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Sources and fluxes of dissolved iron in the Bellingshausen Sea (West Antarctica): The importance of sea ice, icebergs and the continental margin

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ABSTRACT

This study was conducted to estimate the potential for natural iron fertilization in the Bellingshausen Sea, a remote region in the Pacific sector of the Southern Ocean. Seawater samples were collected during early austral spring 2007 near the continental margin, in the wake of an iceberg and near Peter I Island in order to identify and quantify Fe sources to the upper ocean. We concomitantly collected sea ice cores for Fe analysis during a time series sampling program on an ice floe. Looking at the upper 200 m, our seawater data together with other published data suggest a large-scale exponential meridional decrease of DFe concentrations with increasing distance from the coastline noticeable up to 1400 km to the north into the ACC. From this DFe gradient we estimated DFe fluxes into the upper mixed layer of the Bellingshausen Sea using a simple one-dimensional horizontal and vertical diffusion/advection model. We also estimated the melting input from sea ice and icebergs. DFe fluxes were compared for three biogeochemical provinces: ice covered continental shelf, marginal ice zone near the continental margin, and the open ocean. Fe in sea ice decreased with time enabling us to estimate a melt flux of 0.3 μmol/m^2/d DFe. We found that going from the continental shelf to the open ocean the dominant Fe fluxes gradually change from horizontal advection on the continental shelf (54% of a total DFe flux of 7.6 ± 5.0 μmol/m^2/d) via sea ice melt in the pack ice near the continental margin (56% of a total DFe flux of 0.55 ± 0.18 μmol/m^2/d) to vertical advection (58% of a total DFe flux of 0.038 ± 0.027 μmol/m^2/d) in the ice free open ocean. A significant DFe flux of 0.6 μmol/m^2/d was estimated for iceberg melting, but this flux took place below the upper mixed layer and was not taken into further account. Fueling the high horizontal flux on the continental shelf is likely benthic diffusion and sediment resuspension. This is indicated by enhanced total dissolvable Fe (TD-Fe) and dissolved Fe (DFe) in the upper 200 m close to Peter I Island, and near the seafloor at the other stations. Also mid-depth TD-Fe increases near the continental margin were observed.
Comparison of estimates of biogenic Fe fixation (based on estimates for Southern Ocean carbon fixation) with the fluxes computed here, indicates an excess of new DFe input on the continental shelf and increasing Fe limitation going from the continental margin towards the open ocean.

1. Introduction

Iron is well-known as a potentially limiting nutrient for primary productivity and as such plays a key role in the oceanic carbon cycle as a regulating factor of marine primary productivity (Boyd et al., 2007). The Southern Ocean is the largest High Nutrient Low Chlorophyll (HNLC) region of the global ocean, and it is thought that in most of the pelagic Southern Ocean limiting low Fe concentrations (Boyd et al., 2007; Martin et al., 1990) are responsible for low Chl *a* concentrations.

Despite the HNLC status of the Southern Ocean, high biological productivity has been observed in the Marginal Ice Zone (MIZ), in polynyas and in the vicinity of the Antarctic Peninsula and the (Sub-) Antarctic islands, likely due to an apparent alleviation of iron limitation. These modern observations together with the realization that atmospheric CO_2 dynamics over glacial–interglacial cycles could be linked to co-variation in the Fe cycle (Martin, 1990), has led to several investigations into the various Fe sources and their potential for natural Fe fertilization. The main Fe sources are (1) sedimentary input by suspension and diffusion from reducing sediments at the seafloor, which is further

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Table 1
Station list.

NBP0709 station	Fe sampling	Date	Latitude S	Longitude W	Bottom depth (m)	Distance 1000 m isobath (km)
CTD-4	No	Sep 29, 2007	70°33′	92°54′	1683	6
TMC-2	Yes	Sep 29, 2007	70°32′	92°59′	1683	6
CTD-5	Yes	Sep 30, 2007	70°28′	93°32′	2364	9
CTD-6	Yes	Oct 04, 2007	70°10′	94°30′	2785	19
TMC-3	Yes	Oct 04, 2007	70°10′	94°29′	2785	19
CTD-53	Yes	Oct 19, 2007	69°51′	93°01′	3642	80
CTD-59	No	Oct 20, 2007	69°57′	93°16′	3642	80
CTD-67	Yes	Oct 24, 2007	70°01′	94°28′	3000	38
TMC-4	Yes	Oct 24, 2007	70°00′	94°39′	3000	38
TMC-5	Yes	Oct 26, 2007	68°42′	90°48′	1000	0

transported by horizontal and vertical advection/diffusion (2) sea ice melting (3) iceberg melting (4) atmospheric input.

It has been shown that landmasses play a role in supplying Fe to the Southern Ocean as island effects were evidenced in the (Sub-) Antarctic: the Kerguelen archipelago (Blain et al., 2007), the Crozet Islands (Planquette et al., 2007), South Georgia (Nielsdóttir et al., 2012) and the Antarctic Peninsula (Hatta et al., 2013; Measures et al., 2013; Frants et al., 2013; De Jong et al., 2012; Ardelan et al., 2010; Dulaiova et al., 2009; Hopkinson et al., 2007). Passage of the Antarctic Circumpolar Current across ocean ridges and continental and island margins is thought to contribute Fe by sedimentary input, while the proximity of landmasses could also provide atmospheric dust (De Jong et al., 2013; Wagener et al., 2008; Planquette et al., 2007; McConnell et al., 2007). Sedimentary input associated with glacial melt waters have been identified as important Fe sources as well (Gerringa et al., 2012; Statham et al., 2008), a source that is becoming more important in the context of global climate change.

Another potentially important Fe source is sea ice as high dissolved and particulate Fe concentrations in sea ice have been reported in East Antarctica (Van der Merwe et al., 2009, 2011a, 2011b; Lannuzel et al., 2007), the Weddell Sea (Lannuzel et al., 2008), the Bellingshausen Sea (Lannuzel et al., 2010), the Ross Sea (De Jong et al., 2013), the Atlantic Southern Ocean (De Baar and De Jong, 2001; Löscher et al., 1997), the Arctic Ocean (Tovar-Sánchez et al., 2010) and the Bering Sea (Aguilar-Islas et al., 2008). Dissolved Fe in sea ice typically appears to be as much as two orders of magnitude higher than in the underlying seawater. Lannuzel et al. (2007, 2008) proposed that high Fe was due to the fixation of Fe in the sea ice during its formation, and once formed, additional Fe could be added by the fixation of Fe supplied by upwelling through the water column, rather than supplied by atmospheric inputs, which are very low in the Antarctic (McConnell et al., 2007; Wagener et al., 2008). Release of Fe during the spring sea ice melt is thought to be crucial in triggering ice edge blooms (Sedwick and DiTullio, 1997), when the water column stabilizes by increased stratification, and light conditions become favorable due to the decreased ice cover and increased day length (Lancelot et al., 1993).

A potentially important vector of bioavailable Fe to the surface ocean is in the form of melting icebergs (e.g., Lin et al., 2011; Raiswell, 2011; Shaw et al., 2011) shedding entrained sediment in the surrounding waters. It has been hypothesized that Fe oxy-hydroxide nanoparticles adsorbed to the sediment, release Fe upon contact with ice melt or seawater, with the Fe being solubilized by ways of ferrihydrite dissolution, photochemical reduction, complexation with natural organic ligands and zooplankton grazing (Raiswell, 2011; Raiswell et al., 2008).

The SIMBA (Sea Ice Mass Balance in the Antarctic) experiment on board the US RV 'Nathaniel B. Palmer' during early austral spring (September–October 2007) in the western Bellingshausen Sea, was conducted during the International Polar Year (IPY 2007–2009). The experiment was aimed at understanding the coupling between sea ice physics, biology and biogeochemistry and the interaction between ocean, sea ice and atmosphere (Lewis et al., 2011). We present in this study water column profiles from the western Bellingshausen Sea as well as sea ice profiles of dissolved iron (DFe) in filtered acidified samples and total dissolvable iron (TD-Fe) in unfiltered acidified samples, the latter giving an estimate of the amount of labile particulate Fe (LP-Fe). We then attempt to identify sources of Fe to the upper ocean and to estimate their fluxes and relative importance using a simple one-dimensional horizontal and vertical diffusion/advection model as also described in De Jong et al. (2012).

2. Methods

2.1. Seawater sampling

Vertical Fe profiles were collected in the Bellingshausen Sea during the SIMBA expedition on board RV Nathaniel B. Palmer (cruise NBP0709) between 25 September and 26 October 2007, i.e., late winter/early spring. See Table 1 and Fig. 1 for locations and details of stations analyzed in this study. Fig. 2 shows the sea ice distribution and the position of the ice edge in the Bellingshausen Sea on October 25, 2007. All stations occupied during this study were located in the pack ice. For sampling of the upper 1000 m a small polyurethane coated rosette frame fitted with a CTD and 12 ten-liter General Oceanics GoFlo samplers was deployed from a Kevlar coax cable ('TMC' cast). To sample the water column deeper than 1000 m, samples were taken from a large polyurethane coated rosette frame fitted with a CTD and 24 ten-liter General Oceanics Niskin samplers ('CTD' cast). Stations with combined 'TMC/CTD' nomenclature indicate two casts taken at the same location (Table 1). The Niskins had Teflon-coated stainless steel internal springs inside. The CTD rosette was attached to a well-maintained stainless steel cable. Niskin bottles deployed in this way are capable of providing reliable Fe data (De Jong et al., 2012; Measures and Vink, 2001). This can be seen from the excellent link up of DFe and TD-Fe profiles between the combined TMC/CTD casts (see further). Additional unfiltered under-ice seawater samples (1, 2 and 25 m depth) were collected in Nalgene LDPE bottles on the trace metal clean ice coring site away from the ship, using a Masterflex E/S portable peristaltic pump, for later filtration on board.

Upon recovery of the TMC rosette frame on deck, the GoFlo samplers were taken from the frame and brought inside a clean air van with class 100 laminar flow hoods for sub-sampling. The Niskins were however sub-sampled at the CTD rosette frame immediately after return to deck. One-liter sub-samples from GoFlos and Niskins were taken in Nalgene LDPE bottles using a closed system consisting of Teflon tubing and a feed-through bottle cap, to minimize air contamination. From this, aliquots for total dissolvable Fe (TD-Fe, unfiltered) and dissolved Fe (DFe, 0.2 μm filtered) were collected in 250 mL Kartell LDPE bottles. The filtrations were carried out using polycarbonate filtration devices (Sartorius) with polycarbonate membrane filters (Nuclepore, 0.2 μm pore size, 47 mm diameter). Gentle vacuum (<0.5 bar) was applied with a Masterflex hand pump. The samples were acidified to pH 1.9 with 250 μL concentrated subboiled 14 M HNO_3 to 250 mL of sample.