

Winter-time dissolved iron and nutrient distributions in the Subantarctic Zone from 40–52S; 155–160E

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[1] In HNLC oceanic regions, iron (Fe) controls phytoplankton productivity yet large gaps remain in our understanding of iron's biogeochemical cycle. Here we present the first comprehensive winter dataset for dissolved Fe (dFe) and nitrate (NO₃) distributions (0–1000 m depth) between 40S–52S, which transects the Subantarctic zone (SAZ), west of New Zealand. Surface concentrations (<0.2 nmol Fe kg⁻¹) were conspicuously low, i.e., probably biologically limiting even at winter-reserve levels, at frontal zones between 43S (Subtropical Front) and ~51S (Subantarctic Front). A fivefold range in Fe:NO₃ molar ratios was observed along the transect, with Subtropical waters, where blooms occur, having the highest ratios in subsurface waters. The major wintertime supply of dFe in the SAZ is from Ekman advection of waters from the south (but calculated source water dFe is ~0.2 nmol Fe kg⁻¹), suggesting that mixed-layer dFe concentration is controlled by how long these southern waters remain at the surface (~3 years). **Citation:** Ellwood, M. J., P. W. Boyd, and P. Sutton (2008), Winter-time dissolved iron and nutrient distributions in the Subantarctic Zone from 40–52S; 155–160E, *Geophys. Res. Lett.*, 35, L11604, doi:10.1029/2008GL033699.

1. Introduction

[2] In the Southern Ocean, mesoscale Fe fertilization experiments have clearly demonstrated that Fe plays a pivotal role in controlling primary production in polar and subpolar High Nitrate Low Chlorophyll (HNLC) waters [Boyd *et al.*, 2000; Coale *et al.*, 2004]. There has been considerable debate about the relative magnitude of different Fe sources to surface waters in these regions, such as upwelling, dust or entrainment from island and continental self sediments [Blain *et al.*, 2007; Boyd *et al.*, 2004; de Baar *et al.*, 1995]. However, despite the rapidly emerging field of Fe biogeochemistry, there are few vertical profiles of dissolved Fe (dFe) concentration [Parekh *et al.*, 2004], and almost no winter Fe data [Boyd *et al.*, 2005]. The latter are essential to understanding Fe biogeochemistry over annual cycles. There is also evidence that biogeochemical cycles of Fe and NO₃ are decoupled in the upper ocean, but little is understood about the mechanisms behind this [Boyd *et al.*, 2005; Croot *et al.*, 2007; Johnson *et al.*, 1997]. Here, we

present winter dFe and NO₃ distributions, and examine the relationship between them along a meridional transect from 40S to 52S through Southern Ocean waters.

2. Methods

[3] The procedures used to collect and process of samples for iron determination are detailed in the auxiliary material¹. Briefly, samples were collected using 5 L Niskin-X bottles attached to an autonomous rosette (General Oceanics, USA). DFe was determined on acidified samples after dithiocarbamate solvent extraction by inductively coupled plasma mass spectrometry (820-MS, Varian). Three SAFe Fe reference samples [Johnson *et al.*, 2007], and an in-house Fe reference standard, were analyzed to ensure quality control on these measurements (Table S1).

3. South Tasman Sea/Southern Ocean Oceanography

[4] The study region targeted a north-south transect in the south Tasman Sea spanning Subtropical waters to the Subantarctic Front (SAF). This area is characterized by several circumpolar fronts (SAF and subtropical Front (STF)) (Figure 1), and is a key region in the winter formation of subantarctic mode water (SAMW) resulting from deep convection as surface waters cool [McCartney, 1977; Sokolov and Rintoul, 2007; Rintoul and England, 2002]. The STF was present as a broad feature covering several degrees of latitude and is characterized by the transition from warm salty subtropical (ST) water to cold, fresh subantarctic (SA) water. The likely zone for SAMW formation was between around 49S and 51S where the temperature ranges between 8°C and 9°C (Figure 2) and the density was between 26.78 (equivalent to 1026.78 kg m⁻³) and 26.85 (Figure S2). This meridional zonation was also evident from the Si* (Si* = [Si] – [NO₃]) tracer [Sarmiento *et al.*, 2004]. Si* values were between –10 μmol kg⁻¹ and –15 μmol kg⁻¹ between 49S and 51S, which is strongly indicative of SAMW (Figure 3).

[5] The south Tasman Sea receives episodic dust inputs from the arid centre of Australia (Figure 1). These waters are dominated by a classic seasonal cycle in primary production, with high summer rates, and low rates in winter (Figure S3). This seasonal productivity cycle is driven by concomitant changes in light climate, dFe and silicic acid supply [Boyd *et al.*, 1999; Murphy *et al.*, 2001]. During winter months, low phytoplankton productivity (Figure S3) coupled with increased SAMW formation and deepening of

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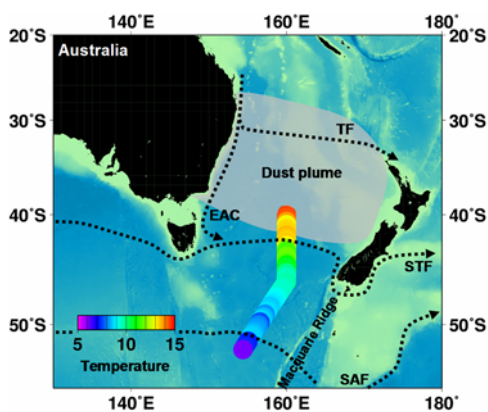


Figure 1. Map of the Tasman Sea region overlaid with sea surface temperature data along the July 2006 voyage track. Dust plume denotes the potential area over which aerosol iron from episodic dust storms might be dispersed. Abbreviations: TF, Tasman Front; EAC, East Australian Current; STF, Subtropical Front; and SAF, Subantarctic Front.

the surface mixed layer to ~ 200 – 400 m depth [Sokolov and Rintoul, 2007] should result in a significant increase in the inventory of both trace metals, like Fe, and macronutrients (such as NO_3) in the upper ocean to winter-reserve concentrations. Such winter reserves largely set the magnitude of seasonal production in the following algal growth season, when the mixed layer shoals to $\ll 100$ m depth [Rintoul and England, 2002; Sokolov and Rintoul, 2007].

4. Results

[6] In general, surface waters had low dFe concentrations, with minima occurring between the two major frontal zones (Figure 2 and Table S2). The ferricline was located at ~ 150 m depth between 40 – 42 S and deepened southward to around 400 m at 48 S in association with the deepening mixed layer. In the remote Southern Ocean, away from continental sources, upwelling/entrainment of dFe from underlying waters into the mixed layer is believed to be the dominant Fe supply for phytoplankton during spring and summer months [de Baar et al., 1995]. However, there was no significant correlation between Fe and temperature, salinity or density (Figures 2 and S2) indicating that dFe supply into this zone is not directly modulated by mixing as the mixed layer deepens. Indeed, the low surface values for dFe are surprising given that we should expect to see winter reserve concentrations approaching ~ 0.4 nmol kg^{-1} i.e. that of the deep water signal (Figure 2) [Sohrin et al., 2000]. In comparison to a typical late summer dFe concentration of ~ 50 pmol kg^{-1} [Boyd et al., 2004; Croot et al., 2007], winter dFe is therefore on average only 150 pmol kg^{-1} higher (Figure 2).

[7] Surface NO_3 concentrations increase southward along the section from the STF to the SAF (Figure 2). Vertical NO_3 profiles reveal an increase in concentration with depth along the transect, with northern waters having a greater vertical gradient at the nitracline than waters to the south. The nitracline was located ~ 50 m shallower than the ferricline between 40 – 46 S, whereas they were co-located

at the same depth stratum from 46 – 52 S (Figure 1) The relationship between dFe and NO_3 was explored by plotting the Fe: NO_3 molar ratios (Figure 3). A fivefold range of ratios were evident, and the waters between 40 – 46 S had much higher ratios than those further south. Fe: NO_3 ratios also increased with depth but with lower values in the south (0.005 – 0.018 nmol: μmol) compared to ratios at the northern stations (0.017 – 0.032 nmol: μmol) (Figure 3). Fe: NO_3 ratios of ~ 0.01 nmol: μmol are consistent with studies from other HNLC regions e.g. the North Pacific [Martin et al., 1989] and with those reported from open-ocean algae cultured under iron-limiting conditions [Maldonado and Price, 1996]. Seasonal Fe and NO_3 datasets for surface waters in the SAZ (~ 46.5 S, ~ 178.5 E) east of New Zealand exhibited Fe: NO_3 ratio's of ~ 0.01 nmol: μmol or less (Figure S4) (M. Ellwood, unpublished data, 2004). It seems that the Fe: NO_3 ratio is not seasonally variable in the SAZ suggesting that either there is strong control of this ratio by supply mechanisms and/or that the resident phytoplankton, due to Fe limitation, are consuming Fe and NO_3 at a set ratio. In the STF and northern waters (where blooms are observed), high Fe: NO_3 ratios are evident at much shallower depths than in the SAZ (Figure 3).

5. Discussion

[8] The major questions that emerge from these findings are: why are dFe levels so low in the subantarctic waters during winter?, such that it may limit phytoplankton growth (i.e. dFe of 0.2 nmol kg^{-1} or less is reported to limit photosynthetic competence of Southern Ocean phytoplankton [Boyd and Abraham, 2001]) even at the onset of the annual growth season, and is this Fe supply sufficient to support significant levels of spring phytoplankton production?

[9] The lateral supply of water into the SAZ is usually from the south via wind-driven Ekman transport [McCartney, 1977; Rintoul and England, 2002]. If this is the main dFe supply mechanism during winter, then wintertime replenishment of the dFe inventory in the SAZ cannot exceed that of source waters to the south. If the dFe concentration in these source waters is low, this would explain the low dFe concentration and the deep wintertime ferricline in waters immediately north of the SAF (Figure 2). To test this idea, some basic calculations are required. Using an Ekman advection rate of 0.01 m s^{-1} for a 100 m thick surface layer entering the SAZ [Rintoul and England, 2002], the transport of water over ~ 1 degree across the SAF into the SAZ will take ~ 4 months. If the apparent age of surface waters entering the SAZ is of the order of years since it was brought to the surface [Rintoul and Bullister, 1999], then it is likely to carry the residue of dFe concentration and Fe: NO_3 signature from the previous phytoplankton growth season plus that of dFe entrained via upwelling. If we assume that the summer background dFe concentration in Southern Ocean surface waters is ~ 0.05 nmol kg^{-1} (Figure S4) [Croot et al., 2007; Sohrin et al., 2000], that upwelled deep water has an Fe concentration of ~ 0.4 nmol kg^{-1} , and that the apparent age of the waters in the surface mixed layer entering the SAZ from the south is ~ 3 years [Rintoul and Bullister, 1999], then the maximum winter dFe concentration in SAZ will be ~ 0.17 nmol kg^{-1} . This

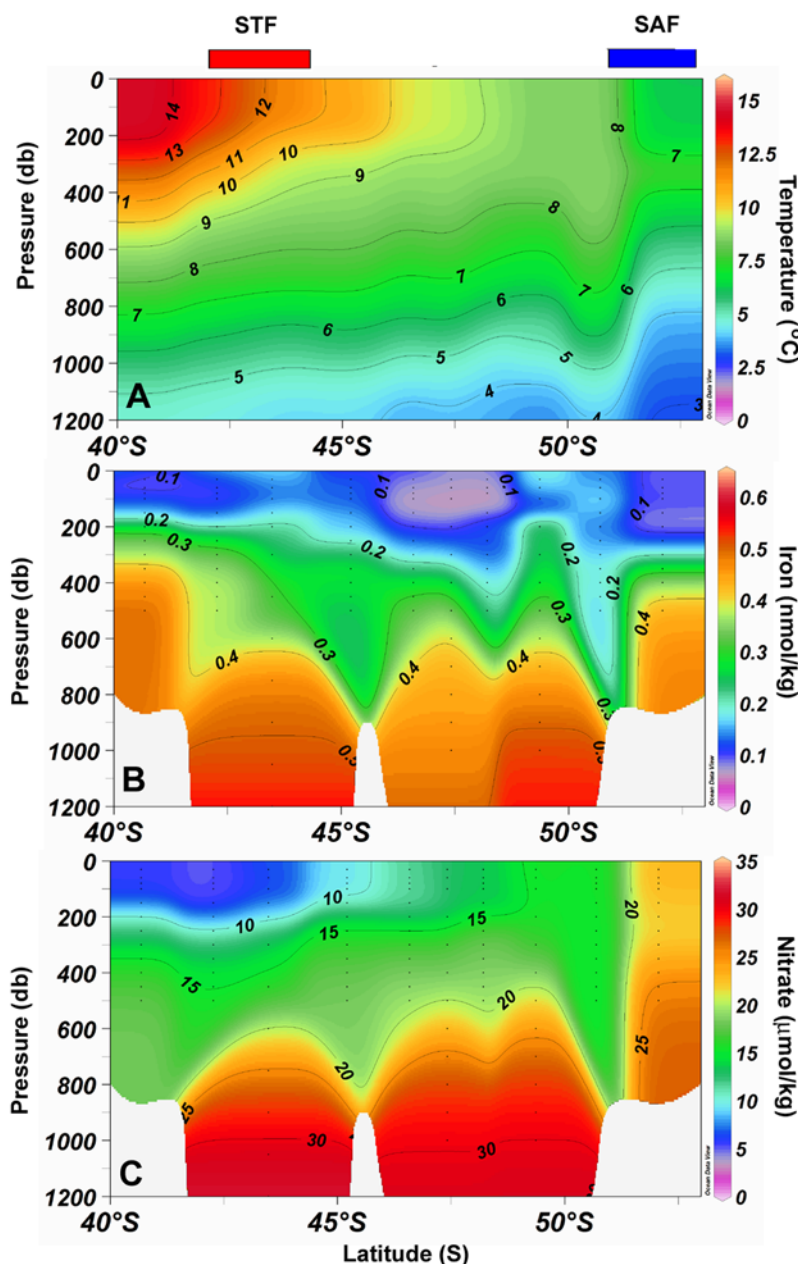


Figure 2. Contour plots of (a) temperature, (b) dFe concentration and (c) NO_3 concentration from 0 to 1200 m. STF and SAF indicate the approximate position of the fronts respectively. Contour plots were generated using Ocean Data View (odv.awi.de/home.html).

calculated concentration is consistent with values estimated using the Fe: NO_3 data and the seasonal difference in NO_3 concentration (Figure S4). During winter, water entering the SAZ from the south has a Fe: NO_3 ratio of between ~ 0.01 – 0.02 nmol: μmol , however winter NO_3 is around $7 \mu\text{M}$ greater than that observed in summer (Figure S4), thus based on this information, the dFe concentration should be 0.07 – 0.14 nmol kg^{-1} higher in winter at around 0.12 – 0.19 nmol kg^{-1} , which is similar to the observed concentration (Figure 2).

[10] These calculations establish that the main supply of dFe into the SAZ during winter months is most likely via Ekman transport (the vertical diffusive supply of dFe into the seasonal mixed layer appears to be minor, based on

estimates derived from sulfur hexafluoride and dFe vertical gradients (Table 1) [Boyd *et al.*, 2005]). The supply flux of Fe entering the SAZ was estimated using a surface transport flux of 44 Sv [Rintoul and Trull, 2001] and a winter dFe concentration of 0.17 nmol kg^{-1} , giving a flux across the SAF of $147 \mu\text{mol dFe m}^{-2} \text{d}^{-1}$. While this supply flux is sufficient to support algal growth at the onset of the growth season, this wintertime dFe concentration is very close to the threshold of that for algal growth limitation [Boyd and Abraham, 2001]. Once production increases, the mixed layer dFe concentration in waters south of the SAZ will decline, by summer, to growth-limiting concentrations of about 0.05 nmol kg^{-1} (Figure S4). As these low dFe waters are transported into the SAZ, the dFe concentration in this

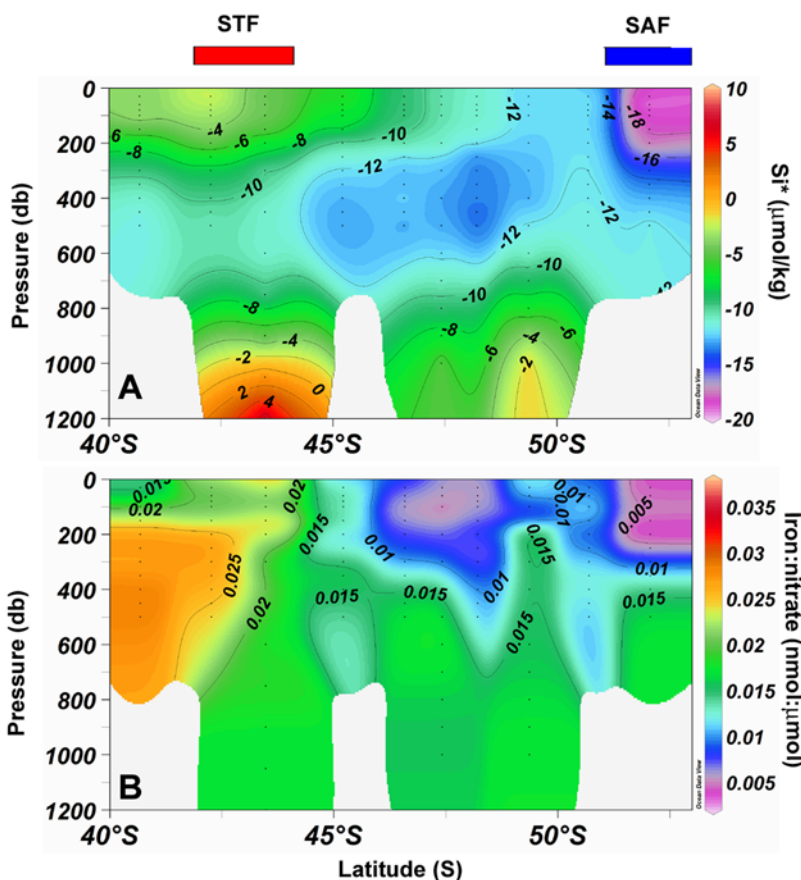


Figure 3. Contour plots of (a) Si^* and (b) the $\text{Fe}:\text{NO}_3$ ratio from 0 to 1200 m depth.

zone will also decline due to both in situ biological activity and this physical transport (Figure S4). This situation is analogous to that of silicic acid where there are strong seasonal changes in concentration leading to the growth limitation of diatoms in the SAZ during summer [Boyd *et al.*, 1999; Falkowski *et al.*, 1998].

[11] Although we can rule out Ekman transport in late spring and summer as a supply mechanism for water with higher dFe concentrations, nevertheless, satellite images of chlorophyll *a* reveal a strong seasonal signal with spring and summer blooms occurring within the frontal features of the STF and northern SAZ (Figure S3). Conversely, the seasonal production signal at the SAF is not pronounced. These contrasts in seasonal production signatures suggest alternative supply routes for Fe into the northern and southern sections of the SAZ. The only supply mechanisms capable of raising dFe concentrations in the surface mixed layer of the SAZ are from Fe associated with atmospheric dust deposition and Fe that diffuses across the pycnocline from below.

[12] The major summertime Fe source into the SAZ, close to continental sources, is thought to be from episodic deposition of eolian dust of an Australian origin [Boyd *et al.*, 2004; Frew *et al.*, 2006]. Although dust deposition is sporadic and spatially variable, the major supply season into the south Tasman Sea region is in the Austral spring and summer [Boyd *et al.*, 2004]. During winter dust supply is low. Indeed, dust activity was low in 2006 according to records from >100 dust monitoring stations across Australia

(G. McTainsh, personal communication, 2008), thus it is unlikely to be a major contributor to the surface dFe pool in the remote waters of the SAZ. This is confirmed using dust flux data from both modeling experiments [Cassar *et al.*, 2007] and observations [Wagner *et al.*, 2008]. Based on our calculations, the atmospheric Fe input flux of $0.027\text{--}0.055\ \mu\text{mol m}^{-2}\ \text{d}^{-1}$ from Cassar *et al.* [2007] (which are ten- to a hundred-fold higher than the observations of Wagner *et al.* [2008]) is not enough to sustain production

Table 1. Flux Calculations for Sources, Sinks and Recycling of Fe to the SAZ During Winter (Summer)

	Source Concentration (nmol kg^{-1})	Flux ($\mu\text{mol m}^{-2}\ \text{d}^{-1}$)
Atmospheric source	-	$\sim 0.027\text{--}0.055^{\text{a}}$ (0.76 ^b)
Wintertime advection source	0.17 (0.05 ^b)	147 (43 ^c)
Vertical diffusive source	~ 0.4 ($\sim 0.7^{\text{b}}$)	0.015 ^b
Biological requirement from new Fe sources ^d		0.25–0.41
Biological requirement from recycled Fe sources ^d		2.25–3.69

^aData taken from Cassar *et al.* [2007].

^bData taken from Boyd *et al.* [2005], Croot *et al.* [2007], and Strzpek *et al.* [2005] for the FeCycle site located in SA waters east of New Zealand.

^cAlthough this flux is high, the dFe concentration associated these waters entering the SAZ is low and comparable to that in the SAZ waters, hence there is no significant change in dFe concentrations.

^dThis is based on an *fe* ratio of 0.1 [Boyd *et al.*, 2005] (*fe* = new/(new+regenerated Fe)).

(cf. primary production driven by 'new' Fe has a demand of $0.25\text{--}0.41 \mu\text{mol m}^{-2} \text{d}^{-1}$), or to raise the wintertime dFe concentration appreciably – based on a mixed layer of 100 m it would take between 275–550 days to raise dFe from $0.05 \text{ nmol kg}^{-1}$ to 0.2 nmol kg^{-1} , assuming no vertical loss from the mixed layer. Using the observations of Wagener *et al.* [2008] these supply times increase to 13–205 years.

[13] The second potential source of Fe into the mixed layer is from the diffusion of iron across the pycnocline. For the southern part of the SAZ and SAF, if we use a vertical dFe diffusive supply rate of $0.015 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Table 1) into the mixed layer it would take approximately 3 years to raise the dFe concentration from $0.05 \text{ nmol kg}^{-1}$ to 0.2 nmol kg^{-1} . Clearly the supply of Fe from atmospheric and diffusional sources is insufficient to fuel summertime production in the STF and northern waters.

[14] The high chlorophyll *a* concentration in the STF region during summer suggests that the dFe levels in this zone are not limiting (Figure S3) [Sokolov and Rintoul, 2007] and likely reflects changes in the concentration and supply of dFe to surface waters [Ridgway, 2007]. The higher Fe:NO₃ values in the waters at and north of the STF, 0.02–0.03 nmol: μmol , confirm this idea as values are higher than typical ratios for HNLC waters. These higher Fe:NO₃ values, especially in deeper waters, may reflect the influence of waters transported eastward by the seasonally variable EAC extension [Ridgway, 2007], which may have entrained Fe of a continental shelf source. Alternatively, the higher Fe:NO₃ values may reflect the influence of a labile particulate Fe source [Frew *et al.*, 2006], which is cycled into the dissolved phase during spring and summer.

6. Conclusions

[15] The first comprehensive winter datasets for south Tasman Sea and Southern Ocean and indicates that dFe concentrations are only slightly elevated over that of summer concentrations. The major wintertime supply of dFe in the SAZ across the APF is thought to be from the Ekman transport of waters from the south; however, the dFe concentration of these southern source waters is $<0.2 \text{ nmol kg}^{-1}$. The major control of dFe concentration in the mixed layer appears to be the age of the surface water entering the SAZ: iron supply from atmospheric dust and vertical diffusivity are relatively insignificant Fe sources to the SAZ. While the advective supply flux of dFe into the SAZ during winter is enough to sustain algal production, albeit at a slightly reduced rate, light and mixed layer depth are not favorable for production during winter months. The fivefold range in Fe:NO₃ ratios was observed along the transect, especially in subsurface waters at and north the STF, which may explain why spring blooms are observed in STF waters.

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