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Variation of the mixing state of Saharan dust particles with atmospheric transport

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ABSTRACT

Mineral dust is an important aerosol species in the Earth's atmosphere and has a major source within North Africa, of which the Sahara forms the major part. Aerosol Time of Flight Mass Spectrometry (ATOFMS) is first used to determine the mixing state of dust particles collected from the land surface in the Saharan region, showing low abundance of species such as nitrate and sulphate internally mixed with the dust mineral matrix. These data are then compared with the ATOFMS single particle mass spectra of Saharan dust particles detected in the marine atmosphere in the vicinity of the Cape Verde islands, which are further compared with those from particles with longer atmospheric residence sampled at a coastal station at Mace Head, Ireland. Saharan dust particles collected near the Cape Verde Islands showed increased internally mixed nitrate but no sulphate, whilst Saharan dust particles collected on the coast of Ireland showed a very high degree of internally mixed secondary species including nitrate, sulphate and methanesulphonate. This uptake of secondary species will change the pH and hygroscopic properties of the aerosol dust and thus can influence the budgets of other reactive gases, as well as influencing the radiative properties of the particles and the availability of metals for dissolution.

1. Introduction

Mineral dust is an important aerosol species in the Earth's atmosphere, involved in several aspect of our climate system. It can influence global climate directly by scattering and absorbing solar and terrestrial radiation, affecting both the regional and global energy balance (Haywood et al., 2003). In the shortwave part of the spectrum, dust scatters radiation back to space but depending on the albedo of the underlying surface it can either increase (over ocean) or make little difference (over desert) to the total albedo. The impact in the longwave depends crucially on the surface temperature and the altitude of the dust layer. Radiation from the earth surface is absorbed in the dust layer and reemitted back toward the ground thereby potentially increasing the surface temperature. Other impacts of mineral dust on the climate system are less well understood, including the fact that even small concentrations of mineral dust are thought to be able to significantly affect cold cloud properties including the radiative properties of cirrus, dehydration of the tropopause and convective cloud dynamics (Haywood et al., 2003).

An estimated 40% of photosynthesis on earth occurs in the marine environment and the turnover time for marine plant biomass is nearly three orders of magnitude faster than that of terrestrial biomass (Behrenfield et al., 1998). There is now considerable evidence that the availability of the nano-nutrient Fe, plays a critical role in regulating phytoplankton primary productivity and microbial diversity in the major High Nutrient Low Chlorophyll (HNLC) regions of the oceans. Nutrients and trace metals are supplied to the surface ocean via the atmospheric transport of dust and its deposition, as well as by the upwelling, entrainment, or mixing of deeper waters relatively rich in nutrients and metals (Jickells and Spokes, 2001; Baker et al., 2003).

The North Atlantic Ocean receives about a third of the global oceanic dust inputs, which are estimated to range between 400 and $1000 \times 10^{12}\ \mathrm{g\,y^{-1}}$ (Jickells and Spokes, 2001). This region receives one of the highest dust loading of any ocean area, with the

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aluminosilicate mineral soil material originating principally from uninhabited Saharan desert regions north of 15°N (Jickells and Spokes, 2001). Long range dust transport requires rapid movement of dust to high altitudes of between 1 and 5 km over the Atlantic Ocean (Fung et al., 2000), and involves an average particle size of ca. 3 μm (Jickells and Spokes, 2001). Long-term aerosol studies have observed a seasonal pattern in the trans- Atlantic transport of Saharan dust, due to the seasonal shift of the Inter Tropical Convergence Zone (Archer and Johnson, 2000; Duce et al., 1991). At the Cape Verde islands in the tropical NE Atlantic, the maximum dust deposition takes place in winter with transport of dust mainly occurring in the lower air masses of the trade winds (Prospero et al., 2002). The winter aerosol concentrations (monthly winter mean 120 $\mu g\ m^{-3}$) at Cape Verde (Prospero et al., 2002) are ca. 5 times higher than in the summer, with an estimated yearly mean dust concentration of 20 $\mu g\ m^{-3}$ (Jickells and Spokes, 2001).

In the atmosphere, the particles are cycled through clouds, which have a low pH as a result of CO_2, HNO_3 and H_2SO_4 uptake and SO_2 and DMS oxidation. Zhu et al. (1992) calculated pH values for the atmospheric particle hydration layer of between 0 and 1, while Keene et al. (1998) calculate a pH of 5.5 for clean marine aerosols as a consequence of carbonate neutralisation. The low pH cloud cycling enhances the lability of aerosol associated nutrients and metals and influences their solubility on wet or dry deposition to seawater (Prospero et al., 1981; Zhu et al., 1992; Keene et al., 1998). Organic complexation of trace metals within the aerosol may also be an important control on solubility, as is photochemistry and the two may well be linked (Jickells and Spokes, 2001). However, the Saharan aerosol as sampled over the tropical North Atlantic is often mixed with anthropogenic pollutants, as the air masses involved travel over European and North African source regions prior to passing over the Sahara (Zhu et al., 1997; Spokes and Jickells, 1996). In the more contaminated urban particles the elements are held in more labile, readily exchangeable fractions compared with mineral aerosols (Spokes and Jickells, 1996; Guieu and Thomas, 1996). Furthermore, the particle concentration plays a critical role in elemental dissolution, with a reported exponential decrease in the percentage dissolution of P (Ridame and Guieu, 2002) and Fe (Formenti et al., 2003) upon an increase in particulate loading in experiments using seawater. These findings were explained by enhanced re-adsorption at higher particle concentrations because of an increase in surface area.

The mixing state (MS) of an aerosol population (AP) can be defined as the distribution of the chemical components within it. Traditional filtration-based aerosol sampling techniques (so called "off-line") provide the average chemical composition over a period of time of the AP and do not allow the determination of the MS. It is not possible to know if the AP is "internally" (each single particle belonging to the AP presents the same chemical composition of the bulk composition) or "externally" (single particles of different chemical compositions) mixed. The aerosol mixing state is the net result of several primary emissions as well as several subsequent chemical and physical processes which influence properties such as solubility. For example, higher acidity in a particle would enhance the solubility of iron within that particle, and therefore knowing the mixing state between iron and particle acidity is a prerequisite to understanding the behaviour of aerosol iron when it deposits into the ocean.

The sulphation and nitration of desert or mineral dust particles due to the interaction of gaseous acidic species, mainly with carbonate species, have been widely described, for African, European, Asian, and Arctic dust (Parungo et al., 1993; Levin et al., 1996; Querol et al., 1998; Alastuey et al., 2005; Wang et al., 2005). These interactions yield mainly the formation of coarse Ca- or $Mg(NO_3)_2$ as well as to Ca- or $MgSO_4$. However, there is also evidence that lesser amounts of NH_4NO_3 and $(NH_4)_2SO_4$ may be present in coatings of dust particles (Sullivan et al., 2007). It should be borne in mind that calcium and magnesium sulphate may also be present as a minor proportion from the original African or Asian dust.

A major parameter for determining the hygroscopicity of aerosols is their chemical composition. The higher the proportion of weakly soluble organic species and elemental carbon relative to more soluble inorganic components such as nitrate and sulphate the more hydrophobic the aerosols will be (Gysel et al., 2007). However, pH is also a very important parameter, as more acidic solutions will have a much greater propensity to take on water (Clegg et al., 1998).

In order to understand aerosol properties including characterizing the sources, transport and transformations of aerosols in the atmosphere, it is no longer sufficient to perform bulk chemical analysis of atmospheric particulate matter; instead, a comprehensive approach that simultaneously characterizes single particles for aerodynamic diameter and chemical composition is needed.

To overcome the weakness of the off-line techniques which are unable to measure the MS of the AP – some particle mass spectrometry techniques (so called "on-line") have been developed to be capable of sizing and chemically characterizing individual airborne particles in real time (Suess and Prather, 1999), allowing the characterization of the MS of the AP. For example, the ATOFMS provides information on the abundance of different types of aerosol particles as a function of particle size with high time resolution (Suess and Prather, 1999; Beddows et al., 2004). While previous ATOFMS studies have focused on the MS of dust particles (Silva et al., 2000; Sullivan et al., 2007, 2009), this is the first time the ATOFMS has been deployed in the laboratory as well as at different outdoor locations in order to determine the MS of dust particles in the Saharan region.

The aim of the work described in this paper was to:

- fingerprint dust sources using single particle characterization and assess their major component composition, including iron content;
- investigate the chemical aging of the mineral dust particles as mixing occurs with trace gases, and natural and anthropogenic aerosols.

Our analysis provides new insights into the varying mineralogy of dust and the uptake of secondary acids by mineral dust.

2. Methods

2.1. ATOFMS

The ATOFMS (Model 3800-100, TSI, Inc.) collects bipolar mass spectra of individual aerosol particles. Ambient aerosol is focused into a narrow particle beam for sizes between 100 nm and 3 μm. Using a 2-laser velocimeter, particle sizes are determined from particle velocity after acceleration into the vacuum. In addition, the light scattered by the particles is used to trigger a pulsed high power desorption and ionization laser ($\lambda = 266$ nm, 1 mJ $pulse^{-1}$) which evaporates and ionizes the particle in the centre of the ion source of a bipolar reflectron ToF-MS. Thus, a positive and a negative ion spectrum of a single particle are obtained. The mass spectrum is qualitative in that the intensities of the mass spectral peaks are not directly proportional to the component mass but are dependent on the particle matrix, the coupling between the laser and the particle and the shot to shot variability of the laser. However, the ATOFMS can provide quantitative information on particle number as a function of composition; providing a measure of all particle components and can be used to assess mixing state.