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Soluble iron dust export in the high altitude Saharan Air Layer

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HIGHLIGHTS

- Soluble iron is observed in the Saharan Air Layer off North African coast.
- Soluble iron occurs in the submicron aerosols in the Saharan Air Layer.
- Enhancement of iron solubility may be linked to dust processing into inner Sahara.

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ABSTRACT

Every summer huge amounts of desert dust particles are exported from the hyperarid subtropical Sahara to the North Atlantic the so-called Saharan Air Layer (SAL), a dry, warm and dust-laden corridor that expands from the North African coast (1–5 km.a.s.l.) to the Americas above the marine boundary layer. Because of the potential impact of the dust deposited on the ocean on marine biogeochemistry and climate, we studied the Fe solubility (in seawater) of atmospheric aerosols samples directly collected in the SAL off the North African coast, i.e. the fresh aerosols recently exported from the Sahara in the SAL. The aerosol sampling was performed at ~2400 m.a.s.l. in Izaña observatory in Tenerife island. In the total aerosols, we found low Fe concentrations and high fractional Fe solubility (FFS ~2%) in the North Atlantic free troposphere airflows and high Fe concentrations and low FFS (~0.7%) within the SAL; the resulting FFS versus total dust (or total Fe) plot shows a hyperbolic trend attributed to the conservative mixing of 'fine combustion aerosols' and 'lithogenic mineral dust'. We then focused on the soluble Fe in the SAL. Our results indicate that ~70% of soluble Fe is associated with the dissolution of submicron dust particles, probably involving Fe-bearing clays. We found a FFS of submicron dust (~6%) higher than that typically observed in submicron particles of soil dust samples (<1%). The correlation between FFS and the ammonium-sulphate/dust ratio and the low variability in the Fe/Al ratio in the dust samples, suggests that the increase in the FFS of submicron dust aerosols (with respect to soil dust particles) may be related to the presence of acid pollutants mixed with dust. Previous studies had focused on dust processing and changes of Fe solubility during the trans-Atlantic transport of dust in the SAL. We found that submicron dust exported off the coast of North Africa may have already experienced acid processing over the Sahara, i.e. before dust export to the Atlantic. Export of soluble submicron Fe dust and deposition of coarse and depleted in soluble Fe dust particles during the trans-Atlantic transport may account for the observed variability in dust, soluble Fe and FFS.

1. Introduction

Deposition of airborne soil dust is a major source of iron, phosphorous and other nutrients to the remote ocean that may influence the phytoplankton growth (De Baar et al., 2005). In high-nutrient low-chlorophylic regions, which compose ~30% of the

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ocean, Fe availability may even limit oceanic primary productivity (Jickells et al., 2005). There is a growing interest about the hypothesis that variability in dust inputs to the ocean may modulate oceanic primary productivity, atmosphere–ocean CO_2 exchange and consequently the Earth's climate (Martin and Fitzwater, 1988). The negative correlation between dust and CO_2 in ice core paleo records suggests that dust-ocean-climate may be subject to important feedbacks (Ridgwell and Watson, 2002) and that increased dust inputs to the ocean may have suppressed CO_2 by 10–20 ppm in glacial versus interglacial periods (Bopp et al., 2003; Rothlisberger et al., 2004).

Knowledge on biogeochemical processes involving dust and its influence on climate is still limited for several reasons. First, the impact of deposited iron on the oceanic biota depends on Fe bioavailability, which can not be directly measured as this is still a poorly understood aspect; measurements of labile/reactive or soluble Fe are being used as a proxy of bioavailable Fe (Fan et al., 2006; Raiswell et al., 2008). Second, there is not a universally accepted (reference) method for measuring iron solubility; methods used in practice (Shi et al., 2012) differ in the extract solvent used (Chen et al., 2006), extraction technique (Wagener et al., 2010) and extraction time (Trapp et al., 2010). Third, the solubility of the Fe bearing dust aerosols depends on dust mineralogy (Shi et al., 2011a) and processes occurring in the atmosphere – before deposition – and in the ocean – after deposition (Baker and Croot, 2010). These, and other limitations on climate research have been discussed in review papers on (i) long term in-situ aerosol dust measurement programs (Rodríguez et al., 2012), (ii) climate relevant physical, chemical and optical dust properties (Formenti et al., 2011; Redmond et al., 2010), (iii) marine biogeochemistry (Schulz et al., 2012), and (iv) on the influence of soil weathering, atmospheric processing and processing occurring in the ocean on iron solubility (Baker and Croot, 2010; Shi et al., 2012).

North Africa is the largest and most active dust source, whose emissions account for 50–70% of global dust emissions (Ginoux et al., 2004, 2012). Dust export occurs in the so-called Saharan Air Layer (SAL), a dry, warm and dust-laden air layer that expands westward from North Africa through the North Atlantic (Prospero and Carlson, 1972). We have focused on the summertime when the SAL (Tsamalis et al., 2013; Rodríguez et al., 2015): (i) is shifted northward linked to enhanced dust emissions in the subtropical Sahara, (ii) is exported at altitudes between 1 and 5 km a.s.l. off the subtropical North African coast (15–30°N) and (iii) results in maximum dust impacts throughout the North Atlantic. During westward transport the SAL shifts downward (down to < 2 km in the Caribbean; Tsamalis et al., 2013) and the aerosol dust population may experience 'aging' by the so-called 'atmospheric processing', a set of processes that may potentially enhance Fe solubility. These processes include (Baker and Croot, 2010; Schulz et al., 2012; Shi et al., 2012): (i) 'acid processing' of dust by reaction with oxidation products of SO_2 and NO_x, (ii) exposure to oxidants and sunlight that may influence dust surface, (iii) in-cloud processing (pass of aerosol through acid-cloud droplets), (iv) evolution from an external to an 'ideally' internal aerosol mixing, and (v) preferential gravitational deposition of large particles. Mixing of dust with combustion (Sholkovitz et al., 2012) and biomass burning (Paris et al., 2010) aerosols may also increase the observed Fe solubility of the resulting aerosol population. Solubility of Fe has been studied in connection to this westward trans-Atlantic SAL movement, e.g. by east-to-west (Baker et al., 2006a) and south-north (Baker et al., 2006b; Buck et al., 2010a,b) cruise measurements, and by collection of samples of 'aged aerosols' of the SAL impacting in the Caribbean (Trapp et al., 2010). A recent global study – which estimated that deposition of soluble Fe on the ocean may have doubled from pre industrial to present times due to combustion emissions of soluble iron and acid processing of dust – found that the highest concentrations of airborne soluble iron are found near North Africa, linked to the desert dust inputs (Ito and Shi, 2016). In this study we have focussed on the solubility of Fe at the beginning of the westward dust corridor–represented by the SAL-that expands from North Africa to the Caribbean. Algae blooms in the Canary Islands have been connected to Saharan dust events (Ramos et al., 2008). In this study we addressed this question: *What are the characteristics of seawater solubility of Fe at the beginning of the North African to Caribbean dust corridor?, i.e. before atmospheric processing potentially occurring during the trans-Atlantic transport may influence dust properties*

The vertical structure of the SAL and the low troposphere of the North Atlantic exhibit some features that should be considered. The dusty SAL expands westward above the marine boundary layer (MBL). The top of this MBL is characterised by the presence of stratocumulus clouds and an inversion layer above them (~1 km.a.s.l.) which hinder vertical mixing processes (Rodríguez et al., 2004), in such a way that sea salt tend to be confined to the MBL, whereas dust concentrations are much higher in the SAL than in the MBL (Prospero and Carlson, 1972). During the westward movement of the SAL, and because of (size dependent) gravitational settling, dust particles move downward from the warm and dry SAL to the cooler and humid MBL where they may experience several processes that may influence Fe solubility, including in-cloud processing, mixing with sea salt and water condensation (with implications on chemical reactions). The comparison of the Fe solubility features of the "fresh aerosols directly collected into the high altitude SAL near North Africa" with those of the "aged aerosols collected in the MBL of the Caribbean and the Western North Atlantic" allows us to assess the role of atmospheric processing during trans-Atlantic transport. In this study we focused on the features of the fresh aerosols recently exported from North Africa, for this reason we collected aerosol samples in the Izaña mountain observatory at ~2400 m.a.s.l. in Tenerife, i.e. directly in the high altitude SAL off the North African coast. As far as we know, these are the first Fe solubility measurements directly in the SAL.

2. Methodology

2.1. Sample collection and aerosol chemistry

The Izaña Global Atmospheric Watch – GAW – observatory (28.309°N, 16.500°W) is located at 2373 m.a.s.l. in Tenerife (Fig. S1 of the Supplementary Material). The site is about 300 km distant to the coast of North Africa; according to the back-trajectories an air parcel may take between 15 and 20 h to travel from the North African coast to Izaña. From 12 to 19 August 2011, we collected aerosol (particulate matter – PM_x) samples in four size fractions: total particulate matter (PM_T) and particulate matter with an aerodynamic diameter smaller than 10, 2.5 and 1 μm (PM_{10}, $PM_{2.5}$ and PM_1, respectively). Sampling was performed in quartz micro-fiber filters (30 m^3/h) at night (22:00 to 06:00 GMT), when upslope winds – that could transport air masses from the boundary layer – have ceased and Izaña is exposed to free troposphere airflows. We refer to samples collected from 22:00 GMT (day D-1) to 06:00 h of day D, as day D. Every night we simultaneously collected samples of PM_T, PM_{10}, $PM_{2.5}$ and PM_1 in different samplers. Thus, a total of 27 PM_x samples were collected along 7 consecutives nights (13–19 August 2011): 7 samples of PM_T, 7 of PM_{10}, 6 of $PM_{2.5}$ and 7 of PM_1. $PM_{2.5}$ was not sampled on the 17 of August 2011 due to sampler failure. Concentrations of PM_x were determined conditioning the filters (before and after sampling) at 20 °C and 30–35%RH and applying the gravimetric method following the EN14907 protocol (except for RH which was set to 30–35% instead of 50%).