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N. J. Wyatt
A. Milne School of Geography, Earth and Environmental Sciences
E. M.S. Woodward
A. P. Rees
T. J. Browning
et al. See next page for additional authors

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Authors
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Biogeochemical cycle of dissolved zinc along the 40ºS South Atlantic GEOTRACES transect

For Submission to Global Biogeochemical Cycles

N.J. Wyatt¹,², A. Milne², E.M.S. Woodward³, A.P. Rees³, T.J. Browning⁴, H.A. Bouman⁴, P.J. Worsfold¹,², M.C. Lohan¹,²

¹Marine Institute, University of Plymouth, PL4 8AA, UK
²School of Geography, Earth and Environmental Sciences, University of Plymouth, PL4 8AA, UK
³Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, UK
⁴Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK

Corresponding author: Neil J. Wyatt, School of Geography, Earth and Environmental Science, University of Plymouth, PL4 8AA, UK (neil.wyatt@plymouth.ac.uk)

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Abstract

The biogeochemical cycle of zinc (Zn) in the South Atlantic, at 40º S, was investigated as part of the UK GEOTRACES programme. To date there is little understanding of the supply of Zn, an essential requirement for phytoplankton growth, to this highly productive region. Vertical Zn profiles displayed nutrient-like distributions with distinct gradients associated with the water masses present. Surface Zn concentrations are among the lowest reported for the world’s oceans (< 50 pM). Highest Zn concentrations were found in Antarctic Bottom Waters (> 8 nM). A strong Zn-Si linear relationship of 65 µmol mol⁻¹ was observed (R² = 0.97, n = 460). Our results suggest that the use of a global Zn-Si relationship would lead to an underestimation of dissolved Zn in deeper waters of the South Atlantic. By utilizing Si* as a tracer for Sub-Antarctic Mode Water, our data indicate that the preferential removal of Zn in the Southern Ocean prevented a direct return path for dissolved Zn to the surface waters of the South Atlantic at 40ºS, and potentially the thermocline waters of the South Atlantic subtropical gyre. The importance of Zn for phytoplankton growth was evaluated using the Zn-soluble reactive phosphorus (SRP) relationship and estimated free Zn²⁺ concentration. We hypothesize that the low Zn concentrations in the South Atlantic may select for phytoplankton cells with a lower Zn requirement. The extremely low Zn concentrations observed in the upper 500 m result in a much deeper kink in the Zn:SRP ratio than observed in other oceanic regions.
1. Introduction

Trace metal micronutrients such as zinc (Zn) play a key role in the productivity of the oceans. Zinc is an essential co-factor in many phytoplankton enzymatic processes [Anderson et al., 1978; Vallee and Auld, 1990; Morel and Price, 2003], and as such is essential for phytoplankton growth. Zinc is used for the uptake of carbon dioxide (CO₂) via the enzyme carbonic anhydrase [Morel et al., 1994; Tortell et al., 2000; Hu et al., 2003] and for organic phosphorus acquisition via the enzyme alkaline phosphatase [Shaked et al., 2006]. In addition, Zn is utilised in both nucleic acid transcription and repair proteins [Montsant et al., 2007]. The vertical profile of Zn in the world’s oceans resembles those of the major nutrients due to biological uptake and utilization [Bruland, 1980; Ellwood, 2008; Lohan et al., 2002; Croot et al., 2011; Jakuba et al., 2012]. The Zn associated with biota and particulates can either be recycled in surface waters, or exported and remineralised at depth. As Zn is essential for phytoplankton growth, it has an impact on the global biological carbon pump. The stoichiometric relationship between Zn and the major nutrients, such as silicate and phosphate, is an important control on the efficiency and size of this pump.

In oceanic surface waters Zn concentrations are < 0.1 nM, with approximately 98 % of this pool chelated by strong organic ligands [Bruland, 1989; Ellwood and van den Berg, 2000; Lohan et al., 2005]. This reduces the bioavailable free Zn²⁺ to concentrations < 2 pM, that have been shown to limit phytoplankton growth in culture experiments [Anderson et al., 1978; Brand et al., 1983; Sunda and Huntsman, 1992, 1995; De La Roche et al., 2000; Saito and Geopfert, 2008]. A Zn concentration of 0.8 pM reduced the activity of carbonic anhydrase in phytoplankton, potentially limiting CO₂ uptake and growth [Morel et al., 1994;
Alkaline phosphatase plays an important role in allowing microorganisms to acquire phosphorus from organic compounds in oligotrophic regimes [Riegman et al., 2000; Dyhrman and Palenik, 2003]. The activity of alkaline phosphatase in phytoplankton was also reduced when grown at 0.4 pM Zn [Shaked et al., 2006]. In diatoms, the uptake of silicate has also been shown to be inhibited by low Zn concentrations [Rueter and Morel, 1981; De La Roche et al., 2000] with possible changes to community structure as a result [Leblanc et al., 2005]. Diatoms are responsible for the majority of carbon exported from the surface to the deep ocean [Nelson et al., 1995; Tortell et al., 2000]. Therefore a community shift, and/or change in silicification rates, under low Zn conditions may alter the silicate to carbon uptake ratio of the phytoplankton community. This in turn has clear implications for the efficiency of the biological carbon pump.

The low Zn concentrations found in open-ocean surface waters are low enough to limit phytoplankton growth based on results from culture studies [Sunda and Huntsman, 1992, 1995; Saito and Goepfert, 2008]. Relatively few shipboard incubation experiments have been conducted with natural assemblages and these showed minimal effects of Zn additions on the bulk phytoplankton community [Coale et al., 2003; Crawford et al., 2003, Leblanc et al., 2005; Lohan et al., 2005; Jakuba et al., 2012]. Consequently, the potential for Zn limitation of phytoplankton growth is still under debate. One possible explanation for the lack of observed Zn limitation during field studies is biochemical substitution. Some phytoplankton have been shown to have a requirement for Zn that can be largely alleviated by either cobalt (Co) or cadmium (Cd) in times of Zn stress [Sunda and Huntsman, 1995; Yee and Morel, 1996; Lee et al., 1995; Saito and Goepfert, 2008]. Furthermore, the evidence for Zn limitation in the oceans may be obscured by the more widespread occurrence of Fe limitation.

What is clear is that our understanding of the impact that dissolved Zn might have on open-ocean primary productivity levels has been hindered by the relative paucity of reliable
Zn data. As Zn is a ubiquitous contaminant and frequently used on marine vessels and equipment, accurate data can only be obtained by adopting strict ultra-clean precautions and protocols during both sampling and analytical procedures [Bruland et al., 1979; De Baar et al., 2008]. Currently, there are no Zn data for the South Atlantic Ocean, although Crook et al. [2011] have reported Zn data from ten profiles along the Zero Meridian between the Antarctic continent and 46° S.

The present study focused on determining the biogeochemical cycle of dissolved Zn along 40° S in the South Atlantic Ocean between South Africa and Uruguay. The South Atlantic is characterised by surface waters that are micronutrient deplete compared with the North Atlantic [Bowie et al., 2002; Ussher et al., 2013] and yet they exhibit considerable surface productivity at 40° S. The enhanced productivity along this section is hypothesised to be derived from the mixing of macronutrient rich waters of the Antarctic Circumpolar Current (ACC) to the south with the phosphate enhanced but nitrate and silicate depleted Sub-Tropical Surface Water (STSW) of the South Atlantic Gyre to the north. However, there is little understanding of the supply of Zn in this region.

2. Methods

2.1. Sampling methods

Seawater samples were collected from 26 stations during two UK-GEOTRACES cruises between South Africa and South America (section GA10, Fig. 1). The first cruise (D357) took place from 18th October – 22nd November 2010, on board the R.R.S. Discovery, whilst the second cruise (JC068) took place from 24th December 2011 – 27th January 2012 on the R.R.S. James Cook. For the D357 cruise, only samples collected below 1000 m are
presented due to the impact of seasonal biological uptake and regeneration processes on Zn concentrations in the upper water column.

All sampling bottles were cleaned according to the procedure detailed in the GEOTRACES sample handling protocols [Cutter et al., 2010]. Seawater samples were collected using a titanium CTD frame fitted with twenty four, 10 L trace metal clean Teflon coated OTE (Ocean Test Equipment) samplers deployed on a plasma rope. Upon recovery, the OTE bottles were transferred into a class 100 clean air container and lightly pressurized (1.7 bar) with high purity compressed air, which was filtered in-line using a 0.2 μm cellulose acetate filter capsule (Sartobran P-300, Sartorius). Samples for dissolved Zn were filtered through 0.8/0.2 μm AcroPak Supor polyethersulfone membrane filter capsules (Pall) into 125 mL low density polyethylene bottles. Each sample was acidified to pH 1.7 (0.024 M) by addition of 12 M hydrochloric acid (HCl, UpA, Romil) under a class 100 laminar flow hood. Vertical profile sampling was augmented by high-resolution underway surface samples. Surface seawater was pumped into the trace metal clean laboratory using a Teflon diaphragm pump (Almatec A-15, Germany) connected by acid-washed braided PVC tubing to a towed ‘fish’ positioned at approximately 2 – 3 m. Underway samples were filtered in-line and acidified as described for samples collected from the titanium sampling system.

2.2. Dissolved zinc determination

Dissolved Zn analysis was carried out in an over-pressurised class 1000 clean air container on-board ship. Dissolved Zn was determined using flow-injection with fluorimetric detection (FI-FL), as first described by Nowicki et al. [1994] and modified by Gosnell et al. [2012]. Briefly, the sample was buffered in-line to pH 5.2 with 0.3 M ammonium acetate before being loaded onto a chelating iminodiacetic acid (IDA, Toyopearl AF-Chelate 650 M) pre-concentration column. The column was rinsed using 0.08 M ammonium acetate to
remove the seawater matrix cations before Zn was eluted from the column with 0.08 M HCl (SpA, Romil). The HCl eluent entered the reaction stream where it mixed with a 40 µM p-tosyl-8-aminoquinoline (pTAQ: Aldrich) solution prepared from a stock solution containing 0.05 M pTAQ, 2 M ammonium hydroxide and 0.5 M boric acid. The emission of the fluorescent complex was detected by a Shimadzu RF-10Ax1 fluorimeter with excitation and emission wavelengths set to 377 nm and 495 nm respectively.

Zinc concentrations were quantified using the method of standard additions to low-Zn (0.08 ± 0.05 nM, n = 10) seawater. Due to the large range of Zn concentrations observed (0.015 - 8.6 nM), it was necessary to use two separate calibration ranges. For samples collected from 0 to 900 m, a calibration range of 0.2 to 1 nM was used, whereas for depths ≥ 1000 m, Zn standards ranged from 1 to 10 nM. All samples and standards were analysed in triplicate.

The accuracy was assessed by the quantification of Zn in surface water (S) and 1000 m water (D2) collected during the SAFe programme [Johnson et al., 2007]. The concentration of Zn measured in the SAFe reference samples during this study yielded values of 0.06 ± 0.02 nM (n = 7) for S and 7.72 ± 0.09 nM (n = 12) for D2 and are in good agreement with the reported consensus values (S = 0.064 ± 0.019 nM; D2 = 7.54 ± 0.14 nM).

Cadmium is known to form a fluorescent complex with the reagent pTAQ. The potential interference from this element on the observed Zn signal was therefore investigated using Cd additions to low-Zn seawater. The interference from Cd contributed up to 67 % of the Zn fluorescence signal. This is comparable to the 70 % reported by Nowicki et al. [1994] and higher than the 30 % reported by Gosnell et al. [2012]. As dissolved Cd exists in seawater at approximately one-tenth the concentration of Zn [Bruland et al., 1978; Bruland, 1980], this resulted in a correction factor of ~ 6.7 % being applied.
2.3. **Nutrients, phytoplankton pigments, temperature and salinity**

The dissolved macronutrients silicate, phosphate, nitrate (determined as nitrate + nitrite, but referred to throughout the paper as nitrate) were determined in all samples for which Zn was determined. In addition, samples for macronutrient determination were collected from a stainless steel rosette. Macronutrients were determined on-board using an AA III segmented-flow AutoAnalyzer (Bran & Luebbe) following colourimetric procedures [Woodward and Rees, 2001]. Clean sampling and analysis procedures were adopted according to international GO-SHIP protocols [Hydes et al., 2010]. Salinity, temperature and depth were measured using a CTD system (Seabird 911+). Dissolved O₂ was determined by a Seabird SBE 43 O₂ sensor. Salinity was calibrated on-board using discrete samples taken from the OTE bottles using an Autosal 8400B salinometer (Guildline) whilst dissolved O₂ was calibrated using a photometric automated Winkler titration system [Carritt and Carpenter, 1966]. For chlorophyll-a analysis, samples were filtered (0.7 µm Whatman GF/F) and then the filters were extracted in 90% acetone overnight [Holm-Hansen et al., 1965]. The chlorophyll-a extract was measured on a pre-calibrated (spinach chlorophyll a standard, Sigma) Turner Designs Trilogy fluorimeter. Phytoplankton pigment samples (0.5 – 2 L) were filtered (0.7 µm Whatman GF/F), flash frozen in liquid nitrogen and stored at -80°C prior to analysis using a Thermo HPLC system. The matrix factorization program CHEMTAX was used to interpret the contribution of taxonomic groups to total chlorophyll-a [Mackey et al., 1996].

3. **Results**

3.1. **Hydrographic setting and macronutrient distributions**
The thermohaline structure of the South Atlantic water column at 40° S is determined largely by water masses that have their origins in the high-latitude regions of the Northern and Southern Hemispheres (Fig. 2A, B). It is at this latitude that the cold and fresh Sub-Antarctic Surface Water (SASW) meets the relatively warm and salty STSW of the South Atlantic gyre. Along the transect, SASW with potential temperature \( \Theta < 15 \, ^\circ \text{C} \) and salinity < 35, occupies large areas within the Cape Basin whereas STSW with \( \Theta > 15 \, ^\circ \text{C} \) and salinity > 35 is more prominent within the Argentine Basin (Fig. 2A, B). The SASW has higher macronutrient concentrations (nitrate > 2.5 µM and silicate > 1.2 µM) compared with those found within the STSW (< 0.1 µM nitrate and < 1 µM silicate) (Fig. 2C, D, E).

Between South Africa and 10° E, the leakage of warm \( (\Theta 15 - 23 \, ^\circ \text{C}) \) and salty \( (S > 35) \) waters from the Agulhas Current (AC) was clearly visible at depths to 200 m (Fig. 2A, B). Nitrate and phosphate concentrations within the AC were extremely low (0.02 µM and 0.1 µM respectively) (Fig. 2C, D).

The Brazil Current (BC) is also clearly distinguishable by the intrusion of warm \( (\Theta 15 - 25 \, ^\circ \text{C}) \) and salty \( (S 35 - 37) \) water to depths of 200 m (Fig. 2A, B). The macronutrient concentrations in the BC were similar to those found within the STSW. Inshore from the BC at 54° W, salinity decreased to 28.5 due to freshwater discharge from the Rio de la Plata estuary. High silicate and nitrate concentrations (22.2 µM and 13.9 µM respectively) were observed within the vicinity of the low salinity signal.

The two primary intermediate water masses are Antarctic Intermediate Water (AAIW) and Upper Circumpolar Deep Water (UCDW) (Fig. 2A). AAIW is thought to be formed by upwelling of circumpolar deep water in either the southeast Pacific Ocean [McCartney, 1977; Talley, 1996] or in the winter waters of the Bellinghausen Sea [Santoso and England, 2004; Naveira Garabato et al., 2009] and was identified along the transect by its salinity minimum \( (S < 34.4) \) between 500 and 1250 m. Below this, the UCDW, the upper branch of circumpolar
deep water that arises from the mixing of upwelled water circulating in the ACC, was located at depths between 1250 and 1750 m. Nitrate and phosphate concentrations within these intermediate waters increased with depth to ~32 µM and ~2.25 µM respectively at 1750 m (Fig. 2C, D). It is these intermediate waters, along with the thermocline waters, that constitute the main return branch of the South Atlantic thermohaline overturning circulation [Donners and Drijfhout, 2004; McDonagh and King, 2005].

The abyssal layer at this latitude is filled by cold, nutrient-rich bottom waters formed around Antarctica, often referred to collectively as Antarctic Bottom Water (AABW) (Fig. 2A - E). AABW macronutrient concentrations were the highest observed with nitrate, phosphate and silicate concentrations of ~36 µM, ~2.6 µM and ~129 µM respectively. At 40°S the southward flowing NADW occupies the majority of water between the intermediate waters at around 1750 m and AABW at around 3500 m and can be identified by its deep salinity maximum (S > 34.75) and reduced macronutrient concentrations (Fig. 2A - E) compared with its encompassing Southern Ocean-derived water masses.

3.2. Distribution of dissolved zinc in the South Atlantic

The vertical profiles of dissolved Zn showed typical nutrient-like distributions for all stations with low Zn concentrations (0.015 - 0.90 nM) in the upper 500 m increasing to values around 8 nM in AABW (Fig. 3). A slight reduction in Zn was observed between 1500 and 2500 m associated with the core of the NADW compared with the Zn-enriched Southern Ocean waters that encompass it. The NADW reduction varied between 0.1 and 0.5 nM along the section with the exception of two stations in the west Argentine Basin where Zn concentrations decreased by 1.3 nM.

The surface waters were sampled in late December and January and therefore represent austral summer conditions. The concentrations of Zn in the upper surface layer (10
averaged 0.13 ± 0.09 nM except for stations close to the South African and South American continents where Zn concentrations of 0.40 nM and 1.15 nM respectively were observed. A sub-surface Zn minimum (0.09 ± 0.07 nM, n = 15) was observed at most stations at depths between 25 and 100 m. The Zn minimum was generally located within the vicinity of the chlorophyll-α maximum, but no relationship (p > 0.05) was observed between Zn and chlorophyll-α concentration in the Cape Basin. However, for the Argentine Basin, a significant negative correlation between Zn and chlorophyll-α concentration was observed ($R^2 = 0.91$, p < 0.01, n = 11).

Zinc concentrations obtained from the underway sampling system (2 - 5 m) were within the range of the averaged upper 25 m samples from the CTD. The highest Zn concentrations were found on the Uruguayan Shelf (0.70 - 1.25 nM) and coincided with elevated silicate concentrations and a decrease in salinity from 32.6 to 29.4, indicating that this region is influenced by freshwater inputs from the Rio de la Plata.

Within the Cape Basin, the stations closest the South African continent displayed the highest upper surface layer Zn concentrations, averaging 0.39 ± 0.01 nM, whilst surface concentrations for the open-ocean Cape Basin averaged 0.05 ± 0.04 nM. Below the upper surface layer, Zn concentrations at all stations increased to ~ 0.50 nM at 500 m, before increasing through the salinity minimum of AAIW to reach values of ~ 3 nM at 1000 m. Below the AAIW, Zn was elevated to ~ 4 nM within the UCDW and remained fairly constant (4 – 5 nM) throughout the underlying NADW. Below the NADW, the northward flowing, cold and nutrient rich AABW was channelled between the South African continental slope and the mid-Atlantic ridge, elevating the Zn concentrations to > 7 nM at all stations.

Within the Argentine Basin, the stations closest to the South American continent displayed the highest upper surface layer Zn concentrations for the entire transect (1.25 nM). Zinc concentrations for the open-ocean Argentine Basin averaged 0.15 ± 0.10 nM. The
Argentine Basin sub-surface minimum of 0.11 ± 0.07 nM was more than double that of the Cape Basin. Unlike the Cape Basin, the Zn concentrations in the Argentine Basin did not increase uniformly to 0.5 nM at 500 m but instead was quite variable in its distribution, reaching concentrations between 0.6 and 0.9 nM at this depth (Fig. 3). Like the upper water column, the Zn distribution in the intermediate and deep waters of the Argentine Basin was not as longitudinally uniform as those in the east (Fig. 3). The Zn concentrations in the NADW and AABW were similar to those found in the Cape Basin. The introduction of Weddell Sea Deep Water (WSDW; θ < 0° C, Fig. 2A), a form of AABW that originates from large-scale mixing in the Weddell Basin [Orsi et al., 1999; Naveira Garabato et al., 2002; Huhn et al., 2008], to the Argentine Basin below 4500 m and the subsequent upwelling of NADW as AABW travelled north over the Southern Ocean ridge systems resulted in higher Zn concentrations at 3000 m relative to the Cape Basin (Fig. 3). At two stations above the South American continental slope, Zn concentrations as low as 1.7 nM were observed between 1750 and 3000 m (Fig. 3), which coincided with reduced potential temperature, salinity and macronutrient values (Fig. 2 A - E), indicating the mixing of different water masses.

### 3.3. The zinc-silicate relationship in the South Atlantic

As widely reported for the ocean environment [Bruland and Franks, 1983; Martin et al., 1990; Lohan et al., 2002; Ellwood, 2008; Croot et al., 2011], the full water column dissolved Zn profile is similar to that of dissolved silicate (Fig. 2E and 3). However, unlike Zn, which decreased to near-zero concentrations at the surface, silicate concentrations at the majority of stations were homogenous within the top ~50 m, suggesting that Zn may become limiting to phytoplankton growth before silicate.
Using the complete data set, a significant Zn versus Si correlation, Zn (nM) = 0.065 Si (µM) + 0.209 (R² = 0.97, n = 460) was observed (Fig. 4). Separate linear regressions of the Zn and Si data from different water masses (Fig. 4) resulted in slopes ranging from 0.020 to 0.066. The highest Zn:Si ratios were observed in the intermediate waters (66 µmol mol⁻¹) that originate in the silicate-deplete regions of the Southern Ocean, whilst the lowest ratios were observed in the upper 500 m (25 µmol mol⁻¹), where Zn concentrations were extremely low, and in AABW (20 µmol mol⁻¹), where silicate concentrations were relatively high.

3.4. The Zn-SRP relationship in the South Atlantic

A relationship between dissolved Zn and SRP similar to that observed between Zn and silicate, was observed for the complete data set, consistent with biological uptake and vertical export of Zn (Fig. 5A). The slopes of the Zn to SRP ratio reflect the aggregate stoichiometry of biological processes [Saito et al., 2010]. As shown in Fig. 5B, this relationship has a ‘kink’ at 500 m, which separates samples from the upper 500 m with a Zn:SRP ratio of 349 µmol mol⁻¹ from samples collected at 500 – 1250 m depth with a ratio of 4604 µmol mol⁻¹ in the AAIW that sits immediately below. For the samples from the upper 500 m a negative intercept was observed (-0.01), an indication that Zn distribution was controlled primarily by phytoplankton uptake.

4. Discussion

4.1. Zinc in South Atlantic surface waters

The concentrations of Zn in the upper 25 m of the open South Atlantic Ocean (0.13 ± 0.09 nM) are much lower than the 0.5 – 0.7 nM reported for both the open North East
Atlantic and Atlantic sector of the Southern Ocean [Nolting et al., 2000; Croot et al., 2011], and are more typical of the concentrations reported for the North East Pacific [Lohan et al., 2002; Jakuba et al., 2012], the Pacific sector of the Southern Ocean [Coale et al., 2005] and the Indian Ocean [Gosnell et al., 2012]. Zinc concentrations observed within the upper 25 m of the central Cape Basin are some of the lowest values reported for the world’s oceans. Such low concentrations may be explained by a combination of the origins of the surface waters present at 40° S and the biological removal of Zn. As the SASW waters travel north into the South Atlantic, the concentrations of both Zn and silicate decrease due to the constant export of biogenic particles, including diatom frustules [Loscher, 1999]. The incorporation of Zn and silicate into diatom opal [Ellwood and Hunter, 2000a; Anderson et al., 2011] allows for a deeper regeneration cycle than those of nitrate and phosphate [Bruland and Franks, 1983; Collier and Edmond, 1984]. In the central Cape Basin, chlorophyll-α was > 0.5 mg m⁻³ in the upper 25 m. The sub-surface Zn minimum for the Cape Basin coincided with the chlorophyll-α maximum, indicating that uptake by phytoplankton, and export from surface waters, is an important mechanism for Zn removal from the mixed layer. This observation is consistent with the findings of Loscher [1999] and Croot et al. [2011] who also reported low sub-surface Zn concentrations in the vicinity of elevated chlorophyll concentrations for the Southern Ocean.

In contrast to the Cape Basin, chlorophyll-α concentrations in the upper 25 m of the Argentine Basin were lower (~ 0.2 mg m⁻³) whilst Zn concentrations were slightly higher, hence phytoplankton growth and productivity may have been primarily limited by the low macronutrient concentrations of the STSW. Another possible explanation for the slightly elevated Zn in the surface waters of the Argentine Basin is the deposition of atmospheric dust transported from the Patagonian Desert. Atmospheric sources are hypothesised to provide a minimal supply of soluble Zn to these waters (R. Chance, 2012, personal comm.). A second
possible source of Zn is through the upwelling of Zn-rich waters from below. The upwelling of AAIW into the upper 500 m due to the introduction of WSDW in the deep Argentine Basin resulted in elevated Zn concentrations of 0.1 - 0.3 nM at 50 to 100 m (Fig. 3), which could potentially penetrate into the upper 25 m.

The coastal waters were enriched with Zn within the upper 25 m compared with the open-ocean. The South African coastal stations had upper surface Zn concentrations similar to those reported for surface waters of the AC in the Indian Ocean, off South Africa [Gosnell et al., 2012]. Reduced macronutrient and chlorophyll-a concentrations in the AC prevented the depletion of Zn in these waters. Higher Zn concentrations were observed on the Uruguayan Shelf and coincided with a decrease in salinity and an increase in temperature and macronutrient concentrations, most notably silicate. These elevated Zn and silicate concentrations result from the discharge of freshwater from the Rio de la Plata estuary.

4.2. Zinc in South Atlantic deep waters

The distribution of Zn in the deep waters (> 1750 m) at 40˚ S is primarily influenced by the inflow of NADW and AABW. The intrusion of NADW is clearly identified by lower Zn (Fig. 3) and nitrate (Fig. 2C) concentrations as it moves southwards between 1750 - 3500 m depth in the Cape Basin and 1750 – 3000 m depth in the Argentine Basin. The Zn concentrations observed in the NADW are consistent with the values of 4.2 – 4.5 nM reported for the NADW by Croot et al. [2011], for a Southern Ocean station north of the Antarctic Polar Front at 50˚ S, 0˚ W.

High Zn concentrations averaging 7.2 nM were observed in the AABW of the Cape Basin below 3000 m (Fig. 3). Our data are higher than the values reported by Croot et al. [2011], who did not observe Zn concentrations above 6.2 nM, and agree more closely with the values of 7 – 8 nM reported by Loscher [1999] for lower circumpolar deep water. Local
enrichments in Zn concentration between 8 - 8.6 nM were observed within the deep Cape Basin at depths just above the sea floor, which coincided with elevated silicate concentrations of 107 µM. This suggests that the re-suspension of opal-rich sediments may be an important source of Zn and silicate to the water column in this region.

Within the Argentine Basin the introduction of WSDW (Fig. 2A) forces AABW to upwell and subsequently Zn concentrations were higher at 3000 m depth in the Argentine Basin compared with the Cape Basin (Fig. 3). Croot et al. [2011] observed no elevation in deep water Zn concentration associated with the Bouvet Ridge system to the south of our transect which may have been a possible source of Zn to the deep waters of the Cape Basin at 40° S as it travelled north with AABW. Furthermore, we observed no Zn inputs from the mid-Atlantic Ridge, suggesting that hydrothermal activity is not a significant source of dissolved Zn to the South Atlantic Ocean and Atlantic sector of the Southern Ocean, as has also previously been reported for Fe [Klunder et al., 2011] and Mn [Middag et al., 2011].

### 4.3. The Zn-Si relationship in the South Atlantic

The overall Zn:Si ratio of 65 µmol mol⁻¹ observed during this study (Fig. 4) is similar to the 77 µmol mol⁻¹ reported for the Southern Ocean [Ellwood, 2008] and the 59 µmol mol⁻¹ reported for both the Drake Passage [Martin et al., 1990] and Indian Ocean [Gosnell et al., 2012]. The ratio observed in the upper water column (25 µmol mol⁻¹) is similar to that reported for the highly-productive surface waters of the Ross Sea (17 µmol mol⁻¹) by Fitzwater et al. [2000]. Culture studies have shown that the majority of Zn in diatoms is incorporated into organic material (> 97%), yet the Zn:Si ratio in the opal of diatom frustules is positively correlated with the availability of free Zn²⁺ in the growth media [Ellwood and Hunter, 2000a]. The physiological mechanisms that determine why Zn and silicate should be correlated in the oceans are unclear. Initial studies have shown that silicate uptake by diatoms...
is inhibited by a Zn deficiency [Rueter and Morel, 1981; De La Rocha et al., 2000; Ellwood and Hunter, 2000]. Recent studies have shown that Zn facilitates the uptake of silicate at low silicate concentrations by its presence in the active centre of silicon containing transmembrane proteins [Grachev et al., 2005, 2008]. Danilovtseva et al. [2009] suggest that it may be polyamine-Zn complexes located within the active centres of these transport proteins that aid the assimilation of silicate from seawater by silicifying organisms.

The observed trends in Zn:Si ratios from seawater have been used to estimate the changes in trace metal availability in surface waters [Ellwood and Hunter, 2000b; Hendry and Rickaby, 2008; Andersen et al., 2011]. Benthic foraminifera Zn:Ca ratios have been shown to reflect bottom-water Zn concentrations and can therefore be used as a sensitive paleo-tracer for the glacial-interglacial interactions between NADW and the Southern Ocean derived deep waters [Marchitto et al., 2000, 2002]. However, owing to a lack of deep water Zn data, the validation of this hypothesis is dependent on the estimation of bottom-water Zn concentrations using a global deep water (>1000 m) Zn-silicate relationship (Zn = 0.052[Si] + 0.79) and measured silicate concentrations [Marchitto et al., 2000]. Our new, large data set suggests that this approach may result in an underestimation of Zn concentrations in the bottom waters of the South Atlantic and subsequently an underestimation of the Zn concentrations in past oceans. By applying our AABW relationship of Zn = 0.02[Si] + 5.13 to the measured silicate values, we estimate a mean AABW Zn concentration of 7.40 ± 0.21 nM compared with the measured concentration of 7.44 ± 0.44 nM. This is higher than the 6.69 ± 0.56 nM estimated by the global deep water relationship of Marchitto et al. [2000]. Our data therefore highlights the requirement for more concomitant deep water Zn and silicate data to accurately determine the relationship between present and past ocean Zn biogeochemistry.

4.4. The biological control on zinc distribution in the South Atlantic
Correlations between Zn and SRP have been reported as evidence for biological uptake and remineralisation [Sunda and Huntsman, 1995]. Studies in the North Pacific, the Southern Ocean, the Indian Ocean and the Ross Sea have shown that the Zn:SRP ratio exhibits a distinct kink in its profile between 20 and 150 m with separate relationships above and below these depths [Martin et al., 1989; Saito et al., 2010; Croot et al., 2011; Jakuba et al., 2012]. The Zn:SRP ratio in this study also showed a kink at ~1.5 µM SRP but at a much greater depth of ~ 500 m (Fig. 5B). The relationship found above and below the kink were similar to values from the sub-arctic North Pacific, with a Zn:SRP ratio of 349 µmol mol$^{-1}$ in waters above 500 m and 4604 µmol mol$^{-1}$ in the AAIW that sits immediately below 500 m.

An explanation for the apparent kinks in these linear relationships is still under debate due to our limited knowledge of Zn biogeochemistry, which is hindered by a paucity of Zn data. The mechanisms proposed for this kink include: (1) the excess uptake of Zn by phytoplankton at the base of the euphotic zone followed by export and remineralisation of high Zn:SRP particulate material in deeper waters [Saito et al., 2010]. The presence of Zn-binding ligands in excess of the Zn concentration may also contribute to this effect as the free Zn$^{2+}$ concentration will decrease concurrently and (2) the influence of Fe limitation, which decreases the uptake P whilst maintaining metal uptake rates, resulting in increased cellular metal:P ratios through a process termed ‘growth-rate dilution’ [Sunda and Huntsman, 2000; Cullen et al., 2003; Cullen, 2006]. Both mechanisms would result in elevated Zn:SRP ratios in phytoplankton that should consequently deplete Zn relative to SRP in the upper water column, followed by export and remineralisation below the euphotic zone.

According to the Redfield theory [Redfield, 1963], if phytoplankton are primarily responsible for the relative changes in Zn:SRP ratio then these values presumably reflect the Zn:SRP ratio in phytoplankton responsible for the removal of these elements. The Zn:SRP ratios observed in the South Atlantic can therefore be compared with the trace metal
requirements of phytoplankton grown in cultures under growth-rate-limiting conditions [Sunda and Huntsman, 1992, 1995] and subsequently used to interpret the biological impact that Zn concentrations have in this region. Based on analyses of pigment markers, the dominant phytoplankton species within the open South Atlantic Ocean during this study were estimated to be haptophytes (approx. 51 % of total chlorophyll-a). In contrast, diatoms made up approximately 11 % of total chlorophyll-a in the open-ocean (approx. 13 – 23 % of total chlorophyll-a). Our upper 500 m Zn:SRP ratio of 349 µmol mol\(^{-1}\) was in excess of the minimum Zn concentration required for optimal growth by the small open-ocean diatom *Thalassiosira oceanica* (~ 110 µmol mol\(^{-1}\)) but not the haptophyte *E. huxleyi* (~ 1100 µmol mol\(^{-1}\)).

Using the variations in Zn:SRP, we estimated free Zn\(^{2+}\) concentrations [Sunda and Huntsman, 1992, 1995] of 0.6 – 80 pM, which are similar to the sub-arctic North Pacific [Jakuba et al., 2012] but lower than the Zn-ligand saturated, high Zn surface waters of the Southern Ocean (Zn\(^{2+}\) >100 pM) [Croot et al., 2011]. At free Zn\(^{2+}\) concentrations of 1 pM, the growth rate of the haptophytes *E. huxleyi* and *Phaeocystis antarctica* as well as the coastal diatoms *T. pseudonana* and *T. weissflogii* was limited in culture studies [Sunda and Huntsman, 1992, 1995; De La Roche et al., 2000; Saito and Goepfert, 2008]. These results suggest that the extremely low Zn concentrations in the South Atlantic Ocean may influence phytoplankton species composition by selecting for phytoplankton cells which have a lower cellular requirement for Zn. This is in contrast to the observed phytoplankton distribution, where the highest haptophyte abundance corresponded with the lowest Zn concentrations. The haptophytes *E. huxleyi* and *P. antarctica*, as well as several diatoms, have been shown to substitute Co for Zn and vice versa in growth-limiting culture experiments [Sunda and Huntsman, 1995; Saito and Goepfert, 2008]. There is also evidence for this substitution in oceanic environments [Jakuba et al., 2008].
During our study, a weak but significant relationship ($R^2 = 0.21$, $p < 0.05$, $n = 21$) was observed between the open-ocean Zn concentration and the marker pigment for diatom distribution (total chlorophyll-$a$ normalized fucoxanthin). This may be in part due to the low cellular Zn requirement of open-ocean diatom species such as *T. oceanica* [Sunda and Huntsman, 1992, 1995], which is a likely evolutionary adaptation to more oligotrophic and Zn-deplete waters. Only at the lowest Zn concentrations (~ 15 pM) observed for the South Atlantic would the estimated free Zn$^{2+}$ concentration (~ 0.6 pM) be potentially growth limiting to *T. oceanica*.

4.5. **The Southern Ocean control on zinc distribution in the upper 500 m**

An intriguing result of this study is the extremely low Zn and silicate concentrations within the upper 500 m (Fig. 2E and 3). This is in contrast to both nitrate and phosphate (Fig. 2C, D) whose concentrations increase significantly below 50 m. One explanation for this may be that unlike nitrate and phosphate, Zn and silicate are not being returned to the upper 500 m at 40˚ S by Southern Ocean mode waters. The Southern Ocean is a critical region for the biological carbon pump, strongly influencing both integrated global export [Sarmiento et al., 2004; Palter et al., 2010] and the overall efficiency of the pump [Sarmiento and Orr, 1991; Marinov et al. 2006, 2008].

Sub-Antarctic Mode Water (SAMW) has been identified as the main conduit returning nutrients from the surface waters of the frontal Southern Ocean to the thermocline waters of the Southern Hemisphere [Toggweiler et al., 1991; Sarmiento et al., 2004; Palter et al., 2010], accounting for about three quarters of biological production north of 30˚ S [Sarmiento et al., 2004]. One unusual characteristic of SAMW is its low silicate:nitrate ratios, generally attributed to the preferential removal of silicate by diatoms under Fe limitation [Franck et al., 2000; Timmermans et al., 2004]. Given the high Zn requirement by diatoms
for silicate uptake and the strong oceanic Zn:Si relationship, it is reasonable to assume that the removal of silicate in the SAMW formation regions would also result in the removal of Zn from these surface waters.

In Figure 6, we have utilised the Si* tracer of SAMW \([\text{Si*} = \text{Si(OH)}^- - \text{[NO}_3^-]\), [Sarmiento et al., 2004] to map this water mass at 40° S. Negative Si* values between 100 and 1000 m indicate that this tracer included the upper portion of AAIW, which is formed immediately to the south of SAMW in the Southern Ocean. Whilst SAMW exhibited elevated concentrations of both nitrate and phosphate at depths of 500 m and above (Fig. 6), the Zn and silicate concentrations however, did not increase until below 500 m, suggesting that SAMW was not a significant return path for Zn or silicate from the Southern Ocean. Instead, Zn was returned primarily within AAIW between 500 and 1250 m depth. This argument is strengthened by the kink in the Zn:SRP ratio being observed at 500 m rather than at the shallower depths reported for other oceanographic regions. Below 500 m, our AAIW Zn:SRP ratio of 4604 µmol mol\(^{-1}\) is slightly higher than the 3800 µmol mol\(^{-1}\) reported for the AAIW formation region of the Southern Ocean [Croot et al., 2011]. The difference between these ratios may reflect the export of Zn-rich biogenic particles out of SAMW as this water mass travels north and their subsequent remineralisation in the underlying AAIW, further reducing the potential for SAMW to return Zn efficiently to the upper thermocline waters of the South Atlantic Ocean.

The Si* tracer can also be used to provide a further insight into the nutrient status of diatoms in the South Atlantic. Diatoms with adequate light and nutrients (including Fe) are reported to contain silicate and nitrate in a mole ratio of about 1:1 [Ragueneau et al., 2000], which requires Si* ≥ 0 [Sarmiento et al., 2004]. The presence of negative Si* SAMW at the base of the thermocline at non-coastal stations along this transect (Fig. 6) is associated with a Si:N ratio of ≤ 0.5, suggesting low diatom production. Using our data at 40° S we hypothesize
that the potential for low diatom production in this region, and most likely throughout the
open South Atlantic Ocean, may be in-part facilitated by the availability of dissolved Zn, which is maintained at extremely low concentrations by the lack of a significant Southern Ocean return path with SAMW.

5.5. Conclusions

We present dissolved Zn data for 556 discrete samples, the largest Zn data set reported to date. Surface Zn concentrations of 0.015 - 0.39 nM are among the lowest reported for the world’s oceans, indicating the absence of a significant source of Zn to these waters and the potential for Zn limitation of phytoplankton growth. Here we suggest, using the Si* tracer, that the low surface Zn concentrations are sustained by the lack of a return path from the Southern Ocean that returns high nitrate and phosphate concentrations to the thermocline waters at this latitude. Despite this, phytoplankton groups with cellular Zn requirements in excess of that available in the surface waters were dominant along the transect, suggesting the potential co-substitution of Zn for alternative trace metals. The kink in the Zn-SRP relationship at ~ 500 m indicates that Zn is returned at this depth primarily by AAIW and that the kink is a result of the relative differences in biological utilization between water masses. A strong relationship between Zn and silicate, Zn (nM) = 0.065 Si (µM) + 0.209 ($R^2 = 0.97, n = 460$), was observed. Separate linear relationships observed between Zn and silicate for NADW and AABW highlight the need for a more deep Zn concentration data for estimating deep water Zn concentrations in paleo-oceanography.

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**Figure 1.** The stations sampled for dissolved Zn along section GA10 during 2 UK GEOTRACES cruises D357 (circled) and JC068. The 3 stations closest to S. Africa were reoccupied during JC068.
**Figure 2.** Distributions of (A) potential temperature, (B) salinity, (C) nitrate, (D) phosphate and (E) silicate showing the water masses occupying 40° S. Abbreviations in alphabetical order: AABW: Antarctic Bottom Water; AAIW: Antarctic Intermediate Water; AC: Agulhas Current; BC: Brazil Current; NADW: North Atlantic Deep Water; SASW: Sub-Antarctic Surface Water; STSW: Sub-Tropical Surface Water; UCDW: Upper Circumpolar Deep Water; WSDW: Weddell Sea Deep Water.
Figure 3. Concentrations of dissolved Zn in the upper 500 m (upper plot) and full depth (lower plot). Water mass abbreviations are outlined in Figure 2.

Figure 4. Concentrations of dissolved Zn versus dissolved silicate for the complete dataset. The Zn:Si ratio varies according to the water mass analysed: upper 500 m (squares, $0.025x + 0.111$); the intermediate waters of AAIW and UCDW (red circles, $0.066x + 0.283$); NADW (grey circles, $0.034x + 2.71$); AABW (triangles, $0.020x + 5.129$).
Figure 5. Concentrations of dissolved Zn versus soluble reactive phosphorus (SRP) for (A) the complete section and (B) the upper 500 m (open circles) and between 500 and 1250 m (AAIW, filled squares).
**Figure 6.** Vertical profiles of dissolved Zn (filled circles), silicate (open circles), nitrate (filled circles) and soluble reactive phosphorus (SRP) (open circles) from stations 3 (Cape Basin) and 16 (Argentine basin) showing the influence of SAMW (Si* < 0). Also shown for each station is the corresponding temperature (black line).