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Iron in East Antarctic Snow: Implications for Atmospheric Iron Deposition and Algal Production in Antarctic Waters

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Abstract. To evaluate the deposition and solubility of aerosol iron in the Antarctic seasonal sea ice zone (SSIZ), iron was measured in snow samples collected from three areas in the SSIZ (Prydz Bay, Dumont d'Urville Sea and Ross Sea) and one continental area (Princess Elizabeth Land) of East Antarctica. Concentrations of total-dissolvable iron (that soluble at pH ~2) ranged from 20-2950 pg g^{-1}, with the lowest concentrations measured in snow from the Dumont d'Urville Sea. Using estimates of snow accumulation rates, we calculate atmospheric iron deposition fluxes of 0.017-0.11 mg m^{-2} yr^{-1} (0.30-2.0 μmol m^{-2} yr^{-1}), which are generally lower than previously published estimates. Measurements of iron in filtered meltwaters of snow samples from Prydz Bay and Princess Elizabeth Land suggest that ~10-90% of the total atmospheric iron is readily soluble. Assuming our results to be broadly representative of atmospheric deposition over seasonally ice-covered, high-nutrient Antarctic waters, we use our mean estimates of atmospheric iron deposition (1.1 μmol m^{-2} yr^{-1}) and solubility (32%) to calculate that atmospheric iron potentially supports annual phytoplankton production of 1.1 x 10^{12} mole C in the Antarctic SSIZ, which is less than 5% of the estimated total annual primary production in this ocean region.

Introduction

Atmospheric deposition of mineral dust is a major source of iron to open-ocean surface waters, and is thought to play an important role in regulating oceanic phytoplankton production and thus atmospheric CO_2 concentration [Martin, 1990; Donaghay et al., 1991; Duce and Tindale, 1991; Broecker and Henderson, 1998; Lefèvre and Watson, 1999; Archer and Johnson, 2000; Fung et al., 2000; Watson et al., 2000]. In order to better understand how atmospheric iron deposition affects algal production and the ocean-atmosphere carbon balance, there is a clear need for improved estimates of the flux and solubility of mineral aerosols entering the surface ocean [Archer and Johnson, 2000; Measures and Vink, 2000]. Such information is of particular importance for remote marine areas such as the Southern Ocean, where it has been demonstrated that phytoplankton growth and community composition are regulated by iron availability [Martin et al., 1990; de Baar et al., 1995;

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Boyd et al., 2000]. In this high-nutrient oceanic region, aeolian iron inputs may influence algal production on a variety of spatial and temporal scales, ranging from short-lived seasonal ice-edge blooms [Sedwick and DiTullio, 1997; Moore et al., 2000] to glacial-interglacial changes in basin-scale export production [Martin, 1990; Watson et al., 2000].

Here we report measurements of the concentration and solubility of iron in snow samples collected from several marine and continental sites in East Antarctica. Based on our current knowledge of mineral dust production and transport [e.g., Duce and Tindale, 1991; Mahowald et al., 1999; Fung et al., 2000], results from these sampling locations are likely to be representative of atmospheric iron deposition over the Antarctic seasonal sea ice zone (SSIZ), with the exception of the region around and immediately east of the Antarctic Peninsula, where higher dust deposition is expected. Combining our results with estimates of snow accumulation rates for the sampling locations, we calculate estimates of (1) the deposition of atmospheric iron over the Antarctic SSIZ, (2) the biologically-available atmospheric iron supplied to SSIZ surface waters during the growing season, and (3) the level of algal production that could be supported by this input of "new" atmospheric iron.

Methods

Snow was collected from seasonal sea-ice floes (70 samples) and elevated continental sites (29 samples) in East Antarctica between the months of August (late winter) and December (early
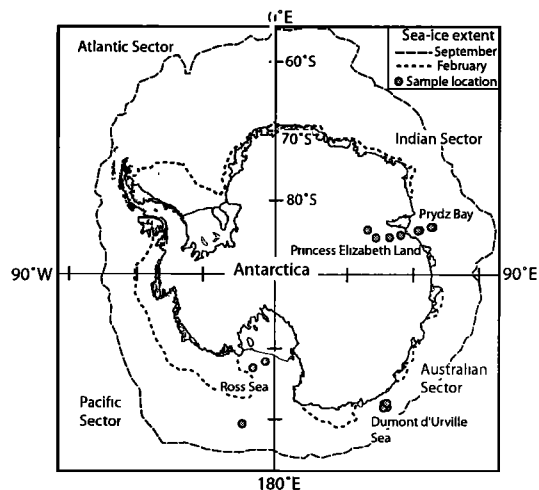

Figure 1. Location map showing snow sampling sites.

Table 1. Summary of snow sampling sites, iron concentrations and atmospheric iron flux estimates

Location and Sampling Date	Site	Position	Elevation (m)	Number of Samples	Geometric Mean TDFe (pg g^{-1})*	Est. Snow Accum. Rate (kg m^{-2} yr^{-1})	Est. Atmos. Iron Flux (mg m^{-2} yr^{-1})
Ross Sea,	1	69.52°S, 170.60°E	0	2	749 (1.1)	100	0.07
Nov-Dec 1994	2	75.00°S, 170.67°W	0	2	918 (1.4)	100	0.09
	3	76.45°S, 175.52°W	0	2	982 (1.1)	100	0.10
Dumont	A	64.60°S, 140.33°E	0	11	42 (1.9)	400	0.02
d'Urville Sea,	B	64.88°S, 141.07°E	0	4	71 (2.4)	400	0.03
Aug 1995	S	64.97°S, 141.45°E	0	8	78 (1.6)	400	0.03
	K	64.93°S, 141.25°E	0	2	85 (1.1)	400	0.03
Prydz Bay,	N	64.57°S, 74.98°E	0	10	376 (3.4)	150	0.06
Sep 1994	O	64.90°S, 75.00°E	0	8	727 (1.8)	150	0.11
	U	66.12°S, 75.32°E	0	12	367 (1.8)	150	0.06
	V	66.30°S, 75.72°E	0	9	505 (2.0)	150	0.08
Princess	LGB70	70.57°S, 76.90°E	1650	6	511 (2.1)	163	0.08
Elizabeth	LGB59	73.43°S, 76.52°E	2520	6	1158 (2.2)	65	0.08
Land,	LGB53	74.90°S, 74.52°E	2430	8	663 (2.3)	78	0.05
Nov-Dec 1994	LGB46	75.85°S, 71.50°E	2413	9	503 (1.5)	50	0.03

*Geometric standard deviations in parentheses.

summer). The sea-ice snow samples were collected from locations in the Pacific, Australian and Indian sectors of the Southern Ocean SSIZ, during voyages of RV *Nathaniel B. Palmer* in 1994 and RSV *Aurora Australis* in 1994 and 1995 (Fig. 1, Table 1). The snow cover at most sites was visibly disturbed by wind and ice movement, although the low salinities (mean = 2 ± 3.5) of the snow meltwaters indicate minimal intrusion of seawater. The continental snow and firn samples were collected from Princess Elizabeth Land during the Australian Lambert Glacier Basin Traverse in 1994-1995, at stations previously established for snow accumulation measurements (Fig. 1, Table 1). These sites were all located on the Antarctic plateau (> 1500 m above sea level), where snow cover is characterized by aeolian micro-relief features, net snow accumulation rates are relatively low, and snow deposits are typically mixed over depths in excess of the annual accumulation [*Higham et al.*, 1997]. All of the snow samples were collected, processed and analysed using the stringent trace-metal clean techniques detailed by *Edwards* [2000], in an effort to avoid sample contamination. Briefly, snow samples were collected in acid-cleaned low-density polyethylene (LDPE) bottles and acrylic tubes by personnel dressed in full clean-room attire, upwind of potential contamination sources such as ships, tractors and other large equipment. Sample containers were then sealed in polyethylene bags and transported frozen to Hobart, Australia, where samples were processed under Class-100 clean-air conditions.

For analysis of total-dissolvable iron (TDFe), unfiltered meltwater samples were acidified to pH ~2 by addition of 0.1% (v/v) Seastar ultrapure concentrated hydrochloric acid. Our preliminary investigations revealed significant increases in meltwater iron concentrations for up to 3 months following acidification, so our acidified samples (and ultrapure deionized water blanks) were stored for > 3 months in acid-cleaned LDPE bottles prior to analysis, to allow for dissolution of iron-bearing mineral particles. Similar acidification schemes have been employed in other studies of trace metals in polar snow, although typically using nitric acid and allowing dissolution times of several days, and it is believed that most of the trace metals

contained in polar snow and ice samples are rendered soluble under such mildly acidic conditions [e.g., *Ng and Patterson*, 1981; *Boutron and Patterson*, 1983; *Dick and Peel*, 1985; *Dick*, 1991; *Barbante et al.*, 1997]. For the analysis of readily-soluble iron (RSFe), snow meltwaters were filtered through acid-cleaned 0.2 μm pore-size polytetrafluoroethylene (PTFE) membranes (Gelman Acrodisc CR) immediately after melting, and the filtrates were acidified to 0.1% (v/v) with ultrapure hydrochloric acid. Ultrapure deionized water was filtered through the PTFE membranes prior to the meltwater samples, and the filtrate was used as an operational blank for the filtration procedure. Both TDFe and RSFe were determined by flow injection analysis without preconcentration using a modification of the method of *Measures et al.* [1995].

Results and Discussion

TDFe concentrations in the snow meltwaters span a wide range, even for samples collected from a single site, with values ranging from 20 pg g^{-1} (0.36 nM) in the Dumont d'Urville Sea to 2950 pg g^{-1} (53 nM) in Princess Elizabeth Land. In order to reduce skewing of our atmospheric deposition estimates by high TDFe values, we have used the geometric mean TDFe concentration for each sampling site (Table 1) in our flux calculations. The mean TDFe concentrations were highest for sites in the Ross Sea (749-982 pg g^{-1}) and Princess Elizabeth Land (503-1158 pg g^{-1}), with slightly lower mean concentrations for the Prydz Bay sites (367-727 pg g^{-1}). These concentrations are similar to values reported for iron in snow and glacial ice from the South Pole, Weddell Sea and Enderby Land [*Boutron et al.*, 1982; *Westerlund and Ohman*, 1991; *Shimamura et al.*, 1995]. Much lower mean TDFe concentrations, ranging from 42-85 pg g^{-1}, were measured in snow from our sampling sites in the Dumont d'Urville Sea. Seasonal variations in mineral aerosol concentrations, with maxima in late spring and early summer, have been documented at the South Pole and in coastal Antarctica [*Tuncel et al.*, 1989; *Wagenbach*, 1996]. Thus the low iron concentrations in our Dumont d'Urville Sea samples may in part reflect seasonal or interannual variations in atmospheric
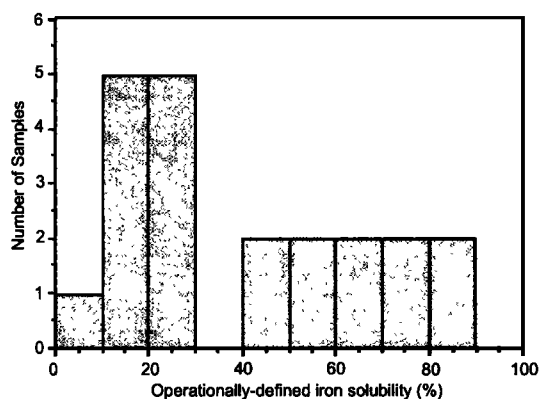
Figure 2. Frequency distribution histogram of operationally-defined iron solubility (RSFe/TDFe).

deposition, rather than regional variations, given that these samples were collected in winter 1995, whereas all our other samples were collected in spring-summer 1994. However, similarly low TDFe concentrations have been measured in recent glacial ice from Law Dome [Edwards et al., 1998], located ~1000 km west of the Dumont d'Urville Sea, which suggests that relatively low iron concentrations (< 200 pg g^{-1}) may be typical of snow accumulating in this region.

We have calculated an average atmospheric iron deposition flux for each sampling site (Table 1), using the geometric mean TDFe concentration in snow and the estimated snow accumulation rate for each site [Edwards et al., 1998]. Net snow accumulation rates for the Princess Elizabeth Land sites are estimated from observed accumulation at snow-depth canes [Higham et al., 1997; M. Craven, pers. comm., 1997], and snow accumulation rates at the marine sites are estimated from the modelled precipitation rates of Cullather et al. [1998]. Our calculated atmospheric iron fluxes range from 0.017 mg m^{-2} yr^{-1} (0.30 μmol m^{-2} yr^{-1}) in the Dumont d'Urville Sea to 0.11 mg m^{-2} yr^{-1} (2.0 μmol m^{-2} yr^{-1}) in Prydz Bay, with a mean of 0.063 mg m^{-2} yr^{-1} (1.1 μmol m^{-2} yr^{-1}). These values are similar to or less than the iron flux estimates of 1.8-18 μmol m^{-2} yr^{-1} derived from aerosol measurements [Duce and Tindale, 1991; Donaghay et al., 1991], and 2.5-32 μmol m^{-2} yr^{-1} estimated from aluminum concentrations in Southern Ocean surface waters [Measures and Vink, 2000].

Our iron deposition estimates are generally much lower than the fluxes estimated from global dust-transport models: Maholwald et al. [1999] estimate atmospheric iron deposition at 0-6.3 μmol m^{-2} yr^{-1} in Princess Elizabeth Land, 3.1-12.5 μmol m^{-2} yr^{-1} in Prydz Bay and the Ross Sea and 12.5-125 μmol m^{-2} yr^{-1} in the Dumont d'Urville Sea, and Fung et al. [2000] estimate an iron flux of ~10-200 μmol m^{-2} yr^{-1} for the Antarctic waters considered in our study. In addition, our mean iron deposition estimate is roughly 4 times higher than the estimated deposition of extraterrestrial iron [Johnson, 2001], which is presumably included within our estimated iron deposition. The fact that our iron deposition estimates are generally lower than other estimates reported for the Antarctic region may in part reflect the incomplete dissolution of Fe-bearing dust in our acidified meltwaters, although the fraction of iron in our samples that is not rendered soluble at pH ~2 is probably not large (see Methods), and is thus unlikely to explain the large differences in flux estimates.

In addition to total-dissolvable iron, we determined readily-soluble iron in a suite of 21 snow samples from Princess

Elizabeth Land and Prydz Bay. Figure 2 shows a frequency distribution histogram of these results, with the operationally-defined solubility of atmospheric iron (RSFe/TDFe) divided into 10% bins. The thus defined iron solubility varied from 9-89%, with a geometric mean of 32%. Although it may be inappropriate to compare these results with other aerosol-iron solubility studies, our data are generally consistent with the 6-60% solubility range suggested for iron in Northern Hemisphere marine aerosols [Zhuang et al., 1990; Zhu et al., 1997] and Greenland glacial ice [Laj et al., 1997], and greater than the ~1-10% solubility range suggested by Jickells and Spokes [2001] and used in recent modelling studies [e.g., Archer and Johnson, 2000; Fung et al., 2000; Watson et al., 2000]. We note, however, that including a 100%-soluble extraterrestrial iron flux of 0.3 μmol m^{-2} yr^{-1} [Johnson, 2001] within our total mean iron flux of 1.1 μmol m^{-2} yr^{-1} with 32% bulk solubility requires a terrestrial iron component with a solubility of ~5%.

Assuming that our mean estimates of atmospheric iron deposition (1.1 μmol m^{-2} yr^{-1}) and solubility (32%) are generally representative of the Antarctic SSIZ, which has a total area of approximately 15 x 10^{12} m^2 [Gloersen et al., 1992], we estimate that some 5.3 x 10^6 moles of dissolved atmospheric iron are released into surface waters of the SSIZ each year during the phytoplankton growing season. If this dissolved iron is biologically available and assimilated by phytoplankton with a typical Fe:C ratio of 5 μmol mol^{-1} [Archer and Johnson, 2000], then we estimate that new atmospheric iron potentially supports an annual algal production of 1.1 x 10^{12} mole C in the Antarctic SSIZ. This value is only 3.2% of the annual primary production in the SSIZ estimated from satellite data [Arrigo et al., 1998], suggesting that the upwelling of dissolved iron, estimated at 8-16 μmol m^{-2} yr^{-1} in the Southern Ocean [Watson et al., 2000], supports most (> 95%) of the phytoplankton production in the SSIZ.

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