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Dissolved aluminium in the Southern Ocean

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ABSTRACT

Dissolved aluminium (Al) occurs in a wide range of concentrations in the world oceans. The concentrations of Al in the Southern Ocean are among the lowest ever observed. An all-titanium CTD sampling system makes it possible to study complete deep ocean sections of Al and other trace elements with the same high vertical resolution of 24 depths as normal for traditional CTD/Rosette sampling. Overall, 470 new data points of Al are reported for 22 full depth stations and 24 surface sampling positions along one transect. This transect consisted of 18 stations on the zero meridian proper from 51°57′ S until 69°24′S, and 4 stations somewhat to the northeast towards Cape Town from 42°20′S, 09°E to 50°17′S, 01°27′E. The actual concentrations of Al in the Southern Ocean were lower than previously reported. The concentration of Al in the upper 25 m was relatively elevated with an average concentration of 0.71 nM ($n=22$; S.D.$=$0.43 nM), most likely due to atmospheric input by a suggested combination of direct atmospheric (wet and dry) input and indirect atmospheric input via melting sea ice. Below the surface waters there was a distinct Al minimum with an average concentration of 0.33 nM ($n=22$; S.D.$=$0.13 nM) at an average depth of 120 m. In the deep southernmost Weddell Basin the concentration of Al increased with depth to ~0.8 nM at 4000 m, and a higher concentration of ~1.5 nM in the ~4500–5200 m deep Weddell Sea Bottom Water. Over the Bouvet triple junction region, where three deep ocean ridges meet, the concentration of Al increased to ~1.4 nM at about 2000 m depth over the ridge crest. In the deep basin north of the Bouvet region the concentration of Al increased to higher deep values of 4–6 nM due to influence of North Atlantic Deep Water. In general the intermediate and deep distribution of Al results from the mixing of water masses with different origins, the formation of deep water and additional input from sedimentary sources at sea floor elevations. No significant correlation between Al and silicate (Si) was observed. This is in contrast to some other ocean regions. In the Southern Ocean the supply of Al is extremely low and any signal from Al uptake and dissolution with biogenic silica is undetectable against the high dissolved Si and low dissolved Al concentrations. Here the Al–Si relation in the deep ocean is uncoupled. This is due to the scavenging and subsequent loss of the water column of Al, whereas the concentration of Si increases in the deep ocean due to its input from deep dissolution of biogenic diatom frustules settling from the surface layer.

1. Introduction

Dissolved aluminium (hereafter Al) occurs in a wide range of concentrations in the world oceans, from as low as 0.1 nM in surface waters of the Pacific Ocean (Orians and Bruland, 1986; Measures et al., 2005) to 174 nM in the Mediterranean Sea (Hydes et al., 1988). Aluminium has been shown to have a quite complex biogeochemistry. Moreover, its residence time is much shorter in the surface ocean than in the deep ocean (Orians and Bruland, 1985, 1986). Fluvial inputs of Al to the open ocean are negligible due to estuarine removal processes (Mackin and Aller, 1984; Tria et al., 2007 and references therein). Maring and Duce (1987) suggested aeolian dust to be the main source of Al to the open ocean, which has since then been confirmed convincingly (Tria et al., 2007 and references therein). In the North West Atlantic Ocean, and also on a global scale, concentrations of Al in the surface ocean have been related to atmospheric dust input (e.g. Gehlen et al., 2003; Kramer et al., 2004; Han et al., 2008). In the surface ocean, Al has a short residence time of only 4 weeks to 4 years (Orians and Bruland, 1986) due to removal from the water column. Several studies have suggested passive, inorganic sorption onto particle surfaces as an important removal mechanism (e.g. Hydes, 1979; Moore and Millward, 1984; Orians and Bruland 1985, 1986). However, there are also indications of active

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uptake of Al by diatoms. These are the nutrient-like increase with depth of Al at several locations (Stoffyn, 1979; Hydes et al., 1988; Chou and Wollast, 1997), as well as the significant correlations often found between dissolved Al and silicate (Mackenzie et al., 1978; Hydes et al., 1988; Kramer et al., 2004; Middag et al., 2009). Moreover, Gehlen et al. (2002) have shown that Al is structurally associated with the biogenic silica of diatom frustules, consistent with earlier studies of Al incorporation in opal frustules of diatoms (Van Bennekom et al., 1989, 1991; Van Beusekom and Weber, 1992). In the deep ocean the concentrations of Al have been suggested to be quasi-conservative (Measures and Edmond, 1990) due to less scavenging. Deep ocean residence times have been estimated to be between 50 and 200 years (Orians and Bruland, 1985, 1986). Additional input in the deeper water column has been suggested via diffusion from the sediments (Hydes, 1977), pressure dependent solubility of Al-containing particles (Moore and Millward, 1984) and shelf water input via deep slope convection (Measures and Edmond, 1992; Middag et al., 2009).

An all-titanium CTD sampling system (De Baar et al., 2008) allows to study complete deep ocean sections of trace elements with the same high spatial resolution of 24 depths as for traditional CTD/Rosette sampling. Here are presented the distributions of Al along a section at (or nearby) the zero meridian (0°W) determined in February–March 2008, during expedition ANT XXIV/3 aboard R.V. Polarstern. This expedition was part of the International Polar Year—Geotraces programme (www.geotraces.org) with the objective to: 'identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions' (Geotraces Science Plan, 2006). Among others, also the distributions of iron (Fe) (Klunder et al., 2011), manganese (Mn) (Middag et al., 2011), zinc (Croot et al., 2011), cadmium and its isotopes (Abouchami et al., in press) and the speciation of zinc (Baars and Croot, 2011) and Fe (Thuróczy et al., 2011) were successfully measured during this expedition. The distributions of Al are compared with the distributions of other variables, notably the salinity and the potential temperature, to gain insight in the sources and cycling of Al in the Southern Ocean and in relation to the world oceans.

2. Methods

2.1. Sampling and filtration

The low density polyethylene bottles (LDPE, Nalgene) used for the storage of reagents and samples were cleaned according to an intensive three-step cleaning procedure as described in Middag et al. (2009). After cleaning, LDPE bottles are suitable for use in the analysis of Al (Brown and Bruland, 2008). Seawater was collected using 24 internally Teflon-coated PVC 12 l GO-FLO samplers (General Oceanics Inc.) mounted on an all-titanium frame that was connected to a Kevlar wire and controlled from onboard (De Baar et al., 2008). Samples were taken at 22 stations along the transect. There were 18 stations on the zero meridian proper from 51°57′ S until 69°24′S near the edge of the continental ice-sheet, and 4 stations on the extension towards Cape Town somewhat to the east in the South East Atlantic Ocean from 42°20′S, 09°E to 50°17′S, 01°27′E (Fig. 1). The 22 deployments of the all-titanium CTD sampling system with 24 GO-FLO samplers resulted in a total of 487 samples that were analysed for Al. This is somewhat less than the theoretical maximum of 528 due to the water requirements of other cruise participants and the occasional malfunctioning of a GO-FLO sampler. Of the 487 samples analysed for Al, 41 samples (8.4%) were suspected outliers and therefore not further used in the data analyses and figures presented. Suspected outliers were labelled as such based on three criteria. When for the sampled GO-FLO the nutrient data (see text Section 2.4.) were anomalous for that depth, indicating closing at the wrong depth, the sample was marked as suspected outlier. In case the trace metal data (Al, Mn and Fe) were elevated for the same GO-FLO for more than one cast, indicating a contaminated GO-FLO sampler, the sample was also marked as a suspected outlier. The third criterion was when 1 data point of Al gave anomalous result for its depth considering the data points at shallower and greater depths. These anomalous data points were identified by visually inspecting the vertical profiles for data points that would not fit in the profile shape. Subsequently, this data point was compared with the values of potential temperature, salinity, nutrients, Mn and Fe to see if those showed a similar trend. If this was the case the data point was left in, if not the following test was applied; a linear regression was determined between the concentrations of Al below and above the suspect data point (2 above and 2 below if possible) versus depth. With the linear regression equation the 'theoretical' concentration was calculated for the depth with the anomalous concentration of Al. When this calculated value was more than 25% lower than the measured value, it was marked as a suspected outlier and not further used in the calculations or graphs.

The complete relational database includes specific flags for suspected outlier values and will be available at the international GEOTRACES data centre (http://www.bodc.ac.uk/geotraces/) and is also available as an Electronic annex with this paper. In between the 22 stations for trace metals and nutrients, another 30 stations were sampled with the regular CTD/Rosette also for nutrients and for other variables (see electronic Supplement).

Samples for Al analysis were taken from the GO-FLO samplers in a class 100 clean room environment. The water was filtered directly from the GO-FLO sampler over a 0.2 μm filter capsule (Sartrobran-300, Sartorius) under nitrogen pressure (1.5 atm). Therefore all data reported in this paper is dissolved Al. The filtered seawater samples were collected in cleaned LDPE sample bottles (125 ml) from each GO-FLO bottle. All sample bottles were rinsed five times with the sample seawater.

Underway surface sampling (target depth of 1.5 m) was conducted during transit between stations from south of 66°01′S onwards until 69°35′S near the continental ice edge. This was done with a towed epoxy-coated stainless steel torpedo deployed off a crane arm on the starboard side of the ship. Water was pumped aboard with an Almatec A-15 Teflon diaphragm pump. A total of 24 samples were sampled inside the same class 100 clean room environment (see above) by in-line filtration over a filter capsule containing a 0.4 μm pre-filter and a 0.2 μm end-filter (Sartrobran P 0.2 μm, Sartorius).

Unfiltered samples for nutrients were collected in high density polyethylene bottles that were rinsed three times with sample water. Samples were stored in the dark at 4 °C prior to analysis (see text Section 2.4.).

2.2. Analyses of dissolved Al

The analyses of dissolved Al were performed on shipboard after the method developed by Resing and Measures (1994) with improvements by Brown and Bruland (2008). This method is a flow injection analysis, based on the fluorescence from the reaction between lumogallion and Al. Samples were stored in a refrigerator (4 °C) and analysed usually within 24 h after sampling but always within 36 h. Samples were acidified 1 h before the start of a run of 10 samples with 12 M ultraclean HCl (Baseline® Hydrochloric Acid, Seastar Chemicals Inc.) to a pH of 1.8. In the flow injection system the samples were buffered inline