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Quantification of trace element atmospheric deposition fluxes to the Atlantic Ocean (> 40°N; GEOVIDE, GEOTRACES GA01) during spring 2014☆

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ABSTRACT

Atmospheric deposition is an important input route of trace elements (TEs) to the global ocean. As atmospheric inputs impact phytoplankton community health and dynamics, atmospheric TE fluxes, and in particular atmospheric iron fluxes, are a key component of marine biogeochemical models. Trace element concentrations were determined in dry (aerosols) and wet (precipitation) deposition samples from the North Atlantic, north of 40°N, during the GEOVIDE cruise (GEOTRACES cruise GA01) in May/June 2014. Atmospheric aerosol loading in the study region was low (~ 2–500 ng m^{-3}) throughout the cruise, as inferred from the very low aerosol Ti concentrations determined (0.0084–1.9 ng m^{-3}). Wet deposition appeared to be of roughly equal or greater importance than dry deposition to the total depositional flux of TEs, which is consistent with other regions of the Atlantic Ocean outside of the influence of the Saharan plume.

It can be challenging to convert aerosol chemical composition data into reliable flux estimates, due to the uncertainties associated with the parameterisation of dry deposition velocity, and precipitation rate.

Therefore, the goal of this study was to compare TE flux estimates derived from two different techniques: (1) the traditional approach of summed wet and dry deposition TE fluxes, using concentration data, precipitation rates, and dry deposition velocities and, (2) using the inventory of the cosmogenic radioisotope beryllium-7 (^{7}Be) in the upper ocean as a proxy for atmospheric deposition. These two approaches yielded TE flux estimates that were in excellent agreement (within one standard deviation) for about half of the TEs under investigation. However, for the remaining TEs differences between the flux estimates ranged from two to forty times, with the traditional approach generally being the higher of the two estimates. Therefore, factors that may contribute to this variation, such as differences in the timescale of integration and selection of representative deposition velocities and precipitation rates, are discussed. Our results suggest that the ^{7}Be approach continues to show promise in this application, particularly in regions where precipitation samples cannot be routinely collected.

1. Introduction

Atmospheric deposition is an important input route of trace elements (TEs) to the global ocean, and can be the principal input in some open ocean regions (Jickells et al., 2005). Atmospheric deposition is delivered to the surface ocean via wet (rain, fog, snow) and dry deposition (dust, soil, ash). It is important to quantify the total atmospheric deposition fluxes of TEs (both essential and potentially deleterious) to the surface ocean as atmospheric inputs impact phytoplankton community health and dynamics. Thus, in this way,

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atmospheric TE inputs may be linked to the global C and N cycles, key players in the global climate system (Morel and Price, 2003; Sunda, 2012). Yet many areas of the global ocean are limited, or co-limited by TE availability (Saito et al., 2008; Moore et al., 2013). Understanding the processes that govern TE supply and availability are key for gaining a mechanistic understanding of the biological carbon pump. However, atmospheric deposition remains poorly constrained, largely due to the difficulties associated with quantifying fluxes (Law et al., 2013).

The magnitude of aerosol input to the atmosphere from dust producing regions is a function of wind speed and precipitation in those regions. The magnitude of aerosol deposition downwind from aerosol source regions is a function of atmospheric loading, particle size and type, wind speed, humidity and precipitation in the receiving areas (Moulin et al., 1997). Even in the North Atlantic Ocean, which receives the largest inputs due to its proximity to the Sahara Desert (~40% of annual global dust deposition; Jickells et al., 2005), aerosol deposition is not uniformly distributed. The Sahara outflow transports vast quantities of mineral dust (~1×10^{12} t a year; d'Almeida, 1986) over the Atlantic Ocean, as far as the Americas, at altitudes above the marine boundary layer (MBL; ~500–6000 m; Prospero and Carlson, 1972), approximately over the latitudinal band 5–30°N. To the south, the Saharan dust plume is largely constrained by the seasonally-migrating intertropical convergence zone (ITCZ; ~5–10°N) (Prospero and Carlson, 1972; Doherty et al., 2012; Schlosser et al., 2013), and to the north by the northern extent of the trade winds (~30°N). North of 30°N, a steep declining gradient in atmospheric aerosol loading, as determined by metrics such as aerosol optical depth (AOD; e.g. http://aeronet.gsfc.nasa.gov), is observed due to a combination of increasing distance from North African dust source regions and large-scale atmospheric circulation. As a result, other aerosol sources (Europe, North America, sea salt and, occasionally, volcanoes) become relatively more important in the north of this ocean basin. Thus, several aerosol sources are likely to contribute to the TE composition of the bulk aerosol.

The objectives of this study were to (1) investigate aerosol sources of a suite of TEs of interest to the GEOTRACES programme (www.geotraces.org); and (2) quantify the atmospheric deposition flux of TEs to surface waters of the North Atlantic at latitudes greater than 40°N. In order to do this, TE fluxes were calculated using, 1) the traditional approach of deriving fluxes from the summation of TE concentration data from wet and dry deposition (e.g., Duce at al., 1991), and 2) a novel tracer approach which uses the natural cosmogenic radionuclide Beryllium-7 (^{7}Be) as a tracer for atmospheric inputs (Cámara-Mor et al., 2011; Kadko and Prospero, 2011; Kadko et al., 2015, 2016). The two approaches resulted in flux estimates that were in excellent agreement for approximately half the TEs under investigation, but performed less well for the remaining TEs, with differences of 2–40 times between them. Therefore, potential sources of uncertainties are discussed.

2. Methods

The *GEOVIDE* campaign (*GEOTRACES* cruise *GA01*; 15 May-30 June 2014), on board the *N/O Pourquoi Pas?*, departed from Lisbon, Portugal, and sailed northwest following the *OVIDE* line (http://wwz.ifremer.fr/lpo/La-recherche/Projets-en-cours/OVIDE) to the Greenland shelf, after which the ship entered the Labrador Sea and sailed for the final port of St John's, Newfoundland, Canada (Fig. 1). In total, 18 aerosol samples and 10 precipitation samples were collected for the determination of a suite of TEs. In addition, ^{7}Be was determined from 18 aerosol samples, 8 precipitation samples, and 9 relatively shallow water column profiles.

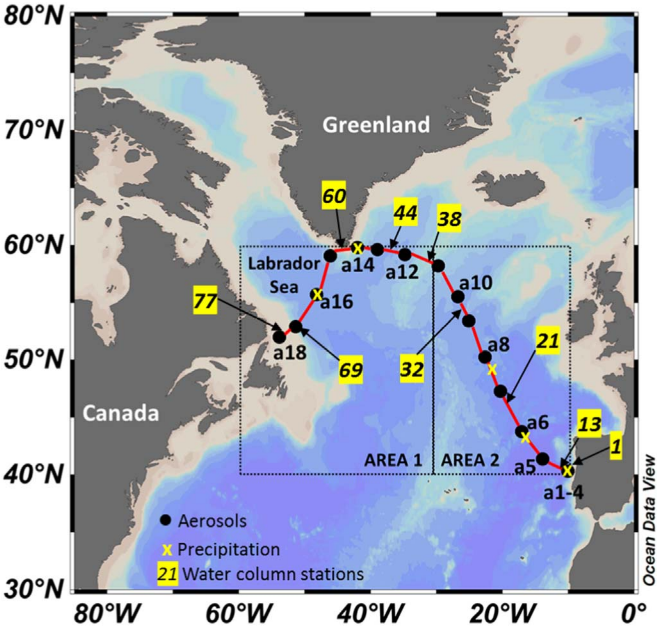

Fig. 1. The *GEOVIDE* cruise track. Aerosol samples *geoa*1–4 (displayed as "a1-4") were collected in close proximity, thus are only shown as one dot on the above map. There were ten precipitation events; the first six ocurred at the same location as aerosol samples *geoa*1–4. The dashed lines indicate the boxes, Area 1 and Area 2; the dividing line is located at 30°W (further details can be found in the Methods). Water column sampling stations are indicated by the arrows; the station numbers are highlighted in yellow. Metadata for the aerosol, rain and water column sample locations can be found in Tables S1, S2 and S3, respectively (Supplemental Material).

2.1. Sample collection and analysis

Aerosol TEs: Samples were collected using a mass flow-controlled, high volume aerosol sampler (~1 m^{-3} min^{-1}; model TE 5171, Tisch Environmental). The aerosol sampler was sector (± 60° from the bow) and wind speed (< 0.9 m s^{-1}) controlled, to minimise the risk of contamination from the ship's exhaust stack, using an anemometer and vane attached to a 3 m pole mounted on the railings near the aerosol sampler. The aerosol sampler was positioned on the forward railings (starboard side) on the flight deck above the bridge (~15 m above sea level). Twelve replicate samples were collected on acid-washed, 47 mm diameter Whatman 41 (W41) ashless filter discs (mixed cellulose esters; total exposed area 149 cm^2), which were positioned on a 12-position PVC adapter plate (Shelley et al., 2015). The first sample collected represented a 24 h deployment (sample time =19.6 h), but after visual inspection of the filters and of air mass back trajectory simulations (using the Hybrid Single Particle Lagrangian Integrated Trajectory Model, HYSPLIT), it became apparent that this sampling duration would be insufficient to collect enough material on the filters. Thus, the deployment time was increased to 48 h (sample time =17.4 – 47.6 h) for all subsequent samples. After recovery, filters were removed from the filter holders inside a laminar flow bench, placed in individual petri-slides (Merck), double ziplock bagged, and immediately frozen (−20 °C) for storage. Three of the twelve replicate samples were reserved for determination of ^{7}Be.

On return to the home laboratory, the aerosol samples were digested to determine concentrations of a suite of TEs by high resolution, magnetic sector field inductively coupled plasma mass spectrometry (SF-ICP-MS; Element 2, Thermo-Fisher). The TEs determined were: Al, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Zr, Mo, Ag, Cd, Ba and Pb. This list includes lithogenic tracers (Al, Ti, Y, Zr), a suite of bioactive elements (P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd), and pollution-derived TEs with no known biological role (Ag and Pb). All filter digestions were performed under Class-100 laminar flow conditions following the protocol of Morton et al. (2013). Briefly, the W41 filter discs were digested in tightly-capped 15 mL Teflon-PFA vials (Savillex) using sequential additions of (1) 500 µL of nitric acid (HNO_3; 15.8 M, Ultrapur, Merck); and (2) 1 mL of HNO_3 (15.8 M, Ultrapur,