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Key Points:

- Fe sources are required to sustain phytoplankton blooms in the Ross Sea
- Local dust on sea ice contributes 2 orders of magnitude more than distal sources
- Fe solubility averages 11% resulting in a Fe flux of $6.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ to SW Ross Sea

Supporting Information:

- Readme
- Figure S1
- Figure S2
- Table S1
- Table S2
- Table S3
- Table S4
- Text S1

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The contribution of aeolian sand and dust to iron fertilization of phytoplankton blooms in southwestern Ross Sea, Antarctica

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Abstract Iron is a limiting micronutrient for primary production in the Ross Sea, Antarctica. Recent observations reveal low dissolved Fe (dFe) concentrations in the Ross Sea polynya following high initial rates of primary production in summer, after the dFe winter reserve has been consumed. Significant new sources of dFe are therefore required to further sustain phytoplankton blooms. Iron from aeolian sand and dust (ASD) released from melting sea ice is one potential source. To constrain aeolian Fe inputs, we determined ASD mass accumulation rates and the total and soluble Fe content of ASD on sea ice in McMurdo Sound, southwestern (SW) Ross Sea. The mean mass accumulation rate was $\sim 1.5 \text{ g m}^{-2} \text{ yr}^{-1}$, total Fe content of this ASD was $4 \pm 1 \text{ wt } \%$, and the percentage of soluble Fe was $11 \pm 1\%$. Our mean estimate of the bulk aeolian dFe flux of $122.1 \mu\text{mol m}^{-2} \text{ yr}^{-1}$ for the McMurdo Sound region suggests that aeolian Fe can support between 9.0×10^9 and $4.1 \times 10^{11} \text{ mol C yr}^{-1}$ ($0.1\text{--}4.9 \text{ Tg C yr}^{-1}$) of new primary production. This equates to only $\sim 15\%$ of new primary production in the SW Ross Sea, suggesting that aeolian dFe is a minor component of seasonal Fe supply. The very high ASD accumulation on sea ice in McMurdo Sound compared to other regions of Antarctica suggests that our results represent the upper limit of dFe supply to the ocean from this source in the Ross Sea.

1. Introduction

The Ross Sea region is the most biologically productive continental shelf region in Antarctica and an important area for both CO_2 sequestration and bottom water formation [Arrigo *et al.*, 2008, 1998; Smith and Gordon, 1997]. The Ross Sea is seasonally iron (Fe) limited, which restricts phytoplankton growth in summer [Fitzwater *et al.*, 2000; Martin *et al.*, 1990; Sedwick *et al.*, 2011]. Evidence from Fe fertilization experiments confirmed the viability of Martin's [1990] "Fe hypothesis," whereby phytoplankton growth, photosynthesis, and community composition are regulated by Fe availability [Boyd and Law, 2001; Boyd *et al.*, 2000; de Baar *et al.*, 1995; Martin *et al.*, 1991; Smetacek *et al.*, 2012]. In spite of a dearth of measurements, atmospheric deposition of mineral dust is thought to be a major source of micronutrient Fe to remote ocean surface waters and consequently plays an important role in regulating marine phytoplankton productivity and atmospheric CO_2 concentration [Arrigo *et al.*, 2008; Broecker and Henderson, 1998; Watson *et al.*, 2000; Martínez-García *et al.*, 2014].

Edwards and Sedwick [2001] suggest that dissolved Fe (dFe, operationally defined as the Fe in solution that passes through a $0.2 \mu\text{m}$ pore size filter membrane) in mineral dust from sea ice fringing Antarctica could account for 5% of annual primary production in the Southern Ocean. Furthermore, a close link has been observed between the timing of sea ice retreat and phytoplankton blooms in the southwestern (SW) Ross Sea [Arrigo and van Dijken, 2004; Smith and Nelson, 1986]. One explanation for this observation is that aeolian Fe-bearing dust that has accumulated on the annual sea ice enters the ocean as the ice breaks up, overcoming the preexisting Fe limitation. More recent studies have shown that there is a winter reserve of dFe in the surface ocean that is progressively depleted from initial values of $\sim 0.2\text{--}1.0 \text{ nM}$ in austral spring (September–November) to $\sim 0.1\text{--}0.2 \text{ nM}$ in austral summer (December–February) [Coale *et al.*, 2005; Fitzwater

et al., 2000; *Sedwick et al.*, 2000; *Tagliabue et al.*, 2012]. Importantly, some observations suggest the winter reserve of dFe can become depleted as early as November, yet phytoplankton blooms continue to occur after this date. This indicates that phytoplankton blooms are responding to a new or at least ongoing dFe supply [*Sedwick et al.*, 2011]. However, the source(s) of this replenishment Fe and its variability in space and time are unclear.

Potential sources of Fe to the Ross Sea include atmospheric fallout of mineral dust [*Cassar et al.*, 2007; *Sedwick et al.*, 2011; *Chewings et al.*, 2014], upwelling/vertical exchange with Fe-rich benthic waters [*Collier et al.*, 2000; *Moore and Braucher*, 2008; *Sedwick et al.*, 2011], resuspension of continental shelf sediments (biogenic and terrigenous) containing particulate Fe [*Elrod et al.*, 2004], extraterrestrial inputs [*Johnson*, 2001], melt from icebergs and sea ice that releases stored dFe from frozen sea water and particulate Fe originally deposited as dust [*Grotti et al.*, 2005; *Lannuzel et al.*, 2008, 2010; *Raiswell et al.*, 2008; *Smith et al.*, 2007; *Smith and Nelson*, 1986; *van der Merwe et al.*, 2009], and Ice Shelf Water from Ross Ice Shelf [*Jacobs et al.*, 1970] which could supply dFe from glacial ice and subglacial debris [*Fitzwater et al.*, 2000; *Sedwick et al.*, 2011]. The few previous studies related to aeolian sand and dust (ASD) concentrations in surface snow on the sea ice in McMurdo Sound, SW Ross Sea (Latitude 77.5°S; Longitude 165°E), suggest that locally derived ASD is in abundance [*Atkins and Dunbar*, 2009; *Barrett et al.*, 1983]. An open question with respect to natural Fe fertilization therefore is “how important is ASD as a source of bioavailable Fe to the seasonally Fe-limited high-nutrient high-chlorophyll (HNHC) regime in the Ross Sea and more broadly to the chronically Fe-limited high-nutrient low-chlorophyll (HNL) offshore waters of the Southern Ocean?”

Here we quantify, for the first time, the importance of ASD as a source of dFe to McMurdo Sound in the SW Ross Sea. McMurdo Sound has the highest reported accumulations of ASD on sea ice fringing Antarctica [e.g., *Atkins and Dunbar*, 2009; *Chewings et al.*, 2014]. Although the sound's spatial extent is small, the abundant sea ice-borne ASD suggests this region represents the upper limit by which dFe can be supplied by this process to the ocean surrounding Antarctica.

2. Regional Setting

2.1. Environmental Conditions

The study area covers 7400 km² of McMurdo Sound (defined by the area 160°E–175°E, 74°S–78°S) (Figure 1). All exposures of unconsolidated subaerial sediment in the McMurdo Sound region are considered as potential source areas of ASD (Figure 1). From a petrological perspective, these can be divided into two, each with distinguishing mineralogical characteristics that aid provenance identification: (i) a southern source, dominated by alkali-rich basaltic volcanic rocks of the McMurdo Volcanic Group (MVG) and distinguished by volcanic lithic fragments and angular, vesicular volcanic glass [*Blank et al.*, 1963; *Kyle and Cole*, 1974; *McCraw*, 1962] and (ii) a western source, the McMurdo Dry Valleys (MDV), dominated by granitic and metamorphic rocks, quartzose sedimentary rocks, and dolerite [*Goldich et al.*, 1975; *Gunn and Warren*, 1992; *LeMasurier and Thomson*, 1990]. Of particular interest is the large volume of exposed unconsolidated sediment, known as the debris bands on the McMurdo Ice Shelf (Figure 1) [*Kellogg et al.*, 1990]. The debris bands are a consequence of basal freezing of the McMurdo Ice Shelf, which incorporates seafloor sediment into the base of the ice shelf, and surface ablation which removes ice but leaves sediment behind. By this mechanism sediment is continuously brought to the surface, providing an extensive area of unconsolidated, very poorly sorted sediment [*Debenham*, 1920; *Denton and Marchant*, 2000; *Kellogg et al.*, 1990]. In comparison, sediments in the MDV have been extensively winnowed, and silt and very fine sand-sized material are rarely exposed at the surface [e.g., *Selby et al.*, 1974]. Aeolian sand and dust and blown snow accumulate on first-year sea ice in Southern McMurdo Sound between April and December and are released into the surface ocean upon its breakout which typically occurs over a 3–4 week period in January and February [*Chewings et al.*, 2014] (Text S1 in the supporting information). The prevailing low-level airflow in McMurdo Sound is from the south [*Sinclair*, 1982]. In particular, storms with wind speeds >15 ms⁻¹, required to transport large amounts of ASD, only blow from the south (Figure 1c) [*Ayling and McGowan*, 2006; *Dunbar et al.*, 2009].

2.2. Previous Dust Transport Studies in Antarctica

Aeolian sand and dust deposited in Antarctica and the Southern Ocean can be divided into two end-member categories: (i) global background dust characterized by its fine grain size (mode <5 μm), modern mass

Figure 1. Map of sample locations and wind field in McMurdo Sound. (a) Location of McMurdo Sound within the Ross Sea. EAIS: East Antarctic Ice Sheet. (b) Map of McMurdo Sound with sample locations and potential source areas of unconsolidated sediment. Grey area: region defined as representative of McMurdo Sound. Transect X-Y is shown in red. MDV: McMurdo Dry Valleys; TAM: Transantarctic Mountains. (c) Wind roses illustrating the direction of storm events at Pegasus North and Marble Point automatic weather stations.

accumulation rates of $0.001\text{--}0.02\text{ g m}^{-2}\text{ yr}^{-1}$ [Duce *et al.*, 1991; Mahowald *et al.*, 2005; Wagener *et al.*, 2008] and $0.0002\text{--}0.0004\text{ g m}^{-2}\text{ yr}^{-1}$ during the Holocene [Albani *et al.*, 2012; Delmonte *et al.*, 2005], and a geochemical fingerprint showing it originates from arid regions in Patagonia and Australia [Basile *et al.*, 1997; De Deckker *et al.*, 2010; Delmonte *et al.*, 2004; Vallenga *et al.*, 2010] and (ii) local ASD, for example, characterized by a modal size of $40\text{--}250\text{ }\mu\text{m}$, modern accumulation rates of up to $55\text{ g m}^{-2}\text{ yr}^{-1}$, and a geochemical composition consistent with derivation from McMurdo Sound [Atkins and Dunbar, 2009; Ayling and McGowan, 2006; Chewings *et al.*, 2014; Dunbar *et al.*, 2009]. Mixtures of these two end-members exist on the polar plateau where Antarctic sourced dust is an important contributor of the total dust flux although the concentration remains low [Delmonte *et al.*, 2010]. As a consequence of the low fallout rate of global dust to the Southern Ocean, it has been suggested that this distal dust flux is insufficient to fertilize observed phytoplankton blooms [e.g., Edwards and Sedwick, 2001; Loscher *et al.*, 1997; Wagener *et al.*, 2008]. To date only two samples from the Ross Sea have been directly measured to assess the contribution of dFe from ASD accumulating on sea ice, yielding an aeolian Fe flux of $0.07\text{--}0.10\text{ mg m}^{-2}\text{ yr}^{-1}$ [Edwards and Sedwick, 2001]. The contribution of Antarctic-derived aeolian dFe and the relationship between sea ice melting and concomitant productivity remain poorly constrained.

3. Materials and Methods

For this study a total of 127 surface snow samples were collected in November 2009 (samples MIS 1–55, GH 1–10) and November 2010 (MPK9–MPS14 (total of 34) CRA6–CRJ11 (total of 27)) on sea ice in McMurdo Sound for mass determinations (Figure 1 and Table S1). Additional snow samples were collected at selected sites along a south to north transect in McMurdo Sound to determine (i) total and soluble Fe concentrations and (ii) particle size. Aeolian sand and dust mass was determined by melting ASD-laden snow and weighing ASD captured on $0.4\text{ }\mu\text{m}$ pore size polycarbonate membranes [e.g., Dunbar *et al.*, 2009]. The particle size

distribution of the recovered ASD was measured using a Beckman-Coulter LS13-320 laser particle size analyzer [e.g., *Atkins and Dunbar*, 2009]. Strontium (Sr) and Neodymium (Nd) isotopes were measured on three samples following the method of *Delmonte et al.* [2008] to determine dust provenance.

The most common approach to understanding the delivery of Fe-bearing dust to phytoplankton has been to quantify the solubility of Fe from dust and assume all soluble Fe is also bioavailable, i.e., the amount available for uptake and utilization by living cells [e.g., *Özsoy and Saydam*, 2001]. However, a major difficulty in assessing the bioavailability of Fe in dust is the lack of consistency in the definition of soluble or bioavailable Fe fractions, making intercomparisons of Fe solubility difficult [*Baker and Croot*, 2010; *Schroth et al.*, 2009]. For simplicity and reproducibility, we follow a modified method of *Aguilar-Islas et al.* [2010] using ultrapure water (resistivity of 18.2 M Ω ; Cascada ultrapure water from Pall Life Sciences) as the leaching solution. We assume that soluble Fe approximates bioavailable Fe, although we acknowledge there are a number of reasons why this may be an over simplification [e.g., *Baker and Croot*, 2010; *Boyd and Ellwood*, 2010; *Boyd et al.*, 2010].

Leaching of soluble Fe was carried out on nine samples, located in Figure 1, using a stepwise leaching method consisting of (a) an initial snow melt leach on the bulk dust fraction and (b) three successive ultrapure water leaches of the fine fraction (0.4–10 μ m). The leaching procedure for each sample took approximately 7 h (4 h to melt the sample and 3 h for the three fine fraction leaches). Acid-washed filter blanks were leached with 180 ml of ultrapure water prior to each leaching experiment.

Each surface snow sample was melted at room temperature, taking ~3–4 h. Immediately after the sample was melted, it was sonicated for 20 min to break up aggregate particles. The snow melt was then filtered on preacid-washed 0.4 μ m and 10 μ m polycarbonate filter papers mounted on separate stages and placed in the reaction chamber. The filtered snow melt of the bulk dust fraction was collected in prewashed bottles.

Successive ultrapure water leaches were carried out on the fine ASD fraction. After the initial snow melt leach, ASD is separated into fine and coarse size fractions on 0.4 μ m and 10 μ m filter papers. The stage containing the 10 μ m filter was removed using acid-washed ceramic tweezers and dried in a desiccator for 48 h. The fine fraction of ASD on the 0.4 μ m filter was leached with 40 ml ultrapure water (maximum volume the reaction chamber can hold) for 1 h. At the end of the leaching time, the leachate was collected in prewashed bottles. Three subsequent 1 h leaches of 40 ml aliquots were carried out.

Fine and coarse ASD-laden filters were later digested for total Fe content using concentrated HF and HNO₃. Digested samples and leachate solutions were acidified using 1 wt % HNO₃ Seastar in a class 100 clean room prior to analysis on an Agilent 7500cs series inductively coupled plasma–mass spectrometry using a hydrogen-flushed collision cell at the SGEES Geochemistry Laboratory, Victoria University of Wellington.

Different Fe fractions are defined as follows: Fe that passed through the 0.4 μ m filter membrane is defined as soluble Fe; Fe that passed through the 0.4 μ m filter membrane during the first snow melt leach is termed instantaneous soluble Fe; the cumulative sum of all the soluble Fe leaches is termed cumulative soluble Fe; Fe >0.4 μ m is defined as particulate Fe; total Fe is the sum of soluble and particulate Fe; and the percentage of cumulative soluble Fe is the cumulative sum of the percentage of soluble Fe from the four leaches.

4. Results

4.1. Mass Accumulation Rates and Textural Trends

The ASD extends as a dust plume on the sea ice downwind from the debris bands [*Atkins and Dunbar*, 2009; *Chewings et al.*, 2014]. The mass accumulation rates decrease exponentially from 26 g m^{−2} yr^{−1} in Southern McMurdo Sound to ~1 g m^{−2} yr^{−1} at Granite Harbour 120 km to the north (Figure 2a and Table S1). Rates also decrease east (to 0.97 g m^{−2} yr^{−1}) and west (to 4.3 g m^{−2} yr^{−1}) of the central axis of the ASD plume. From 20 to 120 km north of the debris bands the mass accumulation rate is reasonably constant at 1.53 g m^{−2} yr^{−1} (Figure 2a), and we use this in our calculations of dFe inputs to the adjacent ocean.

The particle size frequency distribution for samples along the south-north transect X-Y (Figure 1) is distinctly bimodal, with a well-defined fine to very fine sand/coarse silt mode and a secondary broad fine silt mode. The primary mode decreases sharply from ~130 μ m to 76 μ m between 5 and 18 km north of the debris bands and thereafter varies between 25 and 69 μ m. The percentage of sand also decreases between 20 and 120 km from

Figure 2. Physical and chemical properties of McMurdo Sound ASD along transect X-Y (location in Figure 1) with distance north from the debris bands. (a) Mass accumulation rate, (b) percentage of dust $<10\ \mu\text{m}$, (c) percentage of total iron, (d) percentage of cumulative soluble iron, (e) cumulative concentration of soluble iron, and (f) iron flux for the McMurdo Sound region. Black dots: bulk ASD fraction, red dots: fine ($0.4\text{--}10\ \mu\text{m}$) ASD fraction, hashed box: samples used to define Fe flux for McMurdo Sound, DB: debris bands, NH: New Harbour, GH: Granite Harbour, MP: Marble point, and CR: Cape Roberts. First three data points in Figures 2a and 2b are taken from Atkins and Dunbar [2009].

Particulate Fe concentrations along transect X-Y in both size fractions are similar and average $4.08 \pm 1.39\ \text{wt}\%$ (Figure 2c and Table S3). For each sample, the instantaneous soluble Fe concentration ranges from 0.02 to $1.68\ \mu\text{mol L}^{-1}$ (Table S3). The first leach yielded $76 \pm 14\%$ of the total cumulative soluble Fe. Subsequent ultrapure water leaches yield progressively less soluble Fe from the ASD.

The percentage of cumulative soluble Fe in McMurdo Sound ASD ranges from 4.12 to 19.93% (Figure 2d). Cape Roberts and Granite Harbour samples render an average of $10.96 \pm 0.74\%$. This is used as a conservative average to represent Fe solubility on sea ice in McMurdo Sound. This average is similar to or less than the lower limit of Fe solubility from snow samples in East Antarctica ($9\text{--}89\%$) [Edwards and Sedwick, 2001]. It is also less than the value of Last Glacial Maximum dust acid leached from Antarctic ice cores (60%) [Gaspari et al., 2006] and at the lower limit of modeled values from the Southern Ocean of $10\text{--}100\%$ [Baker and Croot, 2010].

the debris bands (Figure S2 and Table S2). Conversely, the fine silt mode remains relatively constant between 4 and $10\ \mu\text{m}$. The $<10\ \mu\text{m}$ fraction typically varies from 2 to 35% (Figure 2b).

In terms of east-west spatial trends of samples in Figure 1, the coarsest sand mode is $185\ \mu\text{m}$ (fine sand) near the center of the transect, decreasing to $\sim 35\ \mu\text{m}$ (coarse silt) in easterly and $120\ \mu\text{m}$ (very fine sand) in westerly directions from this location (Table S2). Granite Harbour samples are sandy silts with a prominent primary mode between 27 and $63\ \mu\text{m}$ and often a poorly defined secondary silt mode at $15\ \mu\text{m}$. The samples become better sorted offshore from the entrance to Granite Harbour.

4.2. Aeolian Sand and Dust Provenance

Strontium and Nd isotopes in two samples from Southern McMurdo Sound ($2.38 < \epsilon\text{Nd}(0) < 3.45$; $0.7053 < {}^{87}\text{Sr}/{}^{86}\text{Sr} < 0.7056$) display ratios characteristic of the MVG ($1 < \epsilon\text{Nd}(0) < 5.7$; $0.703 < {}^{87}\text{Sr}/{}^{86}\text{Sr} < 0.710$) [Delmonte et al., 2004]. Conversely, the sample from Granite Harbour ($\epsilon\text{Nd}(0)$: -6.18 ; ${}^{87}\text{Sr}/{}^{86}\text{Sr}$: 0.7122) is characteristic of Southern Victoria Land sources ($-12.5 < \epsilon\text{Nd}(0) < -3$; $0.710 < {}^{87}\text{Sr}/{}^{86}\text{Sr} < 0.728$) [Delmonte et al., 2010, 2004]. The relative importance of these two isotopically distinct sources to the study region is discussed below.

4.3. Total and Soluble Iron Concentrations

No spatial trend in the percentage of soluble Fe is evident. However, the cumulative soluble Fe concentration exponentially decreases northward with distance from the debris bands ranging from $1.87 \mu\text{mol L}^{-1}$ in Southern McMurdo Sound to $0.06 \mu\text{mol L}^{-1}$ at Granite Harbour (Figure 2e) and correlates directly with the decreasing trend in ASD mass accumulation (Figure 2a).

5. Discussion

5.1. McMurdo Sound as the Dominant Source of Aeolian Fe to SW Ross Sea

The following characteristics identify ASD as being sourced from the McMurdo Ice Shelf debris bands (Figure 1). (i) All samples contain fresh, vesicular volcanic glass sourced from MVG-derived sediments. Such material is only exposed around the southern margin of McMurdo Sound and does not occur in the MDV (Figure 1). (ii) The Sr and Nd isotopic ratios are consistent with ASD originating from MVG, although within the Granite Harbour embayment there is evidence for ASD derived from Transantarctic Mountain lithologies. (iii) Mass accumulation rates and particle size decrease downwind from the debris bands [Atkins and Dunbar, 2009; Chewings *et al.*, 2014]. This northward dispersal is consistent with the local meteorology whereby the highest wind speeds, i.e., those most competent with respect to entraining silt and fine sand, are always from the south (Figure 1c) dispersing ASD from the debris bands north along the Southern Victoria Land coastline. None of the samples show compositional or particle size characteristics that suggest they were derived from distal (i.e., Australian or Patagonian) sources.

Assuming the mass accumulation rate of $1.53 \text{ g m}^{-2} \text{ yr}^{-1}$ on the sea ice also characterizes areas 20–120 km from the source (and perhaps beyond), we suggest these accumulation rates are likely characteristic of at least 7400 km^2 of McMurdo Sound sea ice (grey shaded area in Figure 1 which represents ~5% of the SW Ross Sea). This mass accumulation rate is at least 2 orders of magnitude greater than that measured in ice cores from the polar plateau [Delmonte *et al.*, 2004, 2005, 2002] or estimated from global dust distribution models [e.g., Duce and Tindale, 1991; Fan *et al.*, 2006; Mahowald *et al.*, 2005] and aerosol samples [e.g., Wagoner *et al.*, 2008] in the Southern Ocean.

5.2. Supply of Aeolian Fe to McMurdo Sound

The spatial variability of cumulative soluble Fe in surface snow (Figure 2e) is directly proportional to the ASD mass accumulation rate ($R^2 = 0.89$; Figure 2a). As the mineral composition of the ASD is similar over McMurdo Sound, the concentration of cumulative soluble Fe leached from the samples also decreases northward from the debris bands (Figure 2e). Therefore, in this region, variability in the cumulative soluble Fe concentration is a consequence of variations in the ASD mass accumulation rate, rather than the variability in the Fe content or the percentage of soluble Fe in the ASD.

5.2.1. Timing and Seasonal Variability

Aeolian sand and dust enters the ocean either by transport onto sea ice and subsequent release during melting or by direct deposition into open water during the summer. Sea ice is present in McMurdo Sound for ~9 months per year between April and December based on satellite data. While sea ice is present in McMurdo Sound, the ASD is trapped on sea ice and does not contribute dFe to the ocean. The actual flux of ASD-derived dFe to the ocean during the sea ice melt season is complex as it depends on the rate of ice breakup. Timing and migration patterns of sea ice melt breakup and melting change from year to year [e.g., Arrigo and van Dijken, 2004]. However, for Southern McMurdo Sound an average breakout duration of 20 to 30 days is used (Figure S1).

5.2.2. Particle Size and Potential Contribution to dFe

Although the settling of coarse particles ($>10 \mu\text{m}$) can provide a mechanism for rapid removal of particulate Fe in surface waters, the instantaneous soluble Fe derived from the first leach (bulk dust) provided ~75% of the total soluble Fe. This soluble Fe is derived from dFe in snow, colloidal Fe, and Fe associated with the dissolution of Fe from the surface of particles. Therefore, in spite of the shorter residence time of coarser particles in the upper water column, our measurements suggest they contribute a surprising amount of instantaneous soluble Fe. Fine ($0.4\text{--}10 \mu\text{m}$) particles are suspended in the surface waters for considerably longer periods of time and continue to leach soluble Fe into the water column [e.g., Edwards and Sedwick, 2001] although at a slower rate over time. Our results suggest that most dFe is supplied to the ocean instantaneously upon deposition; therefore, the rate of input of dFe depends on the mass of ASD on the sea ice and the rate at which the sea ice breaks up and not on the particle size distribution of the ASD.

Figure 3. Map of dFe concentrations around the Antarctic coastline highlighting McMurdo Sound which is the largest known source of local ASD in the Ross Sea region. Data sourced from ice cores [Edwards *et al.*, 2006; Gaspari *et al.*, 2006; Vallelonga *et al.*, 2013], aerosols [Wagener *et al.*, 2008], modeling [Lancelot *et al.*, 2009], snow [Edwards and Sedwick, 2001; Lannuzel *et al.*, 2008, 2007; Loscher *et al.*, 1997; van der Merwe *et al.*, 2011a, 2009; Westerlund and Öhman, 1991], icebergs [Raiswell *et al.*, 2008], exposed rock (BEDMAP2), and base maps (derived from Qantarctica, Norwegian Polar Institute). Note the difference in method used to extract dFe from ice cores [Gaspari *et al.*, 2006] and coastal snow [e.g., Lannuzel *et al.*, 2006].

5.2.3. Estimates of dFe Flux

The locally derived soluble Fe flux for the fine fraction ($0.4\text{--}10\text{ }\mu\text{m}$) is $2.1\text{ mg m}^{-2}\text{ yr}^{-1}$ ($36.7\text{ }\mu\text{mol m}^{-2}\text{ yr}^{-1}$), and the bulk fraction is $6.8\text{ mg m}^{-2}\text{ yr}^{-1}$ ($122.1\text{ }\mu\text{mol m}^{-2}\text{ yr}^{-1}$) for our 7400 km^2 study area (Figure 2f). This is 2 orders of magnitude higher than soluble Fe measured in dust-laden snow in East Antarctica ($0.1\text{--}0.3\text{ }\mu\text{mol m}^{-2}\text{ yr}^{-1}$) [Edwards and Sedwick, 2001] and estimated by dust distribution models (Figure 3). Aerosol sampling for the Southern Ocean suggests a flux of only $0.07\text{--}3\text{ }\mu\text{mol m}^{-2}\text{ yr}^{-1}$ [Mahowald *et al.*, 2005; Wagener *et al.*, 2008]. While the importance of global aeolian Fe as a fertilizer in the Southern Ocean is debated [Boyd and Mackie, 2008; Cassar *et al.*, 2007; Lancelot *et al.*, 2009; Measures and Vink, 2001], the flux is known to be among the lowest in the world [Duce and Tindale, 1991; Prospero, 1996; Wagener *et al.*, 2008], and its contribution as a source of Fe appears insignificant compared to locally derived ASD in the SW Ross Sea.

5.3. Ross Sea dFe Limitation Threshold

Boyd and Abraham [2001] reported that dFe concentrations of 0.2 nM in surface waters were required to stimulate phytoplankton blooms during the Southern Ocean Iron Enrichment Experiment. This threshold is consistent with other Fe fertilization experiments in the Southern Ocean [Coale *et al.*, 1996; $0.15\text{--}0.2\text{ nM dFe}$; Olson *et al.*, 2000; 0.15 nM dFe ; Sedwick *et al.*, 2002; $0.05\text{--}0.2\text{ nM dFe}$; Watson *et al.*, 2000; $0.05\text{--}0.1\text{ nM dFe}$], and the authors suggest this threshold response may be applicable to all HNLC waters. Further evidence of this Fe limitation threshold comes from shipboard bottle incubation experiments [Boyd *et al.*, 1999; Hutchins *et al.*, 2001; Sedwick *et al.*, 1999, 2000]. Sedwick *et al.* [2011] measured dFe concentrations in the euphotic zone of the Ross Sea polynya between mid-November and early December before significant sea ice breakup. During this time, the initial winter reserve of dFe decreases from $0.3\text{--}0.4\text{ nM}$ to $\sim 0.1\text{ nM}$. This

Table 1. Iron Supplied to McMurdo Sound From Local Bulk Aeolian Sand and Dust

ASD Deposition ($\text{g m}^{-2} \text{d}^{-1}$)	Mass Fe of ASD (Fractional %)	Leachable Fe (Fractional %)	Fe Instant (nM)	Fe Export and Uptake (nM)	Net New Fe Supply (nM)	Summer dFe (nM)
0.05–0.08	4.08	10.96	0.02–0.12	0.004 ^a	0.02–0.12	0.12–0.32 ^b

^aExport and biological uptake from *Bowie et al.* [2001] and *Boyd et al.* [2010].

^bAssuming the dFe concentration of the surface water is 0.1–0.2 nM after sea ice breaks up and most of the initial winter reserve (0.3–0.4 nM) has been consumed [*Sedwick et al.*, 2011].

suggests winter reserve dFe may be consumed relatively early in the phytoplankton growing season. The residual ~0.1 nM of dFe likely reflects the Fe concentration remaining after substantial biological drawdown by phytoplankton. Considering these observations, we suggest phytoplankton productivity in the Ross Sea is likely Fe limited when Fe concentrations are <0.2 nM and almost certainly when Fe concentrations are <0.1 nM. Local ASD, following melting of sea ice, is among the potential sources of new Fe required to sustain phytoplankton growth that continues beyond the Fe limitation onset.

5.4. The Contribution of Aeolian dFe to Primary Production

Here we estimate the importance of the ASD contribution to phytoplankton blooms using two different approaches. The first utilizes the model of *Boyd et al.* [2010] to calculate the primary productivity resulting from our estimates of dFe supply from local ASD released to McMurdo Sound, and the second approach uses a Fe:C assimilation ratio to estimate the amount of new primary production resulting from the input of locally derived aeolian dFe.

Despite the large number of oceanic dFe measurements in the Ross Sea, *Tagliabue et al.* [2012] note that there is no observational constraint of the seasonal maxima in dFe at the start and end of the growing season in the Ross Sea. In addition, the duration of the sea ice breakout period and the distance over which ASD travels by direct atmospheric fallout during the phytoplankton growth season and by advection and release of ASD from blocks of melting sea ice are also unconstrained. Therefore, we have chosen to “bracket” the likely range of variability by calculating minimum and maximum values for new dFe supplied by locally derived ASD during sea ice breakout in Southern McMurdo Sound (Tables 1 and S4). Upon deposition into the ocean, we assume that coarse particles will reside in the mixed layer for a minimum of 0.5–2 h (if ~90% of the particles are finer than 75 μm , a size range with a settling velocity of $>0.31 \text{ cm s}^{-1}$ [*Gibbs et al.*, 1971]) and fine particles will reside for 1–4 days (if ~25% of the particles are $<10 \mu\text{m}$ which has a settling velocity of $>0.006 \text{ cm s}^{-1}$ [*Gibbs et al.*, 1971]). As our results show, the rate at which soluble Fe is leached from the bulk ASD is more or less instantaneous [e.g., *Boyd et al.*, 2010], i.e., the rate of Fe leached from the ASD surface becomes constant within hours, and the sea ice breakout period in Southern McMurdo Sound occurs over 20–30 days (Text S1), we assume a uniform release of dFe into the mixed layer during this time and that there is no significant Fe leached from ASD beyond the first day of its deposition into the ocean.

Following the procedure of *Boyd et al.* [2010], we have calculated the concentration of dFe from local ASD released to McMurdo Sound using equation (1):

$$\text{dFe} = \text{deposition} \times f\text{Fe} \times f\text{Fe}_{\text{instant}} \times 1/d_{\text{mixed}} \quad (1)$$

where dFe is the concentration increase of dFe in the mixed layer resulting from the release and dissolution of ASD; deposition is the ASD deposition during sea ice breakout ($\text{g m}^{-2} \text{d}^{-1}$); $f\text{Fe}$ is the average mass fraction of Fe in ASD; $f\text{Fe}_{\text{instant}}$ is the fraction of Fe in ASD that is leachable; and d_{mixed} is the depth of the mixed layer (m).

We calculate that local ASD in McMurdo Sound contributes between 0.02 and 0.12 nM of new dFe to the mixed layer per day during sea ice breakout (Table 1). The combined dFe from the winter reserve and new dFe from local ASD within the mixed layer is therefore 0.12–0.32 nM. Using the half-saturation constant (~0.1 nM) with respect to Fe for a number of phytoplankton species [e.g., *Coale et al.*, 2003; *Timmermans et al.*, 2004] to assess potential changes in growth from an addition of Fe depends on the initial conditions. Thus, we presume Monod limitation with a half-saturation coefficient of 0.1 nM. The residual concentration of 0.1 nM of growth is 0.5 of maximum by definition. Supplying an extra 0.02–0.12 nM of Fe from ASD would raise growth to 0.54 to 0.69 of maximum. This represents a growth change of 8–36%. To narrow the summer

background dFe concentration bracket, we assume that any aeolian dFe added in excess of the half-saturation constant will support net primary production. Thus, the upper bound of aeolian dFe addition of 0.12 nM could conceivably support significant primary production. However, even in this high dust flux region of Antarctica, there is insufficient new dFe released from ASD for this to be the sole source of dFe associated with phytoplankton blooms (except very close to the debris bands, which are insignificant in terms of area). This implies that another continuous source of dFe to the mixed layer exists throughout the summer, although the spatial and temporal contributions of other potential sources of new dFe are presently unknown [Sedwick *et al.*, 2011]. Thus, none of the potential sources of Fe (upwelling of Fe-rich benthic waters, continental shelf sediments, extraterrestrial inputs, and iceberg and sea ice melt) can be excluded from consideration [Sedwick *et al.*, 2011; Tagliabue and Arrigo, 2005].

In addition to estimating the impact of locally derived aeolian Fe on the surface water dFe concentration (where surface water has a large input of soluble Fe derived from ASD, but low dFe concentration from rapid phytoplankton uptake), we estimate how much new production could be supported from the input of locally derived aeolian ASD during the summer growing season. Using this second approach, we estimate that locally derived ASD accumulating on McMurdo Sound sea ice may have contributed approximately $1.2 \times 10^4 \text{ mol Fe m}^{-2} \text{ yr}^{-1}$ of aeolian dFe into the surface water of McMurdo Sound during the sea ice breakup in the 2009/2010 summer, assuming that our mean estimate of bulk aeolian dFe flux of $9.1 \times 10^{-5} \text{ mol m}^{-2} \text{ yr}^{-1}$ is representative of the study area of 7400 km². If this dFe is biologically available and assimilated by phytoplankton with a Fe:C ratio between 10,000 and 450,000 mol mol⁻¹ [Coale *et al.*, 2005; Tagliabue and Arrigo, 2005; Twining *et al.*, 2004], we estimate that ASD-derived dFe potentially supports new primary production between 9.0×10^9 and $4.1 \times 10^{11} \text{ mol C yr}^{-1}$ (0.1–4.9 Tg C yr⁻¹). Therefore, our upper estimate could support ~8–15% of new production in the SW Ross Sea based on a new primary production rate for the SW Ross Sea of ~15–30 mol C m⁻² yr⁻¹ assuming an *f* ratio (= new production/total net production) of 0.5 [Asper and Smith, 1999; Long *et al.*, 2011; Sedwick *et al.*, 2011] and primary production rates of 1–2 g C m⁻² d⁻¹ from a regionally calibrated satellite study reported by Arrigo and van Dijken [2004]. This approach suggests that aeolian dFe input from locally derived ASD could only be a minor source of new dFe into the SW Ross Sea. In summary, both methods of calculating the importance of ASD to Fe fertilization in the study area suggest that it likely contributes to, but is clearly not the primary source of dFe, in Ross Sea.

We note that these values could be underestimated due to unquantified ASD accumulation rates supplied by (i) direct deposition to the ocean during the growing season, (ii) the deposition of ASD over a greater area than was sampled in this study, and (iii) other ASD sources along the Victoria Land Coastline, such as Terra Nova Bay, where it is known that dust blows into the embayment. Furthermore, the relative importance of ASD versus other sources of Fe may vary from year to year. Chewings *et al.* [2014] show that windy years correlate to higher dust fluxes in McMurdo Sound. When particularly high velocity southerly storms occur prior to or during the summer, ASD mass accumulation rates (and thus soluble Fe) up to 4–5 times greater than background years have been observed at Windless Bight on the McMurdo Ice Shelf [Dunbar *et al.*, 2009]. The additional dFe supplied during these storm events could therefore extend the influence of McMurdo Sound-derived ASD over a much greater area of the SW Ross Sea.

5.5. Regional Significance

To place the results presented by this study in a regional context, we summarize the sparse measurements of ASD-derived dFe reported elsewhere around Antarctica (Figure 3). In doing so we note that the methodology for determining dFe differs between studies, and in most cases the results are not directly comparable. Nonetheless, the data serve to illustrate several points: (i) the extreme paucity of direct measurements on the contribution of ASD to dFe in the marginal seas around Antarctica, (ii) the large spatial differences in ASD-derived dFe concentrations around the continent, and (iii) the temporal and spatial variability of effectiveness of ASD as an Fe fertilizer, which is dependent on both the input of ASD-derived dFe and the degree of Fe limitation, itself dependent on a number of factors [e.g., Bruland and M. C. L. T., 2004; Morel and Price, 2003; Timmermans *et al.*, 2004].

Direct measurements of dFe from Antarctic ASD are limited to a few studies from three differing localities: (a) the continental interior, which provides a measure of the global background based on provenance data suggesting an Australian and/or Patagonian origin. Notably, to date, of continental ice core sites, ASD-derived dFe has only been analyzed in the European Project for Ice Coring in Antarctica Dome C and Talos Dome

Table 2. Iron Concentration of Coastal Antarctic Snow

TdFe ^a (nmol L ⁻¹)	dFe (nmol L ⁻¹)	Latitude, Longitude	Reference
5.7–16.0	-	Weddell Sea	Westerlund and Öhman [1991]
31.3–52.6	-	58–60°S, 6–7°W	Loscher et al. [1997]
25	4	70°S, 6°W	de Jong et al. [1999]
1.2–31.7	-	64–66°S, 75–76°E	Edwards and Sedwick [2001]
1.8–23.7	1.0–6.5	64–65°S, 112–119°E	Lannuzel et al. [2007]
7.8–22.3	0.7–3.2	67–68°S, 54–55°W	Lannuzel et al. [2008]
-	0.2–1.1	64–65°S, 116–127°E	van der Merwe et al. [2009]
0.7–6.9	0.2–1.1	64–65°S, 116–127°E	van der Merwe et al. [2011a]
3.2–100.8	0.9–7.1	66°S, 110°E	van der Merwe et al. [2011b]
1.2–100.8	0.2–7.1	Antarctic range	
-	28–1871	77.5°S, 165°E	This study, McMurdo Sound

^aTotal dissolved Fe (TdFe) is the Fe concentration of the bulk sample (snow and particulate Fe).

ice cores (Figure 3). (b) The Antarctic margin, which reflects local sources. Dissolved Fe has been measured in a few snow on sea ice studies along the East Antarctic coastline (e.g., sea ice marginal zones off Wilkes Land and the Amery Ice Shelf), in the Weddell Sea and McMurdo Sound (Figure 3). (c) The open ocean, which could receive input from a combination of both local and distal sources. Some indication of the potential dFe contribution from the global background dust is given by values obtained from Holocene intervals of ice cores on the Antarctic Plateau [Vallelonga et al., 2013]. Overlying these observations are modeling studies that estimate 0.01 nmol L⁻¹ dFe is generated from global dust input [Lancelot et al., 2009].

ASD rates are much higher than global background values along Antarctic coastal margins, reflecting proximity to unconsolidated sediment sources (e.g., McMurdo Sound and Granite Harbour) [Atkins and Dunbar, 2009; Chewings et al., 2014]. Figure 3 illustrates the spatial extent of ice-free areas and exposed rock in Antarctica, most of these located on or near the Antarctic coast. Basal marine and glacial sediments exposed by ablation of glacial ice, such as the McMurdo Ice Shelf debris bands, are not necessarily limited to the SW Ross Sea; however, a number of potential source regions (e.g., Terra Nova Bay, Vestfold Hills, and the West Antarctic Peninsula) have not been measured. Regardless, the snow accumulating on sea ice in McMurdo Sound stands out as exceptionally dusty with at least 2 orders of magnitude greater potential for supplying dFe than other sea ice marginal zones. Table 2 shows that our estimates of aeolian dFe from McMurdo Sound snow are substantially greater than the concentration of dFe reported for circumpolar Antarctic snow (0.2–7.1 nmol L⁻¹). McMurdo Sound, therefore, represents the upper limit of the contribution of ASD to sea ice and by implication the upper limit of the amount of dFe that can be supplied by ASD to the Antarctic oceans.

As discussed in section 5.3, the inherent dFe deficiency of HNLC oceans necessitate a dFe limitation threshold to be met for phytoplankton production to occur, and we suggest that an ~0.1–0.2 nM dFe limitation is reasonable for the Ross and Antarctic marginal seas. From the perspective of ASD-derived dFe, for an ocean with an ~0.1–0.2 nM dFe deficit, our results suggest that even in area of high ASD accumulation rates, the Fe fertilization effect of ASD alone is insufficient to drive phytoplankton growth, implying that dFe from another source or sources is relatively more important to biogeochemical cycling in the Ross Sea and offshore Antarctic waters. The identity of other dFe sources and their susceptibility to change in a warming world remain poorly understood.

6. Summary and Conclusions

Recent field observations suggest that seasonal phytoplankton blooms in the SW Ross Sea consume a winter reserve of dFe at the beginning of the season and thus require a new, continuous source of Fe to maintain growth for the rest of the growing season. Based on our measurements of mass accumulation rates, texture, Fe content, and Fe solubility of ASD on sea ice in McMurdo Sound, we conclude the following:

1. The debris bands region of the McMurdo Ice Shelf is the most important known source of ASD to sea ice in McMurdo Sound and the Ross Sea region and contributes >2 orders of magnitude more ASD to sea ice than does global dust supply.

2. The mass accumulation rate of ASD decreases exponentially with distance northwest of the debris bands, from 26 to $\sim 1 \text{ g m}^{-2} \text{ yr}^{-1}$. Between 20 and 120 km from source the mass accumulation rate is relatively constant at $\sim 1.53 \text{ g m}^{-2} \text{ yr}^{-1}$.
3. The total particulate Fe content of this ASD is $4.08 \pm 1.39 \text{ wt}\%$, and the soluble proportion is $10.96 \pm 0.74\%$. The similarity in mineral composition between samples means the flux of soluble Fe for the fine fraction ($2.0 \text{ mg m}^{-2} \text{ yr}^{-1}$ or $36.7 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$) and for the bulk fraction ($6.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ or $122.1 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$) is directly proportional to the mass accumulation rate.
4. The rate of Fe leaching is nearly instantaneous, implying even coarse (sand-sized) grains with a short residence time (hours) contribute to dFe in the water column.
5. Aeolian-derived Fe could potentially support between 9.0×10^9 and $4.1 \times 10^{11} \text{ mol C yr}^{-1}$ of new primary production in McMurdo Sound. The upper estimate is $\sim 15\%$ of new primary production in the SW Ross Sea, suggesting that locally derived aeolian dFe contributes to, but cannot be the primary source of, Fe stimulating new phytoplankton production in the SW Ross Sea.
6. For the marginal seas surrounding Antarctica, with a dFe limitation of $\sim 0.1\text{--}0.2 \text{ nM}$, we suggest the seasonal blooming of phytoplankton is unlikely to be solely driven by dFe deposited by ASD on sea ice as there is currently no evidence of sufficient ASD accumulation to provide the necessary Fe requirements.
7. Lastly, we note the importance of soluble Fe from ASD may change year-to-year depending on the magnitude and timing of storm events which transport proportionately more ASD across the sea ice.

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