading in Sfax can be above 100μg/m^3. Finally, the outdoor deposits of the residues of the local phosphate industry are an occasional source of P-enriched mineral dust (P-Dust) and some heavy metals (Cu, Ni, Zn, Pb). However, their contribution to the aerosol concentration is usually low (0.12–0.25μg/m^3) and does not seem to constitute an important source of contamination.

1. Introduction

Because of the importance of their environmental impacts, solid and liquid air-suspended particles (aerosols) have received increasing attention in the last decades. Aerosols alter the transfer of solar and terrestrial radiation through the atmosphere, and thus affect the Earth's climate at both the regional and global scales. Inhalable particles are also known to have adverse effects on human health (Dockery and Pope, 1994; Abbey et al., 1999; Yang et al., 2005). Therefore, they constitute a matter of concern for the decision makers and the residents of polluted areas. When several sources are active simultaneously, an accurate evaluation of the risk and of the efficiency of the measures adopted to mitigate it supposes that the individual influence of each of these sources has been quantified. This can be achieved by assessing the seasonal variability of the composition of the air-suspended particles and apportioning their concentrations between the potential sources (Schmeling et al., 2000). Enrichment factors (EF) are a useful tool for distinguishing the elements of natural origin from those produced by human activities (e.g., Duce et al., 1975; Ragosta et al., 2008). More recently, mathematical approaches called receptor models have also been developed for assessing the contributions of different potential sources to samples collected at one, or several, sampling sites. Among these methods, one can mention the Principal Component Analysis (PCA) and the Positive Matrix Factorization (PMF). Their advantage is that they provide source profiles from which elemental ratios can be quantified for each resolved source without making any a priori assumption on the composition of these sources. Therefore, combining EF and multivariate analysis is becoming a reference method for the apportionment of air-suspended particular matter (PM) in strongly polluted areas (e.g., Johnson et al., 2006; Sun et al., 2013) as well as in remote ones (Xu et al., 2013; Kang et al., 2016; Tripathee et al., 2017). Unfortunately, this type of method has never been applied so far for the characterization of the aerosol along the North

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African coast of the Mediterranean Sea, a region known to be not only under the influence of local anthropogenic and natural (mineral dust and marine) sources but also at the crossroads of the polluted air-masses coming from Europe and the dust-laden ones coming from the Sahara (Mallet et al., 2016).

In the present work, we first use X-ray fluorescence analysis to determine the elemental composition of 140 daily aerosol samples collected in the industrial city of Sfax (central Tunisia). In a second step, we combine the information drawn from the EF analysis with the results of the PMF to identify the sources active in the area or upwind of it and determine their relative contributions to the overall aerosol loading. Lastly, in order to determine to which extent the conclusions drawn from this study apply at a much larger (regional) spatial scale, these results are compared with those of other measurements performed on the Island of Lampedusa (Marconi et al., 2014) and on the Kerkennah archipelago (Trabelsi et al., 2015). The locations of these two sites are reported on Fig. 1.

2. Material and methods

2.1. Experimental site

The sampling site (lat.: 34.73°N; long.: 10.72°E; alt.: 20 masl) is located on the roof of the Physics Department of the Faculty of Sciences, in the southwestern part of the city of Sfax and 4 km from the seafront. Sfax is the second largest city of Tunisia (pop: 955000). This is an active harbor on the Mediterranean Sea and an important industrial center. The principal industrial activities include phosphate transformation (SIAPE. See Fig. 1), a lead foundry, and agro-industry (SIOS-ZITEX, SATHOP). These industries are located in the coastal area and just a few kilometers away from the town center. At least the first two are known to release heavy metals (Ni, Cu, Zn, Pb, etc.) in the atmosphere (Azri et al., 2000).

2.2. Sampling program

In order to assess the variability of the aerosol's concentration and composition, samples were collected on 47 mm polycarbonate membranes (Nuclepore, Whatman ™) with pore sizes of 0.4 μm. The sampling was performed for 24 h - from 8:00 a.m. of one day to the same hour of the following day- and at a flow rate of 1 m^3/h controlled with a gas counter. However, the pumping was active only for the first 15 min of each hour, which means that it was only active for 6 h in each 24 h-period. This sequential procedure was adopted to 1) collect particles representative of the diurnal variability of the aerosol composition, and 2) avoid collecting a mass of particles too elevated for a correct XRF analysis. From March 2015 to April 2016, five sampling campaigns were organized to cover the different seasons of the period of study. In all, 140 aerosol samples were collected.

2.3. XRF analysis

After collection, the samples were analyzed by wavelength-dispersive X-ray fluorescence (WD-XRF) with a PW-2404 (Panalytical) spectrometer in which the primary X-rays are produced by a Coolidge tube ($I_{max} = 125$ mA, $V_{max} = 60$ kV) with a Rh anode. Wavelength dispersive X-ray fluorescence is a classical technique in qualitative and quantitative elemental analysis and a version was developed specifically to analyze aerosol samples collected on membranes (Quisefit et al., 1996). In this method, the membranes are introduced in the spectrometer without any further preparation and each element is analyzed three times in vacuum for 8–10s.The method is non-destructive, multi elemental, and the measurement time is short. The results of the analyses were corrected for blank membrane counts.

In order to achieve an accurate quantification of the mass of each of the detected elements, the surface concentration of the particles deposited on the membranes must not exceed 200 μg cm^{-2}. This corresponds to an approximate total mass of 1000 μg on a membrane. For each element,

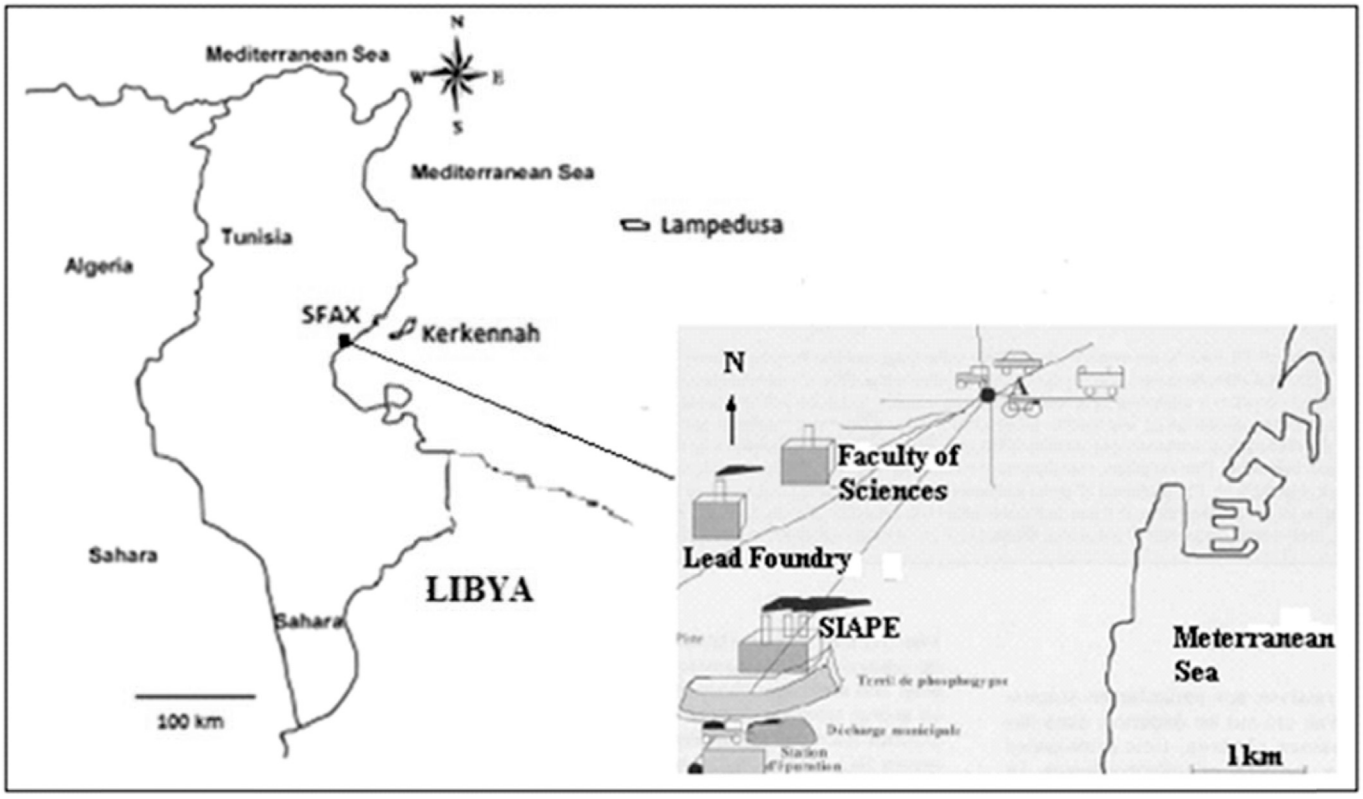

Fig. 1. Location of the city of Sfax, and of the Kerkennah and Lampedusa Islands.