Solubility of aerosol trace elements: Sources and deposition fluxes in the Canary Region

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HIGHLIGHTS

- Solubility is a function of aerosol origin: highest values in anthropogenic aerosols.
- Atmospheric inputs of metals and nutrients are significant for marine biogeochemistry.
- Atmospheric nutrients could enhancement marine production mainly in summer months.

ABSTRACT

African dust inputs have important effects on the climate and marine biogeochemistry of the subtropical North Atlantic Ocean. The impact of dust inputs on oceanic carbon uptake and climate is dependent on total dust deposition fluxes as well as the bioavailability of nutrients and metals in the dust. In this work, the solubility of trace metals (Fe, Al, Mn, Co and Cu) and ions (Ca, sulphate, nitrate and phosphate) has been estimated from the analysis of a long-time series of 109 samples collected over a 3-year period in the Canary Islands. Solubility is primarily a function of aerosol origin, with higher solubility values corresponding to aerosols with more anthropogenic influence. Using soluble fractions of trace elements measured in this work, atmospheric deposition fluxes of soluble metals and nutrients have been calculated. Inputs of dissolved nutrients (P, N and Fe) have been estimated for the mixed layer. Considering that P is the limiting factor when ratios of these elements are compared with phytoplankton requirements, an increase of 0.58 nM of P in the mixed layer (~150 m depth) and in a year can be estimated, which can support an increase of 0.02 μg Chl$a$ L^{-1} y^{-1}. These atmospheric inputs of trace metals and nutrients appear to be significant relative to the concentrations reported in this region, especially during the summer months when the water column is more stratified and deep-water nutrient inputs are reduced.

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1. Introduction

Atmospheric deposition of particles is an important pathway via which nutrients reach the oceans (Baker et al., 2006a), particularly in low-nutrient low-chlorophyll (LNLC) areas (Jickells and Moore, 2015). Dust inputs to the world's oceans are estimated to be around 450 Tg year^{-1}, with around 43% of this depositing to the Atlantic Ocean (Jickells et al., 2005). Anthropogenic and natural atmospheric inputs clearly impact marine biogeochemical cycles in many regions. For example, in the Mediterranean Sea the important role of anthropogenic aerosol inputs (Elbaz-Poulichet et al., 2001), nutrients such as nitrogen and phosphorus (Krom et al., 2010) and micronutrients including Fe (Bonnet and Guieu, 2006) has been demonstrated. Fe is recognized to be a limiting factor for primary productivity (Boyd et al., 2000, 2007; Coale et al., 1996) and nitrogen fixation (Moore et al., 2009; Sanudo-Wilhelmy et al., 2001). In addition, trace elements such as Mn, Co, Zn and Ni are essential micronutrients for marine biota (Butler, 1998; Whitfield, 2001).

Mineral dust is the principal source of soluble atmospheric P, Fe and Si in the North Atlantic subtropical region (Baker et al., 2006a; Mahowald et al., 2008). Biomass burning, anthropogenic

combustion processes, and primary particles derived from vegetation and sea spray also contribute to the aerosol P loading (Mahowald et al., 2005; Ternon et al., 2011). Nitrogen oxides (NO_x) and ammonium emissions derived from combustion processes and agricultural activity, respectively, are the main sources that contribute to the high atmospheric nitrogen concentrations found in the Northern Hemisphere, while biomass burning appears to be a significant seasonal source of atmospheric nitrogen in the Southern Hemisphere. The major pools of soluble nitrogen in aerosol and rainwater are nitrate, ammonium and organic nitrogen. The global nitrogen cycle has been dramatically altered by human activities (e.g. Galloway et al., 2008). Human activities may be exacerbating phosphorus stress through increased atmospheric nitrogen (N) deposition and raised N/P ratios in deposition (Zamora et al., 2013).

The potential impact of dust inputs on the biogeochemistry of surface waters depends on the solubility of the particulate species. Aerosol trace metal solubility is operationally defined and measured under controlled laboratory conditions, but sensitive to extraction volume, solvent pH, mechanical agitation, and other factors. The choice of solvent used in a dissolution experiment (pure water, seawater or buffer acidic solvents) strongly influences solubility measurements made in the laboratory (Anderson et al., 2010; Paris et al., 2011). Differences in aerosol solubility measurements may be the product of particular aerosol characteristics related to aerosol source, transport history, and atmospheric particle processing (Buck and Paytan, 2009). Methodological factors, such as the collection method, storage conditions, or extraction technique employed also influence the result. A necessary standardization of the dissolution methodologies has been claimed for these reasons, particularly to improve the accuracy of biogeochemical models of Fe deposition (e.g. Boyd et al., 2010).

To date there have been no long-term solubility aerosol studies in the Canary Region, with only limited data available from several oceanographic research cruises which have crossed the region during large transects of the Atlantic Ocean, producing deposition estimates for soluble Al, Mn, Fe, P (Baker et al., 2006a; Powell et al., 2015) and N (Baker et al., 2006b, 2010). However, these values are insufficient to characterize dust inputs to the Canary Region adequately.

The main objective of this study is to characterise the soluble fraction of aerosols in the Canary Region and estimated the impact that atmospheric deposition can have in the surrounding waters. Due to the scarcity of aerosol solubility data for this area and the high spatial and temporal variations in concentration and compensation, this work seeks to further understanding of atmospheric inputs to the region.

2. Methodology

2.1. Sampling sites

Pico de la Gorra (27° 56′ N, 15° 33′ W, 1930 m above sea level) is a rural station free of direct influence from local sources of pollution and was used in this and previous studies to investigate variations in the chemical composition of aerosols reaching the Canary Islands (Fig. FS1). A total suspended particles (TSP) concentration time series has been recorded since 1 December 1996 at the Pico de la Gorra station (PG) (see Gelado-Caballero et al., 2012; López-García et al., 2013; Torres-Padrón et al., 2002).

2.2. Aerosol samples

High volume (60 $m^3 h^{-1}$) aerosol collectors (MCV, model CAV-A/M) were used to collect aerosol samples for total and soluble

analysis on acid-washed cellulose filters (Whatman 41) and the TSP in air on glass fibre filters (Whatman GF/A). TSP concentrations were measured by weighing the Whatman GF/A filters before and after sampling and dividing the difference by the sampling volume. The Whatman 41 (WH-41) filters were washed with 10% HCl in order to eliminate metal traces. The collection efficiency of WH-41 is effectively 100% for dust (Savoie, 1984). Procedural blanks were also sampled. Of the samples collected during the period 01/2008-12/2011, 109 cellulose filters were used for solubility experiments (see supplementary material for sampling list, Table S1). All the seasons were proportionally represented. During 2010, sampling was interrupted due to construction work at the station. One eighth of a filter was used in each analysis.

To avoid pollution from local sources (mainly traffic emissions), sampling was conducted during the night (from 6:00 p.m. to 6:00 a.m. UTC). Wind direction and velocity, temperature, humidity and pressure were continuously monitored (Vantage Pro2 Plus) during sample collection in order to aid the identification of African air masses.

To minimise the risk of sample contamination, exposed filters were transferred to individual zip-lock plastic bags immediately after collection and subsequently handled under a laminar flow clean bench. Samples for trace metal and soluble ion analysis were stored frozen (-20 °C) and analysed within a week of collection.

2.3. Chemical analysis

Chemical characterisation of metal composition was made on the WH-41 filters collected at Pico de la Gorra. Analyses of Al, Fe, Mn, Co, Ca and Cu in dust were conducted following total acid digestion and soluble extractions of filters. Extract solutions were analysed by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS, SpectraAA 220Z with Zeeman background correction) for Mn, Co and Cu and soluble Al and Fe and Flame Atomic Absorption Spectroscopy (FAA, SpectraAA 220FS) for Ca and total Al and Fe (Gelado-Caballero et al., 2012).

Soluble trace metals (Al, Fe, Mn, Co and Cu) were extracted at pH 4.7 for 2 h using a 1.1 M ammonium acetate buffer (Sarthou et al., 2003). This pH was chosen initially as a mimic for the release of trace metals from aerosols in rainwater, but it is similar to a procedure employed by Bruland et al. (2001) to examine the bioavailable Fe content of upwelled particulate matter off the coast of California. Samples were placed in an orbital shaker for 2 h and filtered using acid-cleaned 0.2 μm nucleopore filters. With each group of samples analysed, a blank of the procedure was determined. In addition, the CV (%) for WH-41 aerosol-soluble concentrations were estimated analysing all 8-parts of a filter with average aerosol concentration (see Table 1). CV values for Al and Fe (10.2 and 9.6%, respectively) are similar to those reported by Morton et al. (2013) during the GEOTRACES aerosol intercalibration experiment.

Soluble ions (sodium, calcium, nitrate, phosphate and sulphate)

Table 1
WH41 blanks and detection limits and coefficient of variation (CV).

	Average[a] (ng m^{-3})	Detection limits[b] (ng m^{-3})	CV (%)[c]
Al	1.64	0.07	10.18
Fe	2.47	0.36	9.55
Co	0.05	0.02	9.53
Mn	0.11	0.01	26.26
Cu	0.04	0.04	27.29

[a] Filter blank unit (ng m^{-3}) were calculated assuming an average sampling volume of 719.8 m^3.
[b] Detection limits represent 3SD of the filter values (n = 10 filters).
[c] CV (%) was calculated dividing the SD by the average of the concentrations of the 8 parts of each filter and multiply by 100.