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Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic

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ABSTRACT

Total and soluble trace metal concentrations were determined in atmospheric aerosol and rainwater samples collected during seven cruises in the south-east Atlantic. Back trajectories indicated that the samples all represented remote marine air masses, consistent with climatological expectations. Aerosol trace metal loadings were similar to previous measurements in clean, marine air masses. Median total Fe, Al, Mn, V, Co and Zn concentrations were 206, 346, 5, 3, 0.7 and 11 pmol m^{-3} respectively. Solubility was operationally defined as the fraction extractable using a pH 4.7 ammonium acetate leach. Median soluble Fe, Al, Mn, V, Co, Zn, Cu, Ni, Cd and Pb concentrations were 6, 55, 1, 0.7, 0.06, 24, 2, 1, 0.05 and 0.3 pmol m^{-3} respectively. Large ranges in fractional solubility were observed for all elements except Co; median solubility values for Fe, Al and Mn were below 20% while the median for Zn was 74%. Volume weighted mean rainwater concentrations were 704, 792, 32, 10, 3, 686, 25, 0.02, 0.3 and 10 nmol L^{-1} for Fe, Al, Mn, V, Co, Zn, Cu, Ni, Cd and Pb respectively ($n = 6$). Wet deposition fluxes calculated from these values suggest that rain makes a significant contribution to total deposition in the study area for all elements except perhaps Ni.

1. Introduction

The transport and deposition of atmospheric aerosol is a significant source of trace metals to the surface ocean (Jickells et al., 2005) and, in large areas of the open ocean, may represent the dominant supply route for certain elements (Ussher et al., 2013). A range of trace metals (e.g., Fe, Zn, Co) are required for phytoplankton growth, and their availability is limiting or co-limiting in some ocean regions (Saito and Goepfert, 2008; Dixon, 2008; Moore et al., 2013). Consequently, the supply of micronutrients to the surface ocean impacts primary productivity, and thus the potential of the oceans to sequester carbon (e.g., Cassar et al., 2007). In addition to direct impacts on phytoplankton growth, micronutrient availability may also influence functioning of the marine ecosystem via indirect mechanisms, particularly via impacts on nitrogen fixation (Moore et al., 2009, 2013). Another example of an indirect impact is the use of Co by marine prokaryotes in the synthesis of vitamin B12, an exogenous supply of which is required by eukaryotic phytoplankton (Panzeca et al., 2008). Some trace elements present in atmospheric deposition, for example Cu, can also be toxic to marine organisms (Paytan et al., 2009; Jordi et al., 2012).

Micronutrient levels are low in both the oligotrophic subtropical waters of the South Atlantic gyre, and the high nutrient–low chlorophyll waters of the Southern Ocean. Consequently, biogeochemical cycles in both regions are sensitive to atmospheric dust inputs (Cassar et al., 2007; Dixon, 2008). The South Atlantic receives lower atmospheric inputs than the equatorial and northern Atlantic (Sarthou et al., 2003; Ussher et al., 2013). Despite these lower inputs, atmospheric deposition still accounts for more than 50% of the vertical inputs of iron to the surface mixed layer, with the remainder supplied by mixing from below (Ussher et al., 2013). As westerly winds predominate, aeolian and volcanic dust originating in southern South America is considered to be the main source of dust inputs to the South Atlantic (Gaiero et al., 2004; Li et al., 2008; Johnson et al., 2010).

Despite several decades of research, the atmospheric deposition of trace metals to the oceans is not well quantified. Atmospheric loadings of trace metals over the oceans display high variability, reflecting the diversity of source regions and the episodic nature of sources such as dust mobilisation. Understanding the impact of atmospheric deposition on the South Atlantic and Southern Ocean requires improvements in the characterisation of atmospheric trace element (particularly elements other than Fe, Al, Mn) concentrations from sources such as South America (Johnson et al., 2010; Schulz et al., 2012). There is also a need for more information on the solubility and size distribution of aerosol trace metals, in order to better parameterise models (Mahowald et al., 2009; Schulz et al., 2012; Baker et al., 2013).

The aim of this work was to present representative atmospheric aerosol and rain water concentrations for the south-east Atlantic, and use these measurements to estimate atmospheric deposition fluxes to

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the region. A suite of ten elements is included for soluble metal concentrations, and six for total metal concentrations. The data used here comes from four cruises which are previously unpublished (D357 and JC068) or for which only a limited selection of data has been published previously (BGH and ZD; Sholkovitz et al., 2012; Boye et al., 2012; Bown et al., 2011). We also made use of aerosol data for Fe, Al and Mn from three other cruises (AMT15, AMT16 and AMT17; Baker et al., 2013), to provide a detailed study of this historically under-sampled region. We believe that the aerosol and rain trace metal concentrations measured on these seven cruises comprise the most extensive data set for the region currently available. The results presented here are intended as a contribution to the growing global database of marine aerosol measurements, and were obtained under the UK-GEOTRACES research programme.

2. Methods

2.1. Sample collection

Atmospheric aerosol and rainwater samples were collected during seven research cruises that took place between 2004 and 2012. Aerosol sampling mid-points are shown in Fig. 1 and rain sample locations are shown in Fig. 2; further details of the cruises are given in Table 1. The dominant wind direction over the sampling region is from the west/northwest (Barry and Chorley, 1971), so atmospheric deposition to these surface waters likely originated in South America rather than southern Africa. With the exception of AMT16, which took place in May, sampling was conducted during the austral summer (October to March), and in general each cruise took place in a different month.

Atmospheric aerosol was collected using high volume Andersen samplers (flow rate of ~1 m^3 min^{-1}), mounted on the bridge-top deck of the ship. To avoid sampling contaminated air from the ship funnel, the collectors were turned off when the ship was not facing into the wind or there was some other risk of contamination, such as testing of the lifeboat engines on the foredeck. During the more recent cruises (D357 and JC068), power supply to the motors was automatically controlled such that sampling only took place when the relative wind direction was between −80 and 145°, thus avoiding the ship exhaust. Samples were collected over periods of ~24 or ~48 h, depending on the anticipated aerosol loadings. Filter blanks and procedural blanks for the sampling cassette and the motor start up were collected. Bulk aerosol samples were collected using a single Whatman 41 filter paper, and size segregated aerosol samples were collected using a Sierra-type cascade impactor (fitted with two upper stages, with aerodynamic diameter cut-offs of ~2.4 and ~1.6 μm) onto slotted filters and a back-up filter behind (all Whatman 41). Occasionally, samples were collected using a six-stage impactor (also using Whatman 41 filters). Filters for trace metal determinations were washed in at least two consecutive acid baths before use. The filter washing procedures for individual cruises were as follows: AMT15, AMT17, D357, JC068 —

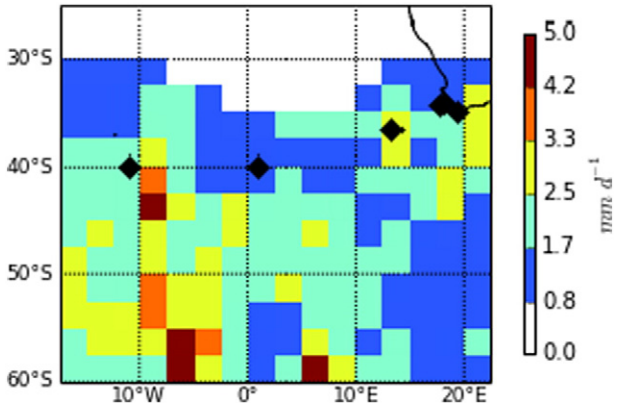

Fig. 2. Rain sample locations (♦) and average long-term monthly mean precipitation rates for the months of October to January. CMAP precipitation data was obtained from NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, via the online portal at http://www.esrl.noaa.gov/psd/ (Xie and Arkin, 1997).

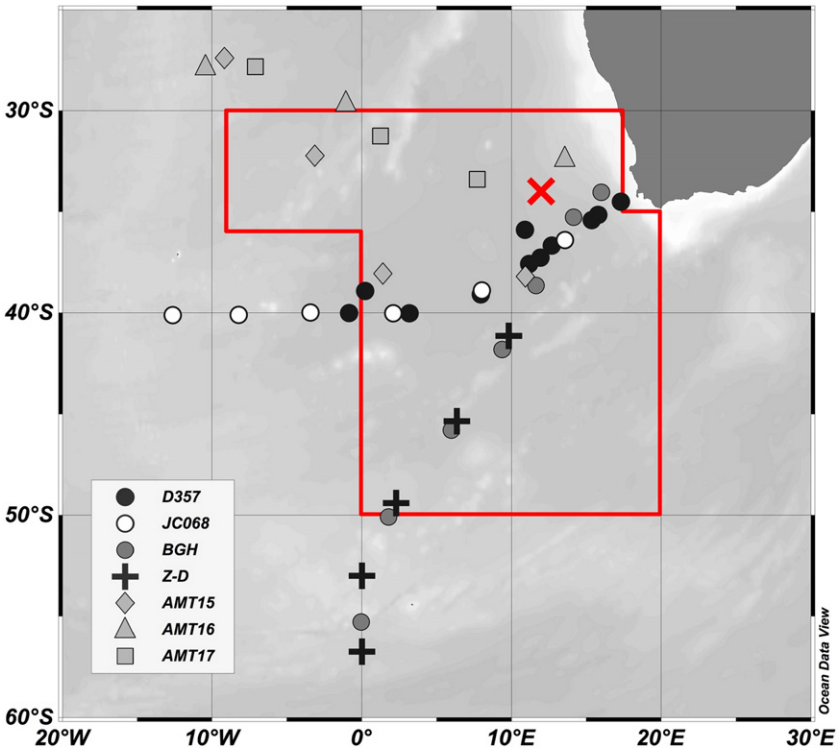

Fig. 1. Aerosol sample mid-points (grey symbols). Region 4d and arrival point of back trajectories used to produce air mass origin climatology in Baker et al., 2010, 2013 indicated by red box and red '×' respectively. Fig. prepared using Ocean Data View (Schlitzer, R., Ocean Data View, http://odv.awi.de, Schlitzer, 2014).