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Aerosol time-series measurements over the tropical Northeast Atlantic Ocean: Dust sources, elemental composition and mineralogy

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ABSTRACT

The North Atlantic receives the largest dust loading of any of the world's oceans due to its proximity to North African deserts and prevailing wind patterns. The supply of biologically important trace elements and nutrients via aerosols has an important influence on biogeochemical processes and ecosystems in this ocean region. In this study we continuously sampled aerosols between July 2007 and July 2008 at the Cape Verde Atmospheric Observatory (CVAO), which is situated on an island group close to the North African continent and under the Saharan/Sahelian dust outflow path. The aim of our work was to investigate temporal variations in aerosol concentration, composition and sources in the Cape Verde region over a complete seasonal cycle, and for this purpose we undertook mineralogical and chemical (42 elements) analyses of the aerosol samples and air mass back-trajectory calculations. Aerosol samples were also collected during a research cruise in the (sub-) tropical Northeast Atlantic Ocean in January 2008. The concentration of atmospheric Al, a proxy for mineral aerosol concentration, at CVAO was in the range of 0.01–66.9 μg m^{-3} (maximum on 28–30 January 2008) with a geometric mean of 0.76 μg m^{-3}. It showed distinct seasonal variations, with enhanced Al concentrations in winter (geometric mean 1.3 μg m^{-3}), and lower concentrations in summer (geometric mean 0.48 μg m^{-3}). These observations have been attributed to dust transport occurring in higher altitude air layers and mainly north of the Cape Verde during summer, while in winter the dust transport shifts south and occurs in the lower altitude trade winds with consequent greater influence on the Cape Verde region. The elemental composition of the aerosols closely agreed with mean upper crustal abundances, with the exception of elements with pronounced anthropogenic sources (e.g. Zn and Pb) and major constituents of sea water (Na and Mg). Mineral analysis showed that clays were the most abundant mineral fraction throughout the whole sampling period, with an increase in quartz and clays during strong dust events and an associated decrease in calcite. This could have important implications for the estimation of release of for example Fe from mineral dust with clays having a higher Fe solubility than quartz.

The elemental composition and mineralogy of aerosol samples collected during the cruise were indistinguishable from those collected at the CVAO during the same period, although mean atmospheric Al was 65% higher at the CVAO than those measured on the ship due to the irregular and uneven nature of dust transport.

Air mass back-trajectories showed an important role for southern source regions of the North African deserts during summer, with 92.5% of the samples indicating a contribution from the Sahel. Significantly elevated ratios of V, Ni, Cu, Zn, Cd and Pb with Al were present in samples originating from the Sahel compared with samples with a more northerly origin. This was likely due to enhanced anthropogenic emissions related to the greater population densities in the Sahel compared with the less developed Saharan regions further north.

Ratios of other elements and trends in rare earth elements could however not be used to distinguish differences in source regions. Similar source material compositions, the mixing of dust from different regions during transport, and the pooling of samples over a 1–3 day collection period appear to have diluted specific signals from source regions.

1. Introduction

Aeolian dust forms an important source of iron (Fe) and other biologically important trace elements and nutrients to microbial organisms in the global surface ocean (Baker et al., 2007; Duce and Tindale, 1991; Jickells et al., 2005). Transport of dust from the Sahara and

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Sahel regions of northern Africa results in increased dissolved Fe concentrations in the North Atlantic Ocean (Measures et al., 2008; Rijkenberg et al., 2008, 2012; Sarthou et al., 2007; Ussher et al., 2013), which influences di-nitrogen fixation (Mills et al., 2004; Moore et al., 2009; Rijkenberg et al., 2011; Schlosser et al., 2014) and the structure and functioning of microbial communities (Hill et al., 2010).

The importance of mineral dust as a source of trace elements and nutrients to the open ocean has stimulated research into its production, transport, deposition and subsequent dissolution in surface waters. Over the last two decades, satellite measurements have proved indispensable in the evaluation of dust sources and the provision of transport pathways. While they provide unparalleled spatial and temporal coverage of dust transport, it is however hard to extract quantitative information on aerosol concentration and composition from satellite observations. In-situ aerosol measurements are therefore essential to obtain accurate data (Mahowald et al., 2005). Due to the sporadic nature of dust transport, long-term measurements of aerosols, such as those made at Bermuda, Miami and in the Canary Islands (Gelado-Caballero et al., 2012; Prospero and Lamb, 2003; Trapp et al., 2010) are essential in order to build up a picture of dust fluxes and composition.

The chemical composition and mineralogy of transported dust can be used to identify the original source of the dust. Through a combination of mineralogical and geochemical measurements, Chavagnac et al. (2007) traced the source of mineral dust particles collected in sediment traps in the Northeast Atlantic to the Anti-Atlas Moroccan mountains. Furthermore, Muhs et al. (2010) identified the source of mineral particles in the soils of the Canary Islands to the Sahara and Sahel desert regions. Recent research indicated the importance of dust composition and mineralogy for trace metal solubility (Aguilar-Islas et al., 2010; Sholkovitz et al., 2012), which highlights the need to link dust samples to specific sources.

Tracing individual Northwest African dust storms to specific source regions may be complicated due to several factors. Desert dust undergoes a continual process of uplift and deposition, mixing soils and smoothing out differences between the original source rocks (Schütz and Sebert, 1987). During long-range transport, homogenisation of air masses and physical selection for particles of similar size and mineralogy result in the composition of the transported dust reflecting the average composition of a large source region (Guieu et al., 2002; Schütz and Sebert, 1987). In addition, air-masses from densely populated or industrialised areas are often mixed with air-masses transporting the mineral aerosols, further altering the chemical composition of the bulk aerosol (Chester et al., 1999).

Aerosols collected at long-term monitoring sites in Barbados and Miami showed a high degree of homogeneity in chemical composition of North African dust by the time it had crossed the Atlantic Ocean. African dust reaches the western Atlantic predominantly during the summer via complex easterly weather systems, which entrain material from a wide area and transport this at high altitude, resulting in large-scale mixing and homogenization (Carlson and Prospero, 1972; Prospero and Carlson, 1972; Trapp et al., 2010). Analysis of aerosol samples collected closer to the North African continent, however, is often able to distinguish dust from different source regions. Various studies, interpreted with the aid of air-mass back trajectory calculations, have detected distinct signatures from aerosols originating in different desert regions for samples collected over the Mediterranean (Guieu et al., 2002), at sites in Spain (Querol et al., 2007), on the Canary Islands (Moreno et al., 2006) and along the West African margin (Stuut et al., 2005). Sample collection over a 3-year period on the island of Sal (Cape Verde archipelago) allowed allocation to one of three African source regions (Chiapello et al., 1997) (Fig. 1). Distinct Fe/Ca, K/Ca, Si/Al and Ca/Al ratios were found for samples originating from each of these regions related to higher amounts of Ca and enhanced Si/Al ratios in northern Saharan soils (Chiapello et al., 1997). Further work on this data set showed that the ratio of the clay minerals illite/kaolinite formed a good indicator of aerosol origin, due to the higher abundance of kaolinite in the Sahel and southern Sahara (Caquineau et al., 1998).

Situated within the main transport area of dust over the tropical North Atlantic, the Cape Verde Islands form an excellent location to study dust inputs to this ocean region. Aerosol measurements over the tropical Northeast Atlantic are limited in both spatial and temporal coverage, with observations restricted to occasional research cruises (Baker et al., 2006; Sarthou et al., 2003; Sholkovitz et al., 2012), land-based observations from the Canary Islands (Gelado-Caballero et al., 2012; Neuer et al., 2004) and a limited number of studies on Cape Verde (e.g. Chiapello et al., 1995, 1997; Fomba et al., 2013). In this article we present a continuously collected set of chemical aerosol measurements covering a complete seasonal cycle for 42 elements in the tropical Northeast Atlantic. It is one of very few sets of long term measurements in the area and is the first study in the eastern tropical North Atlantic to present a continuous set of chemical measurements over a full annual cycle. The data set is supplemented with mineralogical analysis of a selected number of samples, enabling a rare opportunity to interpret mineral composition in conjunction with chemical composition. Furthermore, we present a unique set of concurrent measurements made during a research cruise in the vicinity of Cape Verde in January and February 2008, during which high aerosol dust concentrations were experienced, enabling the comparison of independent measurements of corresponding air-masses on land and at sea.

2. Methodology

2.1. Aerosol sample collection

2.1.1. Aerosol sampling approach

Atmospheric aerosols (total suspended particles — TSP) were collected on 47 mm diameter, polypropylene (0.45 μm nominal pore-size, Sterlitech) and polycarbonate filters (0.4 μm pore-size, Nuclepore). The polypropylene filters were used for leaching experiments to be reported in a separate article, while the polycarbonate filters were used to measure total chemical (via total acid digestion) and mineralogical composition (X-ray Diffraction (XRD) analysis). The polycarbonate filters were cleaned before use by soaking overnight in 1 mol L^{-1} HCl solution (Romil, SpA grade) and then rinsed thoroughly with deionised water (MilliQ water, >18.2 MΩ cm^{-1}, Millipore). The cleaned filters were subsequently dried in a class-100 laminar flow cabinet.

2.1.2. Cape Verde Atmospheric Observatory

Aerosol sampling was undertaken at the Cape Verde Atmospheric Observatory (CVAO) (Carpenter et al., 2010) in the period between 2 July 2007 and 11 July 2008. The CVAO is situated on the northwest coast of the island of São Vicente (16° 51′ N, 24° 52′ W), around 800 km off the west-African coast. Contamination from potential local aerosol sources can be disregarded due to a very stable north-easterly wind direction at the site resulting in sampled air that had not crossed land for more than 900 km since leaving the African mainland.

A low-volume aerosol sampler was installed at the top of a 30 m high sampling tower at the CVAO. The system comprised two rotary vane vacuum pumps (Piccolino VTE 8, Gardner Denver Thomas) drawing air through two pairs of 47 mm filters (two polycarbonate and two polypropylene filters). Thermal mass flow meters (Top Trak 826, Sierra Instruments) monitored the flow rates of air through the filters. A data logger (built in-house) monitored the analogue electrical signal from the mass flow meters and recorded the data on a Compact Flash memory card. For each pair of sample lines, the same type of filter was used in order to achieve an even distribution of flow between the two filters.

Typical flow rates through each filter were ca. 30 standard L min^{-1}, but this decreased as the filters became loaded with dust, particularly for the polycarbonate filters. Filters were changed three times per week (more often during intense dust events) and stored in a freezer (−20 °C) prior to shipment to Southampton for analysis. Filter freezing