

Available at www.scientevents.com/proscience/





Conference Proceedings 1<sup>st</sup> International Conference on Atmospheric Dust - DUST2014

# An integrated approach to characterize long-range transported dust

Giulia Pavese<sup>1\*</sup>, Antonio Lettino<sup>1</sup>, Mariarosaria Calvello<sup>1,2</sup>, Francesco Esposito<sup>3</sup>, Saverio Fiore<sup>1</sup>

<sup>1</sup>Istituto di Metodologie per l'Analisi Ambientale - CNR, Tito Scalo, 85050, Italy <sup>2</sup>OAVDA, Marsico Nuovo, 85052, Italy <sup>3</sup>Scuola di Ingegneria-Università della Basilicata, Potenza, 85100, Italy

## Abstract

An integrated approach, combining columnar and in-situ measurements was used to characterize optical and micro-physical properties of atmospheric aerosols under the advection of Saharan dust airmasses in a site in South Italy. Background and dust-affected radiometric measurements were compared to study their radiative properties. Starting from these radiometric measurements, a source identification technique based on the aerosol components from OPAC (Optical Properties of Aerosols and Clouds) model revealed that mineral dust, soot, water soluble, sea-salt accumulation and sea-salt coarse contribute in a similar way to the solar radiation attenuation. SEM analysis on atmospheric particulate collected at the ground pointed out that crustal elements characterize particles on both fine and coarse stages. Dust particles embedded in soot chains and traces of industrial particles were also detected.

Keywords: Radiometer, source identification, SEM analysis.

## 1. Introduction

Atmospheric aerosols are one of the most important atmospheric constituents because of their potential impact on climate change and human health. From the climatological point of view, they affect radiative properties of both clouds and atmosphere, generally contributing to the "cooling effect" but sometimes, as for carbonaceous particles, to the "warming effect". On the other hand, they may impact on air quality, causing both respiratory and cardiovascular diseases, even for short exposure periods (Vedal et al.,

ISSN: 2283-5954 © 2014 The Authors. Published by Digilabs

<sup>\*</sup>Corresponding Author: giulia.pavese@imaa.cnr.it

Selection and peer-review under responsibility of DUST2014 Scientific Committee DOI:10.14644/dust.2014.030

2009). These effects strongly depend on aerosols chemical composition that can vary according to the air masses mixing during long-range transport phenomena.

Recently, studying Saharan dust intrusion at GAW observatory in Tenerife (Canarian Islands, Spain), Rodriguez et al. (2011) found at the ground mineral particles often mixed with anthropogenic particles emitted by factories (crude oil refineries, power plants, etc.) located along the Northern coast of Africa.

Marconi et al. (2014), from radiometric and ground-based PM10 measurements in Lampedusa island, found in many cases that the dust plume transport occurred above the marine boundary layer.

This study aims to characterize, by an integrated approach, optical, physical, morphological and chemical properties of mineral dust collected in a site in South Italy, and to highlight the variations of atmospheric particulate properties due to the long-range transport. To this purpose, radiometric measurements over the atmospheric column, gravimetric measurements at the ground and HYSPLIT back-trajectories were used to identify days with different particles contents. Poor aerosol loading corresponds to "background" measurements, while high aerosol loading with prevailing large particles, corresponds to desert dust advection. A technique applied to the radiometric data allows the identification of the main aerosol components (Water Soluble, Soot, Sea-Salt Accumulation, Sea-Salt Coarse and Mineral Dust) contributing to the solar radiation attenuation over the atmospheric column. Morphological and chemical characterizations of particulate collected on polycarbonate filters were performed by a SEM-EDX analysis.

Under dust intrusion, preliminary results indicate that crustal elements (aluminosilicates) are already present in finer stages, whereas mineral particles captured in soot chains and traces of industrial particles can be observed in coarse stages. Over the atmospheric column, Saharan air masses are characterized by a quite similar contribution from the five main aerosol components of the OPAC model.

### 2. Measurements site, instruments and methods

Radiometric and gravimetric measurements were collected at the Institute of Methodologies for the Environmental Analysis (40.60° N, 15.72° E, 750 m a.s.l.), in Southern Italy, in a rural area with some factory and private houses. A highway is far 1 km from the sampling site. A continental climate characterizes the site, with sunny days, needed for radiometric measurements, more frequent during spring-summer seasons.

Two instruments for optical and microphysics aerosol properties measurements were used: a wide-range and high-resolution radiometer and a 13-stages impactor. Radiometric measurements were collected, in cloudless conditions, every 15 minutes which is the recording frequency of aerosol optical depth (AOD), Ångström turbidity parameters and aerosol number and volume size distributions, as described in Esposito et al. (2004).

Gravimetric mass distributions (0.03  $\mu$ m – 10  $\mu$ m) were obtained after a 24 h exposure period of polycarbonate filters. The full procedure is described in Calvello et al. (2010). For this study, radiometric and gravimetric measurements have been considered for the period May 2008 – February 2011.

Morphological and chemical analyses were performed by means of a field emission scanning electron microscope equipped with an energy-dispersive X-ray spectrometer.

Samples were carbon-coated and the presence of carbon and oxygen in the polycarbonate filters did not allow to consider elements with Z < 10.

A technique proposed by Satheesh & Srinivasan (2005) to discriminate between absorbing and non-absorbing particles was applied to estimate the main aerosol components contributing to the columnar AOD. To this aim, the five aerosol types used in the OPAC (Optical Properties of Aerosol and Clouds) model by Hess et al. (1998), that is water soluble (WS), soot (S), sea salt coarse mode (SS<sub>coa</sub>), sea salt accumulation mode (SS<sub>acc</sub>) and mineral dust (MD), were considered, each of them characterized by specific physical and optical parameters. A best-fit technique was applied by minimising the following quantity:

$$\chi^2 = \sum_{i=1}^{N} \frac{(\tau_i^{meas} - \tau_i^{comp})^2}{(\Delta \tau_i^{meas})^2}$$

where  $\tau_i^{meas} \tau_i^{comp}$  are, respectively, the measured and computed AOD at the i-th wavelength, obtaining the weight parameters of each component.

#### 3. Data analysis

The scatter-plot  $AOD_{780}$  vs. alpha parameter is shown in Fig. 1 for measurements corresponding both to background (low aerosol loading, small aerosol size) and dust (high aerosol loading, large aerosol size) data.



Fig. 1. Scatter-plot AOD780 vs alpha parameter.

Low alpha values of dust data highlights prevailing large particles, unlike background data characterised by higher alpha values. A small area containing both background and dust data suggests the presence of dust particles also in background conditions, probably due to up-lifting of local winds.



Fig. 2. Percentages of the five aerosol components to the total AOD for background (a) and dust (b) conditions.

The percentages of the five OPAC aerosol components to the total  $AOD_{500}$  are shown in Fig. 2 a-b. Background conditions are characterized by major contributions of WS and Soot and a minor dust component. Mineral dust conditions are characterized, instead, by a quite uniform contribution of all the five atmospheric components. In this case, sea-salts presence can be explained by the air-masses pathways: starting from North-Africa regions, they cross Mediterranean Sea before the arrival at the measurements site, whereas anthropic aerosols could come from oil refineries and plants located in the coastal area of Northern Africa as in Rodriguez et al. (2011).

#### 3. Ground-based size distributions and SEM analysis

The size distributions from impactor sampling in background and dust days are reported in Fig. 3a-b. Differences between the two cases are evident: in background case, the fine mode is centred around 0.4  $\mu$ m and it is dominant over the coarse one. Under dust intrusion the coarse mode is always the highest. An ultrafine (0.05  $\mu$ m) mode is found for background and dust day, probably related to locally produced aerosols.



Fig. 3. Mass size distributions obtained for background (a) and dust (b) conditions.

By analysing the mineralogical and morphological characteristics of particles collected on the fine fraction (EAD <0.94  $\mu$ m) of background samples, FESEM observations revealed a large number of metal particles (Fig. 4a) with prevailing Fe-composition enclosed in a rich K and S amorphous matter.



Fig. 4. SEM images of background fine and coarse particles (a,b) and dust fine and coarse particles (c,d).

This indicates both industrial and biomass burning origins. The background coarse fraction (1.58  $\mu$ m -3.93  $\mu$ m) is characterized by high amounts of carbonate particles (40%), silicates (25%) and soot (11%). A remarkable contribution of industrial spherical particles characterized, in turn, by Fe, Al, Mn, Pb, and Zn was detected. The abundant carbonatic particles, in disagreement with the geology and soil of the site, suggests a local anthropic source. X-ray microanalysis revealed also a small Zn peak in aluminosilicate with morphology and composition referable to smectites. Large soot agglomerates (Fig. 4b) come from re-growth processes on the substrate favoured by relative humidity (Wentzel et al., 2003).



Fig. 5. Percentages of the coarse fraction composition for background (left) and dust (right) particles.

An amorphous material, with nitrates as the main components of the dust finer stages (EAD < 0.16  $\mu$ m), characterizes this fraction, It encloses crustal elements (Si, Al) and gypsum (S-Ca). Fine stages (0.5  $\mu$ m - 1  $\mu$ m) are characterized by sulphates in the amorphous matter and soot chains closely associated to dust particles (Fig. 4c). Most of silicate particles in the coarse fraction appear as single flake-like particles (Fig. 4d) constituted by Si-Al-K-Fe or Si-Al-Ca-Fe-Mg which can be referred to clay minerals (illite

or smectite). Sometime silicates form aggregates plate crystals that can be identified as kaolinite (Caggiano et al., 2011). Carbonate particles are mostly calcite whereas sea-salt particles are both aged and fresh represented, respectively, by sodium nitrate (higher percentage) and NaCl (lower percentage). The air mass pathway moving from North-Africa across the Mediterranean Sea explain these findings. Elongated gypsum crystals can be found in an internally mixed state with clay, or with carbonatic particles not completely transformed. They can be formed by heterogeneous chemical reactions involving atmospheric S-compounds and carbonatic particles. Sulphur deposition on dust particles could derive from sea droplets or from anthropic activities (Lettino & Fiore, 2013). However, soot aggregates externally mixed with dust particles and sulphates support the second hypothesis. The dust coarse fraction composition is marked by a high content of silicate (52%), carbonates (13%), and seawater (13%) particles, with minor amounts of Casulphates, quartz, soot and traces of industrial particles. In Fig. 5 the main groups forming the collected particles are reported. As for columnar data, background composition is dominated by anthropic particles, whereas dust composition is dominated by mineral dust and sea-salt aerosols.

#### 5. Acknowledgements

This study was partially financially supported by the Associazione Italiana per lo Studio delle Argille - onlus.

#### References

- Caggiano R., Fiore S., Lettino A., Macchiato M., Sabia S., Trippetta S. (2011). PM2.5 measurements in a Mediterranean site: two typical cases. *Atmospheric Research*, 102, 157–166.
- Calvello M., Esposito F., Pavese G., Serio C. (2010). Physical and optical properties of atmospheric aerosol by insitu and radiometric measurements, *Atmospheric Chemistry and Physics*, 10, 2195-2208.
- Esposito F., Leone L., Pavese G., Restieri R., Serio C. (2004). Seasonal variation of aerosols properties in South Italy: a study on aerosol optical depths Ångström turbidity parameters and aerosol size distributions *Atmospheric Environment*, 38, 11, 1605-1614.
- Hess M., Koepke P., Schult I. (1998). Optical properties of aerosols and clouds: The software package OPAC. Bulletin of American Meteorological Society, 79, 831–844.
- Lettino A., Fiore S. (2013). Provenance of inorganic aerosol using single-particle analysis: A case study. *Science of the Total Environment* 463-464, 404–413.
- Marconi M., Sferlazzo D.M., Becagli S., Bommarito C., Calzolai G., Chiari M., di Sarra A., Ghedini C., Gómez-Amo J.L., Lucarelli F., Meloni D., Monteleone F., Nava S., Pace G., Piacentino S., Rugi F., Severi M., Traversi R., Udisti R. (2014). Saharan dust aerosol over the central Mediterranean Sea: PM10 chemical composition and concentration versus optical columnar measurements. *Atmospheric Chemistry and Physics*, 14, 2039–2054.
- Rodríguez S., Alastuey A., Alonso-Pérez S., Querol X., Cuevas E., Abreu-Afonso J., Viana M., Pérez N., Pandolfi M., de la Rosa J. (2011). Transport of desert dust mixed with North 15 African industrial pollutants in the subtropical Saharan Air Layer. *Atmospheric Chemistry and Physics*, 11, 6663–6685.
- Satheesh S.K., Srinivasan, J. (2006). A method to estimate aerosol tadiative forcing from Spectral Optical Depths, Journal of Atmospheric Science, 63, 1082-1092.
- Vedal S., Hannigan M.P., Dutton S.J., Miller S.L., Milford J.B., Rabinovitch N., Kim N.S.-Y., Sheppard L (2009). The Denver Aerosol Sources and Health (DASH) study: Overview and early findings. *Atmospheric Environment*, 43, pp 1666–1673.
- Wentzel M., Gorzawski H., Naumann K.H., Saathoff H., Weinbruch S. (2003). Transmission electron microscopical and aerosol dynamical characterization of soot aerosols. *Journal of Aerosol Science*, 34 (10), pp 1347-1370.