PHYSICAL/CHEMICAL CHARACTERIZATION OF TRANS-ATLANTIC AIRBORNE SAHARAN DUST DURING THE AEROSOL AND OCEAN SCIENCE EXPEDITIONS (AEROSE)

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1. Introduction

Transatlantic dust outbreaks emanating from North Africa and their seasonal frequency of outflow across the North Atlantic Ocean have been associated with perturbation processes in the atmosphere (Jeong and Sokolik, 2007), climatic forcing (Haywood and Boucher, 2000), and a variety of health risk factors (Prospero, 2004). The microphysical evolution of these particles from source region depends on air mass pathways and mixing with reactive gas phase species during long distant transport. These processes change the chemistry of the troposphere, and have strong influences on radiative transfer and ensemble optical properties (Otto et al. 2007).

Studies performed over the past few years (Bernadett et al. 2009; Kaaden et al. 2009) have clearly established that dust properties represent one of the greatest uncertainties in both measurement and modeling efforts. As shown by an earlier study (Sokolik et al. 2001), an effective approach in understanding the impact of Saharan dust is to study the size dependent evolution potentials, the surface chemistry, and the microphysical properties of dust plume. The Howard University NOAA Center for Atmospheric Sciences (NCAS) under the framework of the trans-Atlantic AERosols and Ocean Science Expeditions (AEROSE) have conducted a nearly annual interdisciplinary ship-based aerosol field campaigns between 2004 and 2010 with a unique objective of generating a comprehensive data set of complementary atmospheric measurement and Oceanographic observations aimed at characterizing the impact and microphysical evolution of Saharan dust aerosols transported across the Atlantic Ocean (Morris et al. 2006; Nalli et al. 2011, Jimenez et al. 2009).

This study examines the physicochemical characterization and trend in major dust outbreaks of the AEROSE samples obtained during the month of July during the 2006 and 2009 campaigns,. This data set is examined for the purpose of gaining insights on the microphysical evolution of mineral dust during transport across the tropical North Atlantic.

2. Methodology

2.1 AEROSE Research vessel and Sampling

The NOAA research vessel, Ronald H. Brown provided the main sampling

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platform for the AEROSE samples during the transects across the tropical Atlantic Ocean. The instruments were located at the second level of the ship trajectory at 18m high above the sea level and several other instruments were used to study the temporal evolution of the desert dust plume which arrived from the African continent. The cruise tracks were planned on the basis of an aerosol and wind climatology based on aerosol optical depths (AOD) derived from the NOAA Pathfinder Atmospheres Extended (PATMOS-x) dataset, and other satellite and reanalysis products. The Advanced Very High Resolution Radiometer (AVHRR) AOD images shown in figure 1(b) are representative of the retrievals that aided in planning the tracks. AEROSE samples were obtained throughout the research cruise ship using two quartz crystal microbalance (QCM) cascade impactors (California Measurements Inc.). The QCM is used for in-situ mass density distribution monitoring and episodic sampling within the air masses transected.

A six-stage QCM with size bins of 0.15, 0.3, 0.6, 0.12, 2.5, and 5.0 microns and a standard flow rate of 1.5µm, was used for sampling dusty air masses due to the coarse sized particles of dust; while a ten-stage QCM with size bins of 0.05, 0.1, 0.2 0.3, 0.5, 1.0, 2.0, 3.0, 5.4, and 10.0 microns and a standard flow rate of 2.0µm, was used for biomass-burning air masses in order to resolve the size distribution of finer particulate matter that is typical of smoke and other fine mode aerosols. Samples were collected on different days as the dust plume interactions lasted from six to forty-eight hours. Sampling was halted when either the ship was stationary or the smoke stack of the ship moved towards the direction of the sampling instrument to avoid contamination of the data. Upon sampling, the QCM electrodes were extracted, labeled, and stored in a dry encasement at ambient temperature until transferred to the laboratory for physical and chemical analysis. Figure 1(a) shows the cruise track for 2006 and 2009.

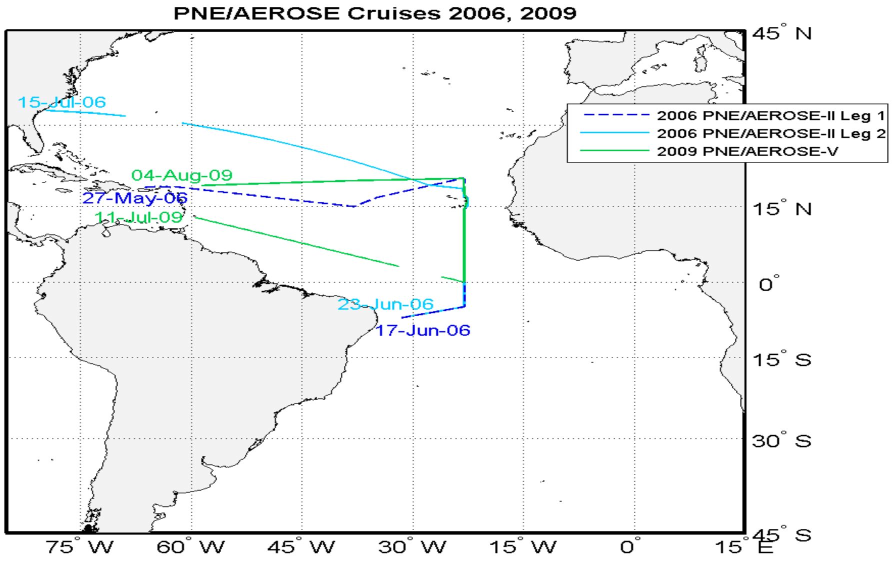


Figure 1(a): AEROSE cruise track for 2006 and 2009.

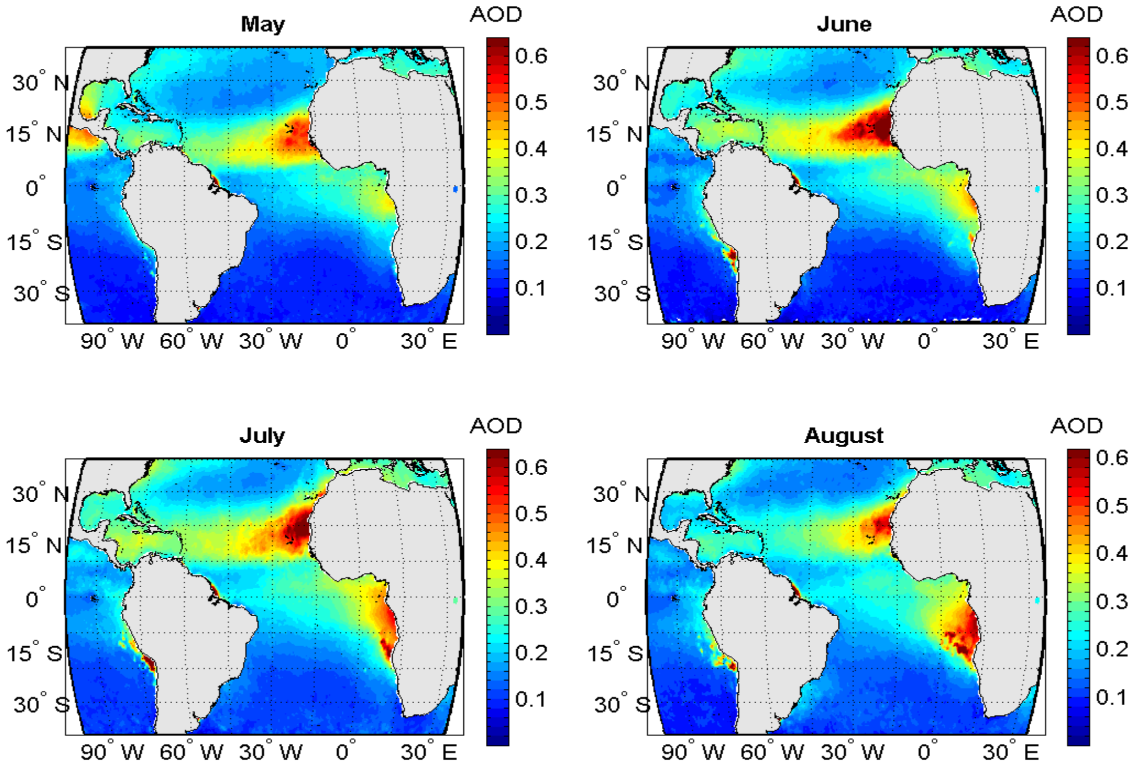


Figure 1(b): AVHRR PATMOS-x Mean AOD 1981-2008 climatology for May-August excluding volcanic eruptions.

2.2 Instrumental analysis

Comprehensive single particle analysis, detailed morphological characteristics, and the element distribution (all elements with Z ≥6) within individual aerosol particles with a Si (Li) detector were performed using the JEOL Oxford JSM 6360-LV Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray (EDX) microanalysis system. The SEM was operated at an electron accelerated voltage of 20Kv, a working distance of approximately 10mm, a spot size of 50µm, and a magnification of X400. Instrument quantization was performed using titanium metal mounted alongside the sample on the sample holder. Automated particle analysis was performed using the secondary electron signal, and the images were obtained without coating.

For all analyzed samples, a mean value for six (6) blank measurements was applied to cancel out the contribution of the sampling substrate. The statistical parameters for the measured elemental composition were computed manually.

3. Results and discussion

3.1 Morphology of the AEROSE samples

Figure 2 shows the morphology of the AEROSE samples for July 2006 (**a**) and 2009 (**b**).

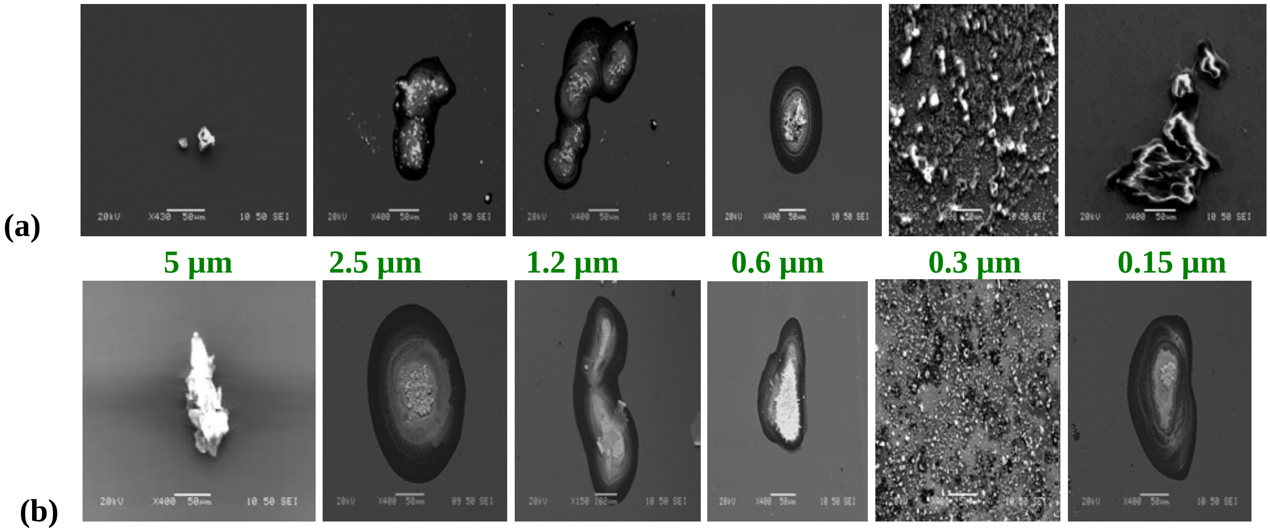


Figure 2a and b: Representative SEM images of the 2006 and 2009 AEROSE samples obtained without coating.

Some of the images (0.6µm size cut for 2006 and 2009) show an agglomeration of particles at the center of the crystal. This is typical of samples collected during high density events that subsequently undergo hygroscopic growth on the QCM substrate. Other samples (2.5µm and 0.15µm for 2009) exhibit a pooling and etching of the electrode from a central impaction, indicating the acidic nature of the new compound formed. The secondary electron images revealed a variety of morphologies dominated by chain-like associations of spherules, flakes, and non-spherical particles. Contrary to the assumption of Barnabas and Gobbi (2001) that dust-like aerosols cannot be assumed to be spherical, SEM results from this study indicate that some of the particles in the July 2006 AEROSE samples assume a spherical shape, and this is consistent with related studies by Iwasaka et al. (2003) that externally mixed aerosols have anthropogenic origin and show different hygroscopic characteristics for a given size, and that carbon is associated with less hygroscopic particles; the more hygroscopic particles containing sulfates, nitrates, oxygen, and sometimes sodium and potassium. Furthermore, Laskin et al. (2005) reported that acidification of mineral dust by nitric acid may lead to a significant uptake of water and thus to an increase in size and a change in shape. The observed variation in shape could also be ascribed to the uptake of moisture by the high-affinity-for-water species present in the AEROSE samples. The most probable explanation at this time is that changes in the surface mixing state of the mineral dust aerosols during long distant transport has led to the observed behavior and different source region characteristics of dust particles. The morphology of July 2006 samples differ from those of July 2009 especially in the 5.0 µm size fraction, where the former appears as a solid non-spherical pebble, and the latter a flaky white longitudinal substance which gradually evolve and presents a surface for chemical reaction.

3.2 Single particle chemical composition

Results from a size resolved single particle analysis of the AEROSE samples are presented in figure (3). Measurements of the atmospheric aerosol size distributions are essential in identifying the various processes involved in the formation and evolution of atmospheric aerosols. As one might expect, there are significant differences in the chemical composition between the July 2006 and July 2009 samples that reflect differences in geology, meteorology, and weathering processes. The chemical composition of the AEROSE samples showed a strong dependence on particle size. In addition, the chemical composition allows us to recognize that the collected dust contains significant amount of silicon, oxygen, carbon, and sulfur for the July 2006 samples; the dominance of SiO_2 probably reflecting the importance of quartz in aeolian dust.

Elemental analyses of the 2006 samples collected during air masses dominated by biomass burning and by Saharan dust encountered in the tropical Atlantic shows the presence of crustal elements and elements associated with biomass burning and anthropogenic activities as a function of size and atomic percent.

These data afford an interpretation of the surface chemical processing and mixing state during long range transport. The presence of Pb, Cd, Ni, and S in the aerosol samples was interpreted as indicators of the anthropogenic fraction, while Fe and K represent a potential source of nutrient to the Mediterranean water. Silicon was used as the primary crustal indicator. Results for July 2006 indicate that the mean Ca/Si ratio varies from 0.02 to 0.05 percent as the size cut decreases from 5 to 0.15 microns. On the other hand, the Al/Si ratio decreases from 0.16 to 0.09 percent, and the Mg/Si ratio from 0.23 to 0.35 percent. This can be used as indicators of dust source region. We also observed a reverse trend in the crustal indicator ratio for some samples examined for this period, which vary according to density distribution, intrusion days, and the sampling geographical latitude and longitude. In addition, figure 3a shows that the distribution of carbon increases as the size cut decreases, and has a maximum mean percentage at the 0.3µm size cut. This is due to the vicinity of source as indicated in the firemap, as well as differences in vertical exchange in the atmosphere. As a highly dynamic system, carbonaceous aerosols are known to evolve by becoming increasingly oxidized, less volatile, and more hygroscopic; leading to the formation of oxygenated organic aerosols. This oxidation process promotes partly the conversion of gaseous sulfur compounds into acidic species and partly the wet removal of elemental carbon from the air (Jimenez et al. 2009). In order to estimate forcing, the highly aged aerosols are characterized by their high oxygen content in relation to carbon.

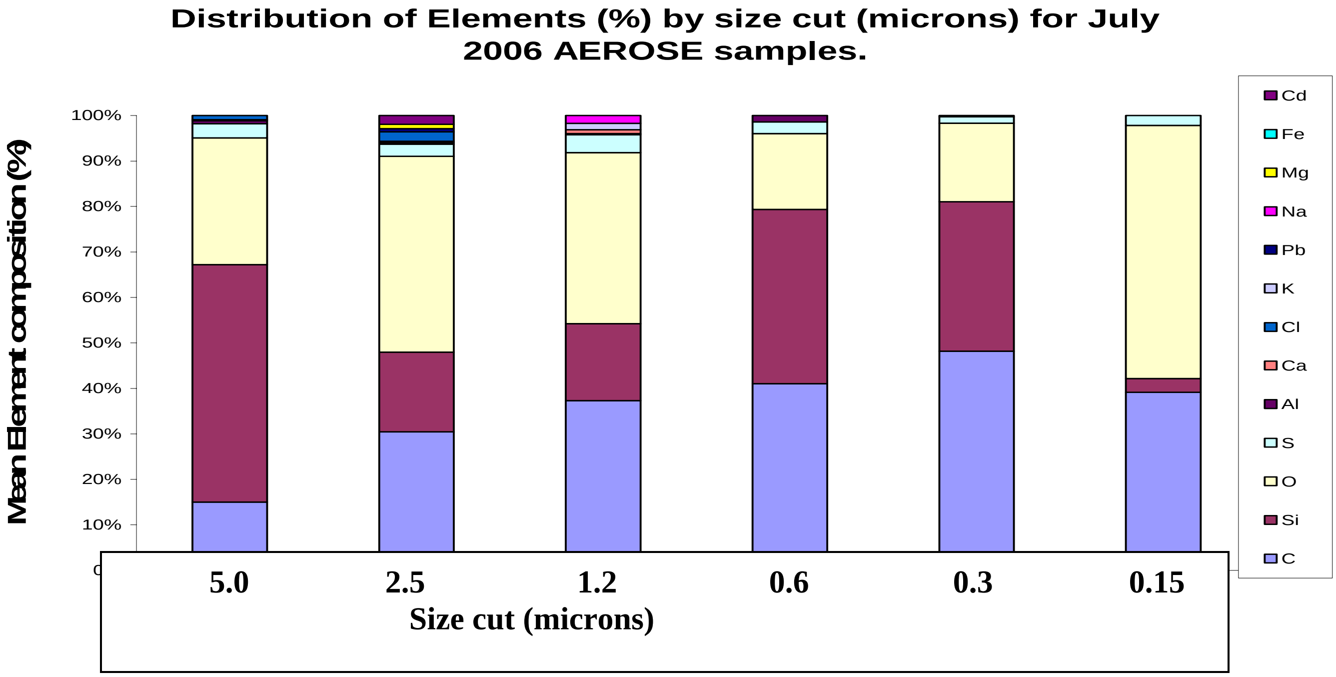


Figure 3(a): Element composition of the 2006 AEROSE samples

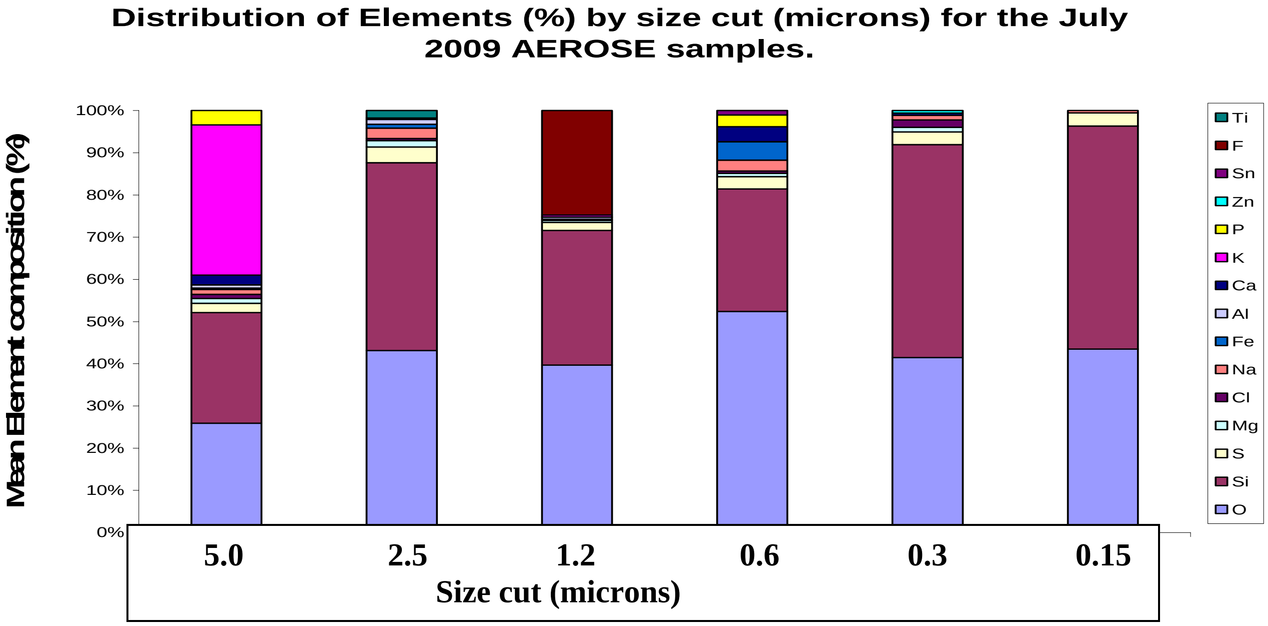


Figure (3b): Element composition of the 2009 AEROSE samples.

The AEROSE data set gives an atomic O: C ratio of 0.5 to 1.3 suggesting highly aged organic aerosols, excepting the 0.15µm size cut which is 2.2 (Jimenez et al. 2009).

Analyses of the AEROSE samples obtained in July 2009 revealed crustal elements from Saharan air mass dominated by Al, Si, Ti, Na, Cl, O, P, Mg, Ca, Fe, and S. The mean Al/Si ratio varies from 0.3 to 0.43 percent. The mean atomic percent of Titanium was very low which agrees with results from previous studies (Reid et al. 2003).

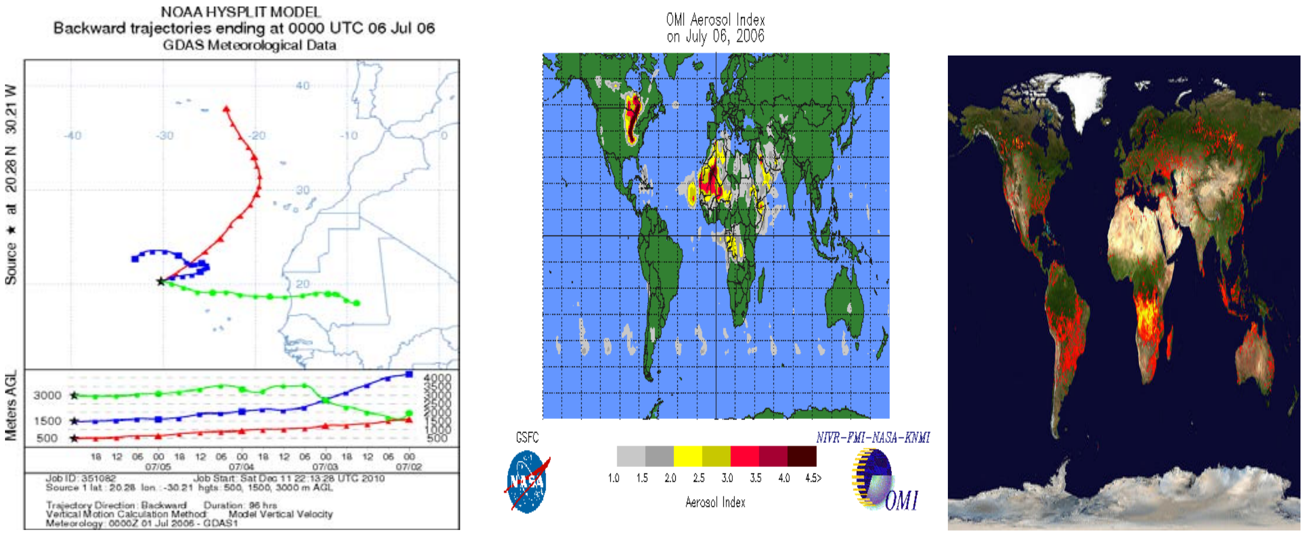
3.3 Source region

The drive for source region identification still remains paramount in understanding dust production, and hysplit back trajectory analysis is a primary tool used to determine the origin of air masses (Draxler and Rolph, 2003; Stohl, 1998).

Back trajectory analysis, the Ozone Monitoring Instrument (OMI) product, and the Modis firemap product for 6 July 2006 and 27 July 2009 which were days of major dust storm event, are shown in figure 4 (a), (b), and (c). The back trajectories for July 2006 reveal a general outflow of air masses from Mauritania, Senegal, and a weak outflow from Algeria – Mali border for samples obtained on five (5) consecutive days. The source regions identified by the OMI satellite appear to be geographically consistent with the hysplit back trajectory model and show the distribution and intensity of UV absorbing aerosols around the implied source area. The four day analytical trajectory with arrival heights of 3000, 1500, and 500 meters AGL points to the fact that the air masses were intercepted during July 2006. The justification for these heights is to enable the identification of pollutants which are conveyed by air parcels near ground level (≤ 500m) and those that may be associated with long-range transport, and rich in mineral dust (≥ 3000m). The wind direction which is a controlling meteorological factor could possibly have influenced the east bound continental trades, thus resulting in a mixing with the combustion sources that is expectedly moving northwards as shown in the MODIS firemap product for July 2006. This strongly correlates with the chemical composition of the July 2006 AEROSE samples which are predominantly dust-urban plume regime

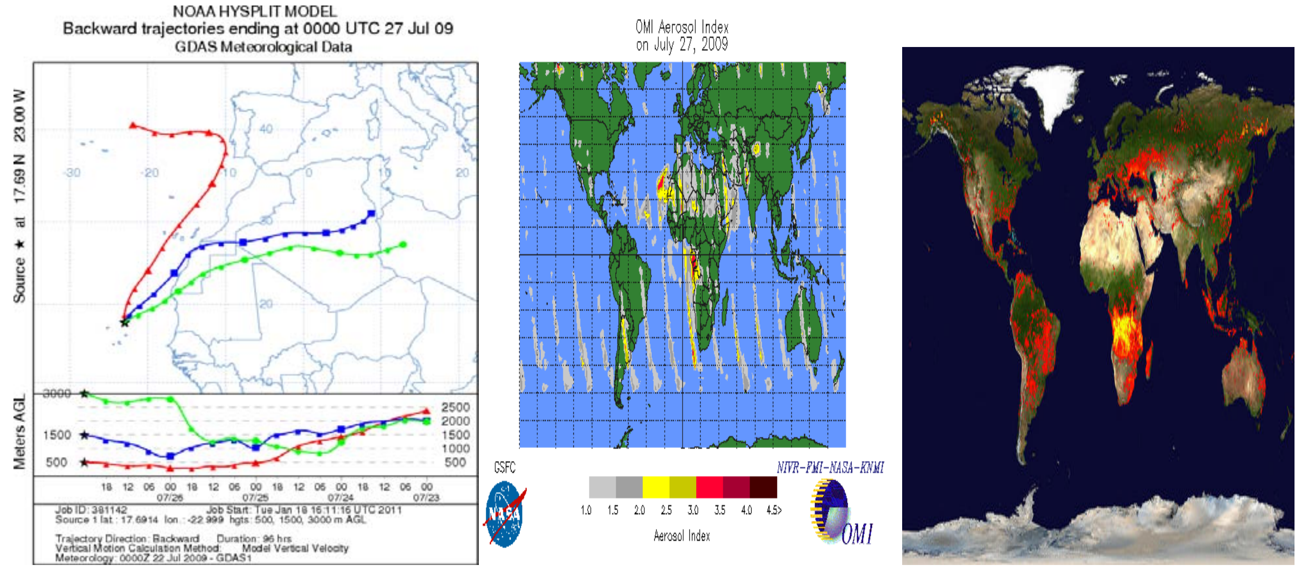
The elemental composition and the morphology of the particles vary from those of the 2009 samples and are characterized by a detailed inventory of anthropogenic emissions of biomass burning due to the vicinity of source. However, in July 2009, the direction of the air flow was northwest; the hysplit and OMI pointing to Libya as the source region. This also is in accordance with the observed physical and chemical characteristics pertaining to this source region, and the surface mixing state of the mineral dust during long distant transport.

(a)



Back trajectory July 2006 OMI July 2006 Modis Firemap July 2006

(b)



Back trajectory July 2009 OMI July 2009 Modis Firemap July 2009

Figure 4(a) and (b): Back trajectory, OMI, and Firemap for July 2006 and July 2009.

4. Summary and Future Studies

African dust events, routinely observed annually, are large scale phenomena that have significant environmental effects that depend on their physical and chemical properties, such as chemical composition, size, and water solubility. In the remote tropical Atlantic Ocean, the AEROSE cruises have measured the physical and chemical properties of Saharan dust aerosol between July 2006 and July 2009. The following conclusions were obtained from the study:

1. The transport of dust across the Atlantic is the homogenized product of a long chain of geological, weathering, and meteorological processes. A good consistency between the results of the various measurements is observed for the 2006 samples which are basically dust – urban plume regime and the 2009 samples which are predominantly dust.

2. Back trajectory analyses and the OMI aerosol product indicate central Mauritania as the source region for the main outflow of air masses for July 2006 and Libya in 2009. In addition, a weak outflow from Senegal and Algeria – Mali border were also observed.

3. The future thrust of this study will extend the chemical analysis of more samples from 2006 and 2009 and include micro Raman Spectroscopy and Power X-ray Diffraction analyses in order to give a robust view of the functional groups and mineralogy present in the AEROSE samples.

We believe that the data set as presented in this study will contribute to the understanding of the physical and chemical processes governing the evolution and transport of Saharan dust from the African continent as it crosses the North Atlantic Ocean.

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