



## Dissolved iron in the Southern Ocean (Atlantic sector)

M.B. Klunder<sup>a,\*</sup>, P. Laan<sup>a</sup>, R. Middag<sup>a</sup>, H.J.W. De Baar<sup>a,b</sup>, J.C. van Ooijen<sup>a</sup>

<sup>a</sup> Royal Netherlands Institute for Sea Research (Royal NIOZ), P.O. Box 59, 1790 AB, Den Burg, Texel, The Netherlands

<sup>b</sup> Department of Ocean Ecosystems, University of Groningen, Groningen, The Netherlands

### ARTICLE INFO

#### Article history:

Received 21 October 2010

Accepted 21 October 2010

Available online 3 December 2010

#### Keywords:

Iron  
Hydrothermal  
Upwelling  
Sea-ice  
Dust  
Antarctic  
Southern Ocean  
Antarctic Circumpolar Current  
Weddell Gyre

### ABSTRACT

We report a comprehensive dataset of dissolved iron (Fe) comprising 482 values at 22 complete vertical profiles along a 1° latitudinal section at the Zero meridian. In addition a shorter high resolution (~00°09') surface section of the southernmost part of the transect (66°00'–69°35'S) is presented. Within the upper surface mixed layer the concentrations of dissolved Fe vary between 0.1 and 0.3 nM. An inverse trend versus fluorescence suggests significant Fe removal by plankton blooms. Vertical mixing and upwelling are the most important supply mechanisms of iron from deep waters to the upper surface mixed layer. At lower latitude (42°S) there is a distinct maximum of 0.6–0.7 nM in the 2000–3000 m depth range due to inflow of North Atlantic Deep Water. In one region (55°S) elevated dissolved Fe found in the surface mixed layer is ascribed to the recent deposition of aeolian dust originating from South America. Close to the Antarctic continent there is an indication of Fe supply in surface waters from icebergs. In the deep waters there is a strong indication of a hydrothermal plume of dissolved Fe and Mn over the ridge in the Bouvet region (52–56°S). In the Weddell Gyre basin the dissolved Fe in the deep water is  $0.47 \pm 0.16$  nM in the eastward flow at ~56–62°S and is lower with a value of  $0.34 \pm 0.14$  nM in the westward flow at high ~62–69°S latitude. At the edge of the continental ice-sheet on the prime meridian, the continental margin of the Antarctic continent appears to be lesser source of dissolved Fe than in any other place in the world; this is likely because it is unique in being overlain by the extending continental ice-sheet that largely prevents biogeochemical cycling.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Dissolved Fe has been recognized to be a key element for phytoplankton growth in the world oceans (Coale et al., 1996). It is needed for important biological processes such as photosynthesis and is used in several enzymes (Sunda, 2001). Although Fe is the fourth most abundant element in the earth crust, it is only available in trace concentrations (generally < 1 nM) in the oxygenated water of the world oceans (De Baar and De Jong, 2001). In the Southern Ocean, the presence of ample major nutrients (N,P, and Si) yet low phytoplankton abundance has been hypothesized to be due to the lack of this essential trace nutrient (Gran, 1931; Hart, 1934, 1942; Martin, 1988) in combination with low light conditions (Sunda and Huntsman, 1997). This was first confirmed in bottle incubations by De Baar et al. (1990) and Buma et al. (1991), and since then has been verified by others—see review by De Baar and Boyd (2000). During *in situ* Fe fertilization experiments the effect of extra Fe was shown repeatedly; however the light limitation effect of deep Surface Mixed Layers due to high wind velocity also plays a key role (see reviews by De Baar et al., 2005; Boyd et al., 2007). More recently natural Fe

fertilization was reported over shallow plateau regions around subantarctic islands (Blain et al., 2007; Pollard et al., 2009).

Because of the low concentration of dissolved Fe in open ocean waters, the sampling, filtration and analysis are very sensitive to contamination. As a result the world ocean dataset of dissolved Fe in the published literature is quite small in number of datapoints and in geographical and vertical distribution, notably in the Southern Ocean.

Recently, more ocean datasets of dissolved Fe have become available in the Southern Ocean (Sedwick et al., 1997, 2008; Sohrin et al., 2000; Boye et al., 2001; Measures and Vink, 2001; Croot et al., 2004; Nishioka et al., 2005; Planquette et al., 2007; Blain et al., 2008a; Lai et al., 2008), and elsewhere (Bell et al., 2002; Laës et al., 2003, 2007; Sarthou et al., 2003; Boyle et al., 2005; Measures et al., 2008). Recent world ocean data compilations have also been made (Gregg et al., 2003; Parekh et al., 2004; Moore and Braucher, 2008) and include Fe values in the Southern Ocean. Nevertheless, determination of the concentration and basin wide gradients of dissolved iron in the deep ocean basins remains a challenge in oceanography, mainly in the (less studied) deep Southern Ocean.

With the purpose of addressing this issue, two new developments have allowed major progress in sampling trace metals over the recent years. Firstly, a new ultra clean sampling system has been developed and successfully tested (De Baar et al., 2008)

\* Corresponding author. Tel.: +31 222 369 459.

E-mail address: Maarten.klunder@nioz.nl (M.B. Klunder).

(see Section 2), allowing faster and more reliable clean sampling at higher resolution, of specifically the deep waters. Secondly, international exercises (Bowie et al., 2003, 2006; Johnson et al., 2007) have eventually led to the availability of certified reference samples of dissolved Fe in seawater.

Several sources of dissolved Fe to the Southern Ocean can be envisioned. The Fe in surface waters may come from above by dust input originating from adjacent continental source regions, notably Patagonia (South America), South Africa and Australia (Jickells and Spokes, 2001; Sedwick et al., 2008). Alternatively Fe may come from below by upwelling and upward mixing of deeper waters containing higher dissolved Fe than the surface waters (Löscher et al. 1997; Croot et al., 2004; Lai et al., 2008). Obviously the deep waters would in turn need a source as well, where reductive dissolution within suboxic marine sediments and remineralization of particles are known sources of Fe (De Baar and De Jong, 2001) and Mn (Froelich et al., 1979). Hydrothermal vents at active mid-ocean ridges are another known source of dissolved Fe and Mn (Klinkhammer et al., 2001). The parallel determination of dissolved Mn (Middag et al., 2011) may provide clues as to these source terms. Finally in the polar oceans, meltwater from the continental Antarctic ice-sheet continuously flows into the sea where some of its Fe contents may become dissolved. Moreover, icebergs broken off from the ice-sheet often become temporarily grounded on the shelf and entrain dirt hence Fe from the shelf sediments (Löscher et al., 1997). Finally, the seasonal sea-ice also comprises some Fe (Lannuzel et al., 2008) which upon melting may contribute to the Fe content of the surface waters.

Here we present the distribution of dissolved Fe at a high resolution ( $1^\circ$  latitude) transect (Fig. 1) over the complete 4–5 km depth of the water column, overall 482 dissolved Fe values at 22 stations with 20–24 sample depths. This section is designed across the Antarctic Circumpolar Current (ACC) as to be representative of the ACC flowing all around Antarctica. Moreover the southernmost part of the section represents the eastern extent of Weddell Gyre. Within the Weddell Gyre, an additional small set of 24 samples for dissolved Fe was collected in the very same surface waters from  $66^\circ 02.18'S$ – $69^\circ 35.15'S$  by deployment of a towed fish so as to obtain high ( $\sim 00^\circ 09'$ ) resolution surface water concentrations. This sampling scheme allowed us to accurately determine the distribution of dissolved iron, and establish its sources in the Atlantic sector of the Southern Ocean.

## 2. Materials and methods

### 2.1. Sampling

#### 2.1.1. Vertical profile sampling

Seawater samples were collected during the ANT XXIV/3 expedition of the R.V. Polarstern (Cape Town to Punta Arenas: 10 February until 14 April 2008) on its first transect from Cape Town to the Antarctic ice-sheet of Antarctica (Fig. 1). Here, in total 22 stations were sampled for analyses of dissolved Fe and other trace metals (see Section 2.4). On the prime meridian transect, the resolution is typically  $1^\circ$ , except for a station at  $66^\circ 30.06'S$  instead of  $\sim 66^\circ S$  and the southernmost station at  $69^\circ 24.03'S$  close to the approximately 200 m thick ice-sheet extending beyond the Antarctic continent over the shelf seas.

All bottles used for storage of reagents and samples were cleaned according to an intensive three step cleaning protocol extensively described by Middag et al. (2009). Samples were taken using 24 internally Teflon-coated PVC 12 l GO-FLO Samplers (General Oceanics Inc.) mounted on a Titanium frame which was connected to a Kevlar hydrowire with internal signal cables for data transfer and control from the ship. Directly upon recovery the complete frame with samplers was placed inside a class 100 clean

container (De Baar et al., 2008). Seawater was filtered in line over a  $0.2 \mu\text{m}$  filter cartridge (Sartrobran-300, Sartorius) under 1.5 bar nitrogen pressure. Before seawater collection, the first 0.5 l of seawater was filtered and disposed for rinsing purposes. Two (one for measuring, one for back-up) LDPE sample containers (NALGENE, 60 ml) were filled from each GO-FLO sampler for analyses of dissolved Fe.

#### 2.1.2. Surface water sampling

In the Weddell Gyre, close to the Antarctic continent 24 additional samples were collected along the southernmost part of the transect ( $66^\circ 02.18'S$ – $69^\circ 35.15'S$ ) using a towed epoxy-coated stainless steel torpedo deployed off a crane arm on the starboard side of the ship, after De Jong et al. (1998). In between vertical sampling stations, a seawater sample was collected every hour, and was analyzed as described in Section 2.5. Due to differences in ship speed this resulted in a slightly unequal resolution of  $00^\circ 09'$  on average.

## 2.2. Analysis of Fe

### 2.2.1. Chemicals

A solution of 0.4 M hydrochloric acid was made by diluting 30% concentrated HCl (Merck, suprapur, 10 M), 0.35 M  $\text{H}_2\text{O}_2$  solution by dilution of 30%  $\text{H}_2\text{O}_2$  (Merck, suprapur) and the 0.96 M  $\text{NH}_4$  solution was made from 25%  $\text{NH}_4\text{OH}$  (Merck, suprapur). A luminol stock solution was prepared by dissolving 270 mg luminol (3-aminophthalhydrazide, Aldrich) and 500 mg potassium hydroxide in 15 ml Milli-Q (MQ) water (MQ water is defined as ultrapure water with resistance  $\geq 18.2 \text{ M}\Omega$ ). To prepare the final reagent used in this system 3 ml of luminol stock solution and 60  $\mu\text{l}$  triethylenetetramine (TETA) (Merck) were diluted in 1 l of MQ. The 0.12 M ammonium acetate buffer (pH=6.5) was made by diluting a 2.0 M buffer solution. This 2.0 M buffer solution was obtained by a tenfold dilution of a saturated solution of ammonium acetate crystals after Aguilar-Islas et al. (2006).

### 2.2.2. Method

The shipboard analysis method used is by Flow Injection—Chemiluminescence method with preconcentration on iminodiacetic acid (IDA) resin as described by De Baar et al. (2008), with some minor modifications. One modification is the initial acidification of the samples; here the samples were acidified to pH=1.8 by adding 120  $\mu\text{l}$ /60 ml sample (2%) of ultraclean HCl (12 M) (Seastar Baseline<sup>®</sup> Hydrochloric Acid, Seastar Chemicals) and left for at least 12 h before analyzing.

The method detects Fe (III). Here, we ensured that all the Fe was in the Fe (III) form, by adding 60  $\mu\text{l}$  of a 1% hydrogen peroxide (Merck suprapur 30%) solution at least 1 h before measuring as recommended by Johnson et al. (2007).

All samples from one station were measured within one run, from surface to deep and each sample analyzed in triplicate as follows. Each sample was buffered in-line to pH=4.0 by mixing it with a 0.12 M acetate buffer (pH=6.5). After buffering, the sample passed over a chelating iminodiacetic acid (IDA, Toyopearl, AFChelate 650 M)) column for 120 s. The column was rinsed by flow-through of MQ for 1 min before the Fe was eluted with 0.4 M HCl (Merck suprapur). A four port selection valve (VICI, Switzerland) was used for switching between buffer/sample and MQ passing over the IDA—preconcentration column.

The eluent was mixed with 0.96 M ammonia, 0.35 M hydrogen peroxide and the luminol solution. The mixture passed through a 5 m length mixing coil in a constant  $35^\circ\text{C}$  water bath, before injection in a Hamamatsu (HC 135) photon counter. This injection step took 180 s.

A six port injection valve (VICI, Switzerland) was used to switch between inflow of sample, rinsing MQ over the column and elution

Download English Version:

<https://daneshyari.com/en/article/4536896>

Download Persian Version:

<https://daneshyari.com/article/4536896>

[Daneshyari.com](https://daneshyari.com)