# Nitrate-rich inland waters of the Ross Ice Shelf region, Antarctica

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Abstract: Nutrient and major ion concentrations were measured in surface water samples from lakes, ponds and streams at sites 30–320 km south of McMurdo Sound: the Darwin Glacier region (79.7–80.0°S), Pyramid Trough in the southern Dry Valleys (78.2°S), and the McMurdo Ice Shelf ablation zone (77.8–78.4°S). These aquatic environments ranged from dilute meltwaters (conductivity < 0.05 mS cm<sup>-1</sup>) to concentrated brines (> 50 mS cm<sup>-1</sup>). The lowest nitrate concentrations were recorded at the sites closest to the seasonally open waters of the Ross Sea. Much higher values (100–142000 mg NO<sub>3</sub>–Nm<sup>-3</sup>) were recorded at sites further south. These observations support the hypothesis that NO<sub>3</sub><sup>-</sup> precipitation over Antarctica is of stratospheric rather than coastal marine origin. The nitrogen-rich waters contained chloride and nitrate in the ratio 5.45 g Cl : 1 g N (C.V. = 8.4%) which is within the range for Antarctic snow, and indicative of nitrate enrichment by freeze concentration processes. Cyanobacterial mats were conspicuous elements of the biota across the full range of salinities, and were usually dominated by oscillatoriacean species. Nitrogen-fixing cyanobacteria and diatoms were also represented in these benthic microbial communities at the more northern sites, but were absent from all samples from the Darwin Glacier region.

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## Introduction

High nitrate concentrations in natural waters are often attributed to industrial or agricultural sources (e.g. Saull 1990, Spalding & Exner 1993) but there is a paucity of data from pristine areas where these local anthropogenic inputs are minimal. The lack of measurements from remote sites has been emphasized by Lyons *et al.* (1990) who draw attention to the importance of such data in better understanding the background variability in natural NO<sub>x</sub> concentrations. However, snow and ice cores from Greenland (Mayewski *et al.* 1990) and Antarctica (Mayewski & Legrand 1990) show a marked near-surface increase in nitrate concentration. These observations suggest that even remote polar regions are sensitive to the global emission of nitrate by industry, biomass burning and other human activities.

Nitrate has now been measured in the snow at many sites around the Antarctic continent but there are still few data for surface meltwaters. The source of this nitrogen in Antarctic snow has remained controversial for many decades. Virtually all of these south polar sites lie well beyond the immediate influence of human activity, and local anthropogenic inputs are likely to be negligible. *In situ* biological activity (nitrogen fixation, ammonification, nitrification) is also likely to be minimal in these deep frozen snow and ice environments. While some authors have suggested that precipitation of marine aerosols is the primary source term in the Antarctic nitrate budget (Claridge & Campbell 1968, Keys & Williams 1981), others have favoured a stratospheric origin for this biologically active anion (e.g. Parker *et al.* 1978, Zeller & Parker 1981, Legrand & Kirchner 1990).

The nitrate content of Antarctic surface waters may largely reflect the characteristics of the inflowing snow-melt or other external inputs. For example, inorganic nutrients including nitrate are usually in high concentration (often 300-400 mg NO<sub>3</sub><sup>-</sup>N m<sup>-3</sup>) in the surface mixed layer of the Southern Ocean (Vincent 1988), and Antarctic coastal ponds experience direct nitrate enrichment by sea spray. However, a variety of physical and biogeochemical processes operating within the waterbody can substantially modify the local nitrate regime. Certain meromictic lakes in the Dry Valleys of southern Victoria Land contain deep-water nitrate maxima (e.g. up to 6426 mg N m<sup>-3</sup> in Lake Bonney (Torii 1975) and up to 3200 mg N m<sup>-3</sup> in Lake Vanda (Vincent et al. 1981)) that have been attributed to the slow but long-term activity of nitrifying bacteria. Some of the highly saline ponds of the Dry Valleys are enriched in nitrate as a result of freeze concentration and evaporation e.g. up to 24 400 mg N m<sup>-3</sup> in the Wright Valley (Webster et al. 1994) and up to 347 200 mg N m<sup>-3</sup> in the Labyrinth (Torii 1975). The ephemeral streams of this region carry their highest nitrate concentrations during the early flow period, reflecting freezeconcentration and evaporation processes at the source glacier, and over the streambed (Vincent & Howard-Williams 1986). Nitrate stripping by biological processes can deplete the concentration of this nutrient in some Antarctic lakes and streams (Canfield & Green 1985, Howard Williams et al. 1989a).

This paper presents nitrate and associated chemical and biological analyses from a set of remote, south polar aquatic environments between 77 and 80 °S. They represent the southernmost environments thus far sampled for surface water chemistry. From the combination of limnological data obtained in this study we consider the relative importance of nitrate

160<sup>°</sup>E 160<sup>°</sup>E 164<sup>°</sup>E McMurdo Sound McMurdo Bratina Island A 78°S Pyramid Trough Mt. Discovery C Minna Bluff 90°E 90°E 180°

Fig. 1. Location of sampling sites. Three sites were located on the McMurdo Ice Shelf: near Bratina Island (A), near the base of Mountt Discovery (B) and the northern side of Minna Bluff (C).

source and sink processes for these Antarctic inland waters.

## Study sites

Three geographically distinct regions were sampled over a broad area between latitudes 77–80 °S, 156–166 °E, at altitudes from sea level to 1000 m. The regions were centred on or near the following geographic features which we subsequently adopt as regional names: McMurdo Ice Shelf ablation zone, Pyramid Trough, and the Darwin Glacier, (Fig. 1). All sites lay within 5–75 km of the Ross Ice Shelf, and ranged from 30–320 km from the sea, as defined by the late summer ice edge in McMurdo Sound (Fig. 1). The sampling was conducted between 31 December 1990 and 26 January 1991, the late summer period of maximum meltwater production. Air temperatures at this time ranged from -7 to  $+4^{\circ}$ C.

#### McMurdo Ice Shelf ablation zone

This is a 1200 km<sup>2</sup> region of moraine-covered ice with 10–60% coverage by lakes, ponds and streams. The ice sheet is mostly derived from the basal freezing of seawater, but the surface meltwaters range from relatively fresh to hypersaline. Further background information on the limnology of this region is given in Vincent (1988) and Howard-Williams *et al.* (1989b, 1990). Three sites on the ice shelf were sampled (A, B and C): Minna Bluff (C, 90 km south of McMurdo Sound); Mount Discovery Site (B, 60 km south of McMurdo Sound); and near Bratina Island (A, 30 km south of McMurdo Sound).

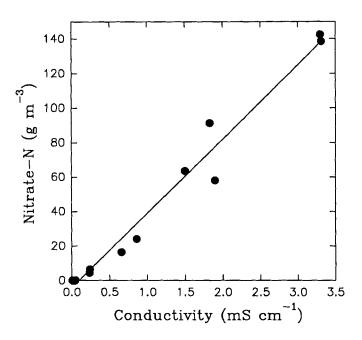


Fig. 2. The relationship between nitrate concentration and conductivity for waters in the Diamond Hill region. The line is a fitted regression line for the data.

## Pyramid Trough region

This is an area of abundant lakes, ponds and streams at the southern end of the Dry Valleys region, c. 75 km from the open sea. The Trough is a deep valley at 400 m altitude that terminates in proglacial Trough Lake. The upper portion of the Alph River, fed primarily by the Koettlitz Glacier, flows down the valley and through Trough Lake (Howard-Williams *et al.* 1986, de Mora *et al.* 1991).

#### Darwin Glacier region

This was the southernmost region of the study, c. 300 km south of McMurdo Sound. Lakes and pools on the lower Darwin Glacier were originally identified from satellite images (Swithinbank 1988). On visiting this area we found pools (such as LDP1) of clear water up to 0.5 km long and 0.1 km wide mostly overlain by a thin (<0.5m) layer of ice. Several streams up to 1 m wide of greenish coloured water were flowing over the glacier surface. Ponds with open water up to 0.5 km long were also observed in the pressure ridges further up the Darwin Glacier at the confluence with the Hatherton Glacier. Diamond Hill is an ice-free region with many small valleys, each of which contains small ponds and interconnecting streams. Samples were collected from a downslope sequence of ponds and streams, from DHS1 at c. 650 m altitude to DHP5 at c. 450 m altitude. A large, permanently ice-covered lake, Lake Wilson, lies at the base of this region between Diamond Hill and the Ross Ice Shelf. Samples from this lake were restricted to the surface waters from the melted edge region (the moat). A deep moraine-filled valley was visited to the south of Mount Ash in the Darwin Mountains, at an altitude of 1000 m. The highly undulating surface of this valley was occupied by several hundred ponds of variable size, but typically 40 m by 40 m or less.

## Methods

Conductivity was measured in the field and corrected to 25 °C using a Hanna combined temperature and conductivity probe. Field measurements of pH were made with a Hanna pH electrode. Water samples were collected in acid-washed (0.1N HCl) polyethylene bottles that were rinsed with deionized water and then with the filtered or unfiltered sample water, each three times. The samples were stored cool ( $<5^{\circ}$ C) but unfrozen for 2 –24h prior to filtration through sample-washed Whatman glass fibre filters (Grade GF/F). The filtrates and filtered particulates were then stored frozen until analysis up to 4 weeks later.

The benthic microbiological samples were cut with a 1 cm diameter plastic coring device from areas of highest standing stock. These were then stored frozen until subsequent microscopic and chlorophyll a analysis.

Dissolved reactive nutrients were subsequently measured on duplicate samples of thawed filtrates using a Technicon II AutoAnalyser system. The nitrate plus nitrite concentrations were determined using an automated cadmium column method with Tris-ammonium chloride buffer modified from Nydahl (1976). Nitrite was measured by the same method, but without the cadmium reduction step. The highest concentration samples were diluted with milli-Q water before final analysis. Dissolved reactive phosphorus (DRP) was measured by the autoanalytical method of Downes (1978) modified by eliminating the metabisulphite-thiosulphite reagent. Ammonium was measured by an automated version of the phenol hypochlorite method of Solorzano (1979). The analytical detection limits were 0.5 mg N m<sup>-3</sup> for nitrite, nitrate and ammonium, and 0.3 mg P m<sup>-3</sup> for DRP. The duplicate samples for each nutrient analysis typically agreed to within 20%.

Total dissolved nitrogen was measured by persulphate oxidation of the sample to nitrate and nitrite (Solorzano & Sharp 1980) and dissolved organic nitrogen (DON) was then calculated by difference. For waters high in nitrate (> 2 g m<sup>-3</sup>) DON was measured by Kjeldahl digestion to ammonium of filtered samples. Total dissolved phosphorus (TDP) was measured as DRP following UV-digestion. Dissolved organic phosphorus (DOP) was calculated as TDP minus the DRP in undigested samples.

The major ion analyses were determined using a Dionex 2000i SP ion chromatograph. Cations were resolved using isocratic elution on the Dionex Fast Sep Cation I and Dionex Fast Sep Cation II column pair. Anions were analysed following isocratic elution on a Dionex AS 4A column.

The filtered particulates and the benthic samples were analysed for chlorophyll *a* by grinding and extraction into 90% acetone, subsequent centrifugation, and assay by fluorometry before and after acidification (Strickland & Parsons 1968). **Table I.** Limnological properties of the surface waters sampled near the RossIce Shelf. Location codes: Alph R-, Alph River site; BIP-, Bratina IslandPonds reference site; DH-, Diamond Hill; DM-, Darwin Mountain; LD-,Lower Darwin Glacier; MB-, Minna Bluff site; MD-, Mount Discovery site;PT-, Pyramid Trough site. Type codes: -P, pond; -S, stream; -, not measured.

Site	Conductivity	Temperature	pH
	(mS cm <sup>-1</sup> )	(°C)	
McMurdo Ice Shelf			
BI-P1 (Fresh)	0.11	1.7	8.8
BI-P2 (Duet)	0.72	3.0	8.9
BI-P3 (Fogghorne)	0.95	5.1	9.0
BI-P4 (Skua)	1.11	4.0	8.4
BI-P5 (Conophyton)	1.00	6.5	9.2
BI-P6 (Nostoc)	1.60	5.7	9.1
BI-P7 (IRP)	2.17	2.8	7.6
BI-P8 (Orange)	2.59	6.1	8.6
BI-P9 (P70-E)	5.3	4.9	8.0
BI-P10 (Brack)	10.3	3.9	8.9
BI-P11 (Salt)	53.9	6.3	8.3
MB-P1	0.81	0.0	-
MB-P2	1.09	0.9	-
MD-P1	0.66	0.5	-
MD-P2	19.0	0.0	-
Pyramid Trough			
PT-P1	0.22	8.4	9.6
PT-P2	0.08	9.5	-
PT-P3	0.07	0.0	10.3
PT-P4	0.11	0.0	10.3
PT-P5	1.47	4.1	9.3
PT-P6	0.07	2.6	9.6
Trough Lake	0.07	0.0	9.8
Alph - R1	0.03	1.6	6.9
Alph - R2	0.05	4.6	8.6
Alph - R3	0.07	5.0	8.4
Darwin Glacier			
LD-P1	0.01	0.0	7.3
DH-S1	0.24	3.5	7.7
DH-P1	0.86	7.2	7.6
DH-S2	0.56	0.0	-
DH-P2	1.9	6.2	8.0
DH-P3	1.5	4.5	-
DH-P4	3.3	4.5	-
DH-P5	3.3	4.4	-
Lake Wilson	0.03	3.2	7.4
Lake Hendy	0.05	0.8	9.5
DM-P1	0.04	1.9	8.6

## Results

The surface waters spanned a wide range of conductivities and pH values, from the dilute meltwaters of neutral pH on the Darwin Glacier to hypersaline, alkaline ponds on the McMurdo Ice Shelf (Table I). Ponds and/or streams with conductivities in excess of 1 mS cm<sup>-1</sup> were found in all three regions, with the highest values on the McMurdo Ice Shelf of  $53.9 \,\mathrm{mS} \,\mathrm{cm}^{-1}$  in Salt Pond (site BIP11) and 19 mS cm<sup>-1</sup> in a Mount Discovery Pond (MDP2). The ponds near Bratina Island encompassed an extremely broad range of salinities with lowest values around 0.1 mS cm<sup>-1</sup>. Their pH was almost always above 8, with extreme values above 9.

Table II. Reactive and organically bound nutrient concentrations in surface waters from the McMurdo Ice Shelf and Pyramid Trough sites. The site codes are as in Table I. ND, not detectable; -, not measured. Values are in mg N or  $P \text{ m}^{-3}$ .

Site	NO3-N	NH4+-N	DON	DRP	DOP
McMurdo Ice Shelf					
(31 Dec. 1990)					
BI-P1 (Fresh)	6	4	133	48	8
BI-P2 (Duet)	1	3	191	128	4
BI-P3 (Fogghorne)	ND	4	387	25	9
BI-P4 (Skua)	215	8	324	63	24
BI-P5 (Conophyton)	ND	5	539	6	10
BI-P6 (Nostoc)	600	6	264	5	11
BI-P7 (IRP)	88	5	-	107	5
BI-P8 (Orange)	5	ND	-	1	-
BI-P9 (P70-E)	2	2	-	ND	-
BI-P10 (Brack)	1	-	-	9	ND
BI-P11 (Salt)	10	ND	-	364	-
McMurdo Ice Shelf					
(26 Jan. 1991)	ND	7		36	5
BI-P1 (Fresh)			-	122	3
BI-P2 (Duet)	1	6 9	-	2	8
BI-P3 (Fogghorne)	ND	9 7	-	50	0 16
BI-P4 (Skua)	ND		-		9
BI-P5 (Conophyton)	2	7	-	1	6
BI-P6 (Nostoc)	ND	6 7	-	1 12	3
BI-P7 (IRP)	45		-		
BI-P8 (Orange)	2	ND	-	2 4	-
BI-P9 (P70-E)	8	ND	-	4 11	-
BIP-10 (Brack)	1	40	-		-
BI-P11 (Salt)	121	ND	-	573	-
MB-P1	14	2	43	27	2 3
MB-P2	26 20	3	118	4	-
MD-P1	20	2	52	16	1
MD-P2	30	1	46	4	1
Pyramid Trough					
(17 Jan. 1991)					
PT-P1	138	4	145	2.3	3
PT-P2	20	8	189	6.3	6
PT-P3	6	2	95	6.0	2
PT-P4	8	2	106	6.0	4
PT-P5	4	5	199	0.8	1
PT-P6	3	1	32	0.4	2
Trough Lake	4	1	3	22.3	2
Alph - R1	62	2	13	4.6	3
Alph - R2	5	1	17	0.8	1
Alph - R3	4	2	34	0.4	1

Nitrate concentrations varied between sites to a greater extent than any other measured constituent, ranging from below the limits of detection (0.5 mg N m<sup>-3</sup>) to > 100 000 mg N m<sup>-3</sup>. The lowest values were recorded in the ponds at the Bratina Island site (Table II). In the early melt period, three of these ponds had nitrate concentrations > 50 mg N m<sup>-3</sup>, but by the end of the January the values in almost all of the ponds had fallen to <0.5 mg N m<sup>-3</sup>. These waters also contained low concentrations (<0.5 to 8 mg N m<sup>-3</sup>) of ammonium throughout the season, but many had high concentrations of DRP, up to a maximum of 573 mg P m<sup>-3</sup> in Salt Pond (Table II). Unlike the nitrate trend, there was no consistent change in the concentration of DRP between dates. **Table III.** Reactive and organically bound nutrient concentrations in the Darwin Glacier region sampled 8–9 Jan. 1991. Site codes are as in Table I. ND, not detectable; -, no data. Values are in mg N or P m<sup>-3</sup>.

Site	NO3-N	NO <sub>2</sub> <sup>-</sup> -N	NH4+-N	DON	DRP	DOP
LD-P1	121	ND	22	615	4.1	0.3
DH-S1	6447	3	3	150	2.0	0.4
DH-P1	24091	69	5	-	0.7	0.7
DH-S2	16385	15	7	100	1.6	0.3
DH-P2	58138	132	7	50	2.1	0.3
DH-P3	63639	161	4	-	1.0	0.1
DH-P4	142380	-	22	-	1.0	0.6
DH-P5	138550	-	5	-	0.5	0.4
Lake Wilson	156	ND	2	16	1.1	ND
Lake Hendy	230	3	14	300	3.9	0.5
DM-P1	147	ND	5	112	1.4	0.1
DM-P2	142	ND	8	78	1.4	0.7
DM-P3	4520	19	3	128	1.7	0.8
DM-P4	91396	204	45	60	1.2	0.8

For example, DRP values decreased in Skua Pond (BIP4), rose by several hundred mg m<sup>-3</sup> in Salt Pond, and remained unchanged in Duet (BIP2). As a result of this combination of low NO<sub>3</sub><sup>-</sup>, low NH<sub>4</sub><sup>+</sup> and high DRP the Bratina Island pond waters had the lowest inorganic N/P ratios for any of the study sites. Similarly high DRP (with N/P ratios at and below 1) occurred elsewhere on the McMurdo Ice Shelf (Mount Discovery Ponds, Minna Bluff) but at these sites nitrate concentrations were consistently in excess of 8 mg N m<sup>-3</sup>. DON values varied greatly between ponds with the highest values in excess of 500 mg m<sup>-3</sup> in Conophyton Pond on the McMurdo Ice Shelf (Table II) and on the lower Darwin Glacier (Table III), and minimum values less than 20 mg m<sup>-3</sup> in the Pyramid Trough region.

The Pyramid Trough waters ranged from fresh  $(0.032 \text{ mS cm}^{-1})$  in the headwaters of the Alph River to saline  $(1.5 \text{ mS cm}^{-1})$  in pond PTP5 (Table I). In most of these ponds, lakes and streams the nutrient concentrations were below  $8 \text{ mg N or P m}^{-3}$ , with the exception of Trough Lake which had > 20 mg DRP m<sup>-3</sup> (Table II).

In sharp contrast to these northern sites, all of the surface waters in the Darwin Glacier region contained concentrations of NO<sub>3</sub> above 100 mg N m<sup>-3</sup> (Table III). The lowest concentrations were recorded in the meltwaters running over the Darwin Glacier, with values up to three orders of magnitude higher in a number of saline ponds. For all sites in this southernmost region there was a close, positive relationship between nitrate concentration and conductivity (Fig. 2; df=12, r<sup>2</sup>=0.974), and between nitrate and chloride concentrations. Nitrite values were always a small percentage of the total dissolved inorganic nitrogen, but attained high absolute values in the nitrate-rich ponds, to a maximum of 204 mg N m<sup>3</sup> in DMP4 (Table III). In the ponds with nitrate concentrations below 200 mg NO<sub>3</sub>- m<sup>-3</sup> the nitrite levels were at or below our limits of detection, as in the McMurdo Ice Shelf and Pyramid Trough waters. For all the Darwin site nitrite data there was a positive correlation with conductivity (df=  $11, r^2 = 0.970$ ). Neither ammonium nor DRP correlated with conductivity or chloride.

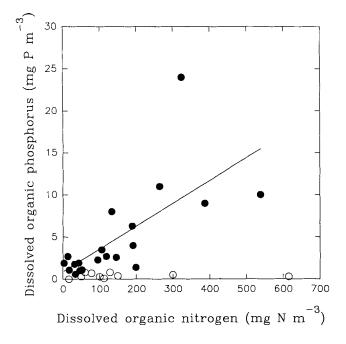


Fig. 3. The relationship between dissolved organic phosphorus and dissolved organic nitrogen for the Pyramid Trough and McMurdo Ice Shelf waters (●). The line is the fitted regression for these data. (O) are data for the Darwin Mountain region.

In all samples, excluding the Darwin Glacier region, DON and DOP were positively, although not closely, correlated (df = 17,  $r^2 = 0.485$ , p < 0.001). The Darwin Glacier samples were anomalous in that relatively high DON occurred without DOP (Fig. 3).

Sodium was the dominant cation at all three sites on the McMurdo Ice Shelf, but calcium was also important and sometimes dominant in the Darwin Glacier region (Table IV). Chloride was the dominant anion in the Diamond Hill waters but sulphate made an equal or greater contribution (on a g m<sup>-3</sup> basis) in the Darwin Mountains. Sulphate was also the dominant anion in some of the McMurdo Ice Shelf environments.

A scatter plot of the ratio Mg/Ca (a measure of evaporative concentration) against Mg/Na (a measure of rock interaction; cf. Webster *et al.* 1994) underscores the geochemical diversity of the inland waters of Antarctica (Fig. 4). Most of the samples cluster according to their regional origin: for example, the McMurdo Ice Shelf data embrace a range of Mg/Ca ratios but at consistently low Mg/Na. These data suggest their marine origin with varying degrees of evaporation or redissolution of marine salts. The Diamond Hill data encompass a similar Mg/Ca range, again pointing to the variable importance of evaporative concentration, but at much higher Mg/Na implying strong geochemical interactions with the surrounding rock catchment. The Darwin Mountain data spread over a wide range of Mg/Na ratios but at low Mg/Ca ratios.

At many of the sites in all three regions the ponds and streams contained benthic microbial mats (Table V). These communities contained chlorophyll a concentrations spanning two orders of

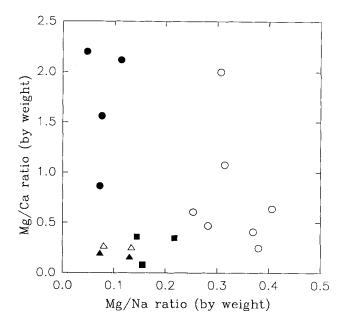


Fig. 4. Cation ratio plot for waters from the Diamond Hill sites (O), McMurdo Ice Shelf ablation zone ( $\bullet$ ), Trough Lake and Alph River ( $\blacktriangle$ ), Lake Hendy and the lower Darwin Glacier ( $\Delta$ ), and the Darwin Mountain ponds ( $\blacksquare$ ).

magnitude  $(0.4-55 \text{ g cm}^2)$  but there was no statistical relationship with inorganic or organic nutrient concentrations in the overlying waters. At most sites the benthic mats were dominated by oscillatoriacean cyanobacteria. Nitrogen-fixing cyanobacteria

Table IV. Major ion concentrations in meltwater environments near the Ross Ice Shelf. The site codes are as in Table I. -, no data. All values are in  $g m^{-3}$ .

Site	Na <sup>+</sup>	K+	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl-	SO42-
McMurdo Ice S	helf					
MB-P1	180	1.9	15	13	180	161
MB-P2	234	1.4	5	11	209	135
MD-P1	132	1.3	6.4	10	162	85
MD-P2	4215	146	226	478	6210	1830
Pyramid Troug	h					
Trough Lake	18	1.9	6.7	1.3	6.1	4.5
Alph - R3	10	1.3	8.4	1.3	2.3	7.7
Darwin Glacier						
LD-P1	1.5	0.4	0.8	0.2	1.5	1.2
DH-S1	20	4.6	18	7.4	35	2.6
DH-P1	85	24	15	24	143	110
DH-S2	50	10	76	19	80	120
DH-P2	197	51	125	80	350	230
DH-P3	178	28	52	56	309	100
DH-P4	453	18	189	115	772	533
DH-P5	417	7.6	64	128	779	54
Lake Wilson	2.4	0.2	1.2	-	2.8	2.3
Lake Hendy	10	0.4	3	0.8	7.1	12
DM-P1	-	0.2	-	1	1.8	2.1
DM-P2	4.5	0.2	8.5	0.7	3.4	4.6
DM-P3	29	0.6	18	6.3	18	33
DM-P4	479	8.6	190	69	354	320

**Table V.** Biological characteristics of the meltwater environments sampled in the Ross Ice Shelf region. The site codes are as in Tables I. Key to benthic dominants: An, Anabaena sp; Ca, Calothrix sp.; Chl, Chlorocapsa sp.; Chr, Chroococcus sp; Co, coccoid chlorophytes; Nc, Nostoc commune; Nm, Nostoc microscopicum; No, Nodularia sp.; Osc, oscillatoriaceans of mixed trichome dimensions; O2, oscillatoriaceans with trichome diameters less than  $2 \mu m$ ; O5, oscillatoriaceans with trichome diameters m; Pa, Phormidium autumnale; Pf, Phormidium fragile; Sch, Schizothrix sp; -, no data. Further descriptions of each of the BI-P microbial mats are given in Vincent et al. (1993).

Site	Chlorophyll a		Benthic dominar	nts Mat surface properties
	Plankton (mg m <sup>-3</sup> )	Benthos (g cm <sup>-2</sup> )		<b>r</b> - <b>r</b>
McMurdo Ice Shelf	f (26 Jan.	1991)		
BI-P1 (Fresh)	0.6	24	02	grey-pink
BI-P2 (Duet)	0.7	-	O2	grey-pink
BI-P3 (Fogghorne)	2.1	11	Nc, Nm, Osc	grey-green, leafy Nc, Osc in tall brown columns
BI-P4 (Skua)	4.0	31	Osc,No, An	pink
BI-P5 (Conophyton		-	Nm, Osc	orange cones
BI-P6 (Nostoc)	0.2	-	Nc, Nm	grey-green leafy mats
BI-P7 (IRP)	2.3		O2, O5, diatoms	grey
BI-P8 (Orange)	4.9	39	O5	bright orange
ВІ-Р9 (Р70-Е)	1.0	16	O2, O5, Nc	orange-brown
BI-P10 (Brack)	3.2	43	O2, O5, many	mucilaginous,
			ciliates	orange
BI-P11 (Salt)	1.3	-	02, 05	dull green
MB-P1	0.5	7	Osc	sparse
MB-P2	0.4	32	Osc	brown
MD-P1	1.8	-	Osc	brown
MD-P2	0.6	-	Osc	pink-brown
Pyramid Trough				
PT-P1	0.7	19	Osc, Nc	-
PT-P3	0.5	31	Nc, Osc	blue-green, leafy
PT-P4	3.2	17	Nc, Osc, Chr, Co	blue-green leafy
PT-P5	3.0	55	Nc, Osc, Chr	red crusts
PT-P6	0.2	17	Chl, Sch, Osc	black crusts
Trough Lake	0.7	13	Nc, Osc, Ca	grey-green
Darwin Glacier				
LD-P1	0.06	<1	-	no visible mats
DH-S1	0.10	15	Osc, Pa, O2	green-brown
DH-P1	0.09	<1	02	brown film
DH-S2	-	30	Pa, Pf, O2, O5	green-brown
DH-P2	0.07	<1	-	no visible mats
DH-P3	0.11	<1	-	no visible mats
DH-P4	0.05	<1	-	no visible mats
DH-P5	0.11	0.4	-	no visible mats
Lake Wilson	0.06	12	-	-
Lake Hendy	0.04	-	02	thin film
DM-P1	0.20	12	O2, Sch	pink-brown
DM-P2	0.21	6.5	Osc, Sch	red-brown
DM-P3	0.62	13	Osc, O2	sparse growth
DM-P4	0.68	8.2	Osc, O2	sparse growth

were absent from our samples in the Darwin Glacier region, but were well-represented at sites in the two northern regions. Diatoms were also absent from the Darwin Glacier samples, but were sometimes encountered as minor constituents of the more northern mat communities. Planktonic biomass levels were typically low in all waters, ranging from less than 0.1 mg Chl a m<sup>-3</sup> in lakes and ponds in the Darwin Glacier region, to 4–5 mg Chl a m<sup>-3</sup> in certain ponds on the McMurdo Ice Shelf. There was no correlation between benthic and planktonic biomass concentrations.

## Discussion

Physico-chemical rather than biological processes are likely to have given rise to the high nitrate concentrations observed in the present study. All of the waters contained low concentrations of ammonium, and NH<sub>4</sub><sup>+</sup> oxidation by nitrifying bacteria is therefore unlikely to have been a major source term for their nitrate budgets. The Darwin Glacier NO, data showed a strong, positive relationship with conductivity, suggesting that concentration mechanisms such as freezing and evaporation were the primary cause of nitrate enrichment. Several of the Diamond Hill waters had elevated Mg/Ca ratios which further indicate evaporative concentration effects. In these nitraterich environments the chloride-to-nitrate ratio averaged 5.45g Cl/g N (n = 7, C.V.= 8.4%) which is within the range reported for Antarctic snow (e.g. Wilson & House 1965, Legrand et al. 1984). This ratio, and its relative constancy despite a 20-fold variation in nitrate levels, give additional support to the hypothesis that the nitrate was largely derived from snowmelt and concentrated by physical enrichment rather than biotic processes.

The nitrate levels were consistently high  $(> 100 \text{ mg N m}^{-3})$  in all of the aquatic environments sampled in the Darwin Glacier region. These sites were c. 300 km from the open sea, and local marine inputs cannot therefore be considered the dominant source for these waters. Nitrate has been measured in snow from several sites in the Antarctic interior (Parker et al. 1978, Legrand & Kirchner 1990), and snow core analyses indicate that its concentration has recently begun to increase (Mayewski & Legrand 1990). Whether this trend reflects increased anthropogenic inputs to the Antarctic region remains speculative at present. The polar stratospheric clouds which form above Antarctica and which catalyse the ozone-CFC reactions appear to be substantially composed of nitrate, specifically nitric acid trihydrate (Schoeberl & Hartmann 1991). The exact link between stratospheric processes and the chemical composition of snowfall in the Antarctic interior is not yet fully understood (see Mayewski & Legrand 1990, Legrand & Kirchner 1990) but the nitrate measured at our remote southern sites was probably derived from long-range transport and reaction processes in the upper atmosphere.

Long-range transport and precipitation may have also contributed to the high DON values found in the Darwin Glacier region waters. In certain Antarctic lakes (e.g. Lake Vanda, Matsumoto *et al.* 1992) and streams (e.g. Downes *et al.* 1986) DON accumulation has been attributed to microbial activity. This source mechanism seems relatively unimportant in the Darwin waters where the microbial biomass was low, and the DON uncorrelated with DOP or autotrophic biomass. Freezeconcentration effects are known to influence the dissolved organic carbon levels in a variety of Antarctic environments (Matsumoto *et al.* 1992, Schmidt *et al.* 1991, Tominaga & Fukui 1981), but the lack of correlation observed here between DON and chloride indicates that such a mechanism is not a primary control. However, the chemical nature of the large DON pool in these southern waters is completely unknown and will require much closer attention before the source and sink mechanisms can be resolved.

The waters sampled in this study spanned the pH range 6.9–10.3, with most of the values above 8. The alkaline nature of many Antarctic freshwaters has been previously noted by Matsumoto *et al.* (1992) who attribute these conditions to the continuous photosynthetic activity during summer.

Despite the great chemical diversity of the environments sampled in the present study, most contained oscillatoriacean cyanobacterial mat communities. N<sub>2</sub>-fixing genera such as Nostoc and Calothrix were also represented in these communities in the northern sites, but were completely absent from the Darwin Glacier region. Species such as Nostoc commune can withstand prolonged periods of desiccation and freezing (Hawes et al. 1992), and the observed distributional limit of this species is therefore unlikely to reflect the severe physical environment at 80 °S. More likely factors are the high nitrate concentrations of the Darwin Glacier region coupled with the low phosphate levels. Neither condition is likely to favour nitrogen-fixing cyanobacteria. Dissolved inorganic N/P ratios were within an extremely high range (59-142 380, by weight) that would not select for N<sub>2</sub>-fixers. Nitrogen fixing species would have a much greater competitive advantage in the Pyramid Trough and McMurdo Ice Shelf waters where the nitrogenous nutrient concentrations were generally much more dilute, and where N:P ratios were often below 10.

The almost complete absence of diatoms from the Darwin Glacier region, in spite of the relatively high abundance of cyanobacteria (Table V) also differs from all of the more northerly sites in this study. Broady (1989) reported the puzzling absence of diatoms from remote areas of Marie Byrd Land in spite of the presence of ponds and some running waters with filamentous and coccoid chlorophytes and mats of oscillatoriaceans. These observations further underscore the enormous resilience of oscillatoriacean cyanobacteria to geographical extremes in the Antarctic environment, and/or their superior dispersal capabilities.

The present study has shown that even remote polar sites can be highly enriched in inorganic nutrients, specifically nitrate. Much remains to be learned about the exact transport and biogeochemical control mechanisms that produce such conditions. Future studies will require close attention to the atmospheric exchange processes, as well as to the biogeochemical source, sink and concentration mechanisms operating in these south polar environments.

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