

Chemistry of streams of Signy Island, maritime Antarctic: sources of major ions

A.P. CAULKETT and J.C. ELLIS-EVANS

British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, UK

Abstract: A general study of the streams of Signy Island, South Orkney Islands, was undertaken to identify the effects of catchment, distance from source, and time on concentrations of dissolved ions. In the majority of cases catchment did not affect the chemistry of streams, although marine-derived ions were affected by distance from the sea. Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and NH_4^+ were derived from the thawing of the winter snowpack. NO_3^- was derived from areas of permanent ice. SiO_4^{4-} , Ca^{2+} , Mg^{2+} and CO_3^{2-} were derived from crustal weathering. Although PO_4^{3-} was also derived from crustal weathering, it was released as a pulse related to the thawing of the soil.

Received 5 September 1996, accepted 10 December 1996

Key words: geochemistry, maritime Antarctic, streams

Introduction

The majority of stream studies in Antarctica have been undertaken in the Dry Valleys, southern Victoria Land which are ice free polar deserts (e.g. Green & Canfield 1984, Canfield & Green 1985, Green *et al.* 1988, de Mora *et al.* 1991, Howard-Williams *et al.* 1986, 1989). However, the streams of the maritime Antarctic have received comparatively little attention (Hawes 1989). The maritime Antarctic is subject to an entirely different climatic regime compared to that of the Dry Valleys; mean winter temperatures rarely drop below -15°C whilst in the summer period, of 1–4 months, daily mean temperatures exceed 0°C (Smith 1984). The region is subject to high levels of precipitation (400 mm y^{-1} , Greenfield 1992) falling both as rain or snow as atmospheric conditions dictate. Snow accumulation during the winter is significant, the melting of which results in a period of high discharge in the streams during the first few weeks of summer (Hawes 1988). Heywood (1967a) carried out some basic chemical studies of the streams of Signy Island but more recent studies of maritime Antarctic streams have concentrated on biological aspects of the stream environment (Hawes 1988, 1989, Hawes & Brazier 1991, Davey 1993). There has been no substantial study of the chemistry of maritime Antarctic streams.

Geochemical studies in the Dry Valleys have linked stream chemistry to the development of the soluble chemistry of the permanently ice covered, closed-basin lakes of the area (e.g. Green *et al.* 1989). In order to facilitate this understanding, workers in the Dry Valleys have identified the sources of various dissolved ions in the streams (e.g. Canfield & Green 1985, Green *et al.* 1989) by studying the variation of concentrations of dissolved ions with distance from source.

The aim of the present study was to identify the primary controls of catchment and abiotic sources of ions in the streams of Signy Island.

Sites and methods

Sites

Signy Island lies in the South Orkney Islands (Fig. 1) in the maritime Antarctic. It is small ($8 \times 5\text{ km}$) and comprised of a central ice cap and areas of coastal plains that are separated by a series of ridges. The geology is predominantly quartz-mica-schist with some outcrops of marble and amphibolites (Mathews & Maling 1967) and the deglaciated areas are either covered by frost shattered rock or undifferentiated glacial till. A system of radiating ridges roughly divides the island into six catchments (Heywood 1967b).

The only previous study of the streams of Signy Island was primarily a study of the filamentous green algae found in the streams (Hawes 1988, 1989). However, there was a small chemical component to the work and several consistent temporal trends were identified. The streams of Signy Island are subject to a highly seasonal regime, typically flowing for less than six months of the year. The streams are shallow and range from meltwater runnels of low and erratic flow to larger streams that form the outflows of lakes or glacial streams that consist of well defined beds and substantial flows. The length of streams is limited by the small size of the island and the longest streams are of the order of 500 m (Hawes 1989). Streams are predominantly fed by melting snow in the early part of the summer, but as the season progresses meltwater is derived from melting of the island's areas of permanent ice that are currently in a period of retreat (Smith 1990).

The aim of this work was to identify the influences of catchment on stream chemistry and identify the sources of various dissolved ions to facilitate the understanding of more complex influences on stream chemistry. Therefore, the streams chosen for this study are generally high in the catchments to avoid any complicating issues of lakes, flora and fauna associated with the lower reaches. In general, these

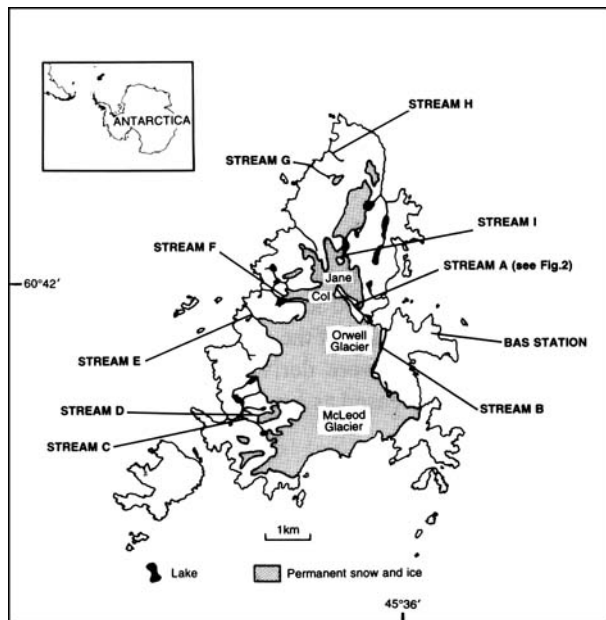


Fig. 1. Map of Signy Island ($60^{\circ}43'S$ $45^{\circ}38'W$) and its location in relation to the Antarctic Peninsula.

fall into Category 1 (meltwater runnels) using the rudimentary classification of the streams of Signy Island devised by Hawes (1989).

Stream A (Fig. 1) drains Jane Col and the ice cap. It flows east down Limestone Valley which is an area where rapid deglaciation has occurred in recent years. The stream flows within the confines of a well defined channel after the initial spring melt. There are significant marble outcrops in the valley. This stream was chosen for more intensive study by studying five sites along the reach of the stream (Fig. 2). These were sampled at weekly intervals to provide data on the temporal and spatial changes of concentrations of dissolved ions.

Stream B (Fig. 1) flows in a broad, well defined channel alongside the lateral moraine of the Orwell Glacier (one of the island's two active glaciers). The bed is rocky, but with areas of sand and silt accumulation. Its source is a pair of newly formed lakes, which are fed by meltwaters from the snowfield associated with the eastern side of the McLeod Glacier. Its volume is swelled by run-off from the sides of the valley and the Orwell Glacier. No other streams exist in this catchment, so it was necessary to study this stream with its lake influences. Stream C (Fig. 1) is the outflow from a small pool that consists entirely of meltwater. For most of the summer the stream flows through a channel cut through a semi-permanent snow field. Water flowing from the southern end of the ice cap constitutes Stream D. The stream is poorly defined with substantial sand and silt in its bed. It flows in part over some marble outcrops. There was some cyanobacterial mat development around the selected site. Stream E emerges from directly under the ice cap and is

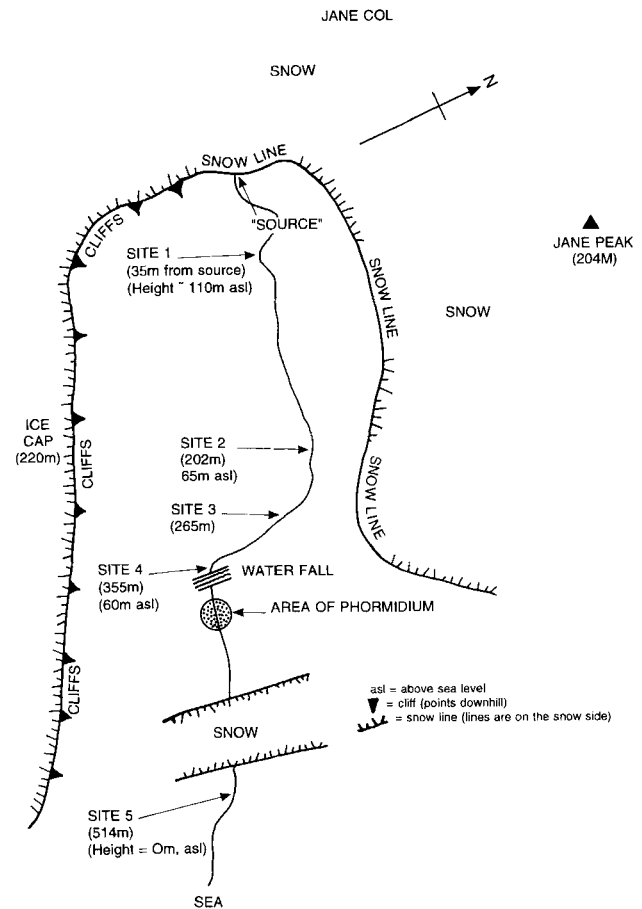


Fig. 2. Map of Limestone Valley.

consequently often very turbid with suspended glacial sediment. It flows west, down a steep boulder-filled channel. Stream F is the inflow to an oligotrophic lake. The stream carries meltwater from the valley that extends from the lake toward the ice cap. The valley floor is covered by a receding icefield. The stream is broad and has a very rocky bed free of smaller particles. Streams G and H (Fig. 1) are derived from meltwater flowing from the high ground at the north of the island. They are shallow channels with very rocky beds. Stream I (Fig. 1) flows from Jane Col to an oligotrophic lake. It is poorly defined in its upper reaches and at times of low flow the water often percolates through the regolith to emerge significantly further down the slope.

Sampling and analytical methods

Streams were sampled on a weekly basis and three water samples were collected from each stream site: a 2 l sample for general analysis, a 150 ml sample for determination of pH and alkalinity and a 50 ml sample was collected in an acid washed bottle for metals analysis. Before filling, the sample bottles were washed three times with water from the stream. On return to the research station, samples for general chemical analysis and cation analysis were stored in a refrigerator at

$4 \pm 1.5^\circ\text{C}$ whilst samples for pH and alkalinity determination were allowed to equilibrate in a constant temperature room also maintained at $4 \pm 1.5^\circ\text{C}$.

The samples for pH and alkalinity analysis were collected in narrow necked bottles to ensure a close fit of the pH probe in the neck of the sample bottle, so minimizing gas exchange with the atmosphere. A Corning 145 pH meter and Hamilton single pore pH probe with good stability characteristics in low conductivity waters were used to determine pH. Prior to sample analysis the probe was recalibrated with two buffer solutions (pH 4.00 and 7.00 at 5°C). A magnetic stirrer was introduced to each sample bottle and the sample gently stirred during all measurements. Alkalinity was then determined in the same bottle by titration of the sample with hydrochloric acid (0.05M) from a Metrohm piston burette. Three readings of pH and titrant volume were taken at about pH 4.5, 4.0 and 3.7 and used to determine the actual end-point by the Gran plot method (Talling 1973).

To remove particulates from the water and prevent exchange of ions between the dissolved and particulate phases the 2 l samples were filtered through GF/C filters prior to analysis. The filters were dried and weighed prior to use and then dried and re-weighed after filtering to determine the mass of suspended particulate material (SPM) in the sample.

A Pye Unicam SP6-550 UV/Vis spectrophotometer equipped with 1 cm and 4 cm cells and a sipper unit was used for colorimetric determinations. Ammonium, nitrate, soluble reactive silicate and ortho-phosphate ions were determined using the methods described by Mackereth *et al.* (1978). Chloride was determined by the mercuric nitrate and diphenylcarbazone titration (Goltermann *et al.* 1978). The precision and detection limits of the methods are given in Table I. The precision was determined as three standard deviations of ten replicate analyses of a standard solution and the detection limit was determined as three standard deviations of ten replicate analyses of a reagent blank.

For samples which contained significant concentrations of suspended matter the method of Mackereth *et al.* (1978) yielded low concentrations of silicate (even with pre-filtering). The method is subject to interference by various ions (Mackereth *et al.* 1978), so in order to eliminate a methodological problem, samples were spiked with aliquots of a standard solution and the concentration of silicate determined. Spiked samples gave concentrations that were the sum of the sample concentration and the standard concentration. Therefore, the method was judged to be working correctly and the low silicate results admissible.

The 50 ml samples for determination of cations were

filtered through acid washed 0.45 mm Nucleopore filters, acidified with 5 ml of undiluted hydrochloric acid (AAS grade, 18M) and stored at -20°C in acid washed bottles for analysis on return to the UK.

An Instrumentation Laboratory Video 11 AA/AE spectrophotometer operated in atomic emission (AES) and atomic absorption (AAS) modes was used to determine the concentrations of dissolved cations: sodium and potassium (AES) and magnesium and calcium (AAS) both using an air-acetylene flame. Where the absorbance of an element (notably sodium and magnesium) was outside the linear response of the equipment the samples were diluted with double distilled, deionized water. Due to the complex nature of the stream water matrix the technique of standard addition (Ewing 1975) was used. A mixed standard was prepared and acidified to prevent adsorption of ions such that the concentration of acid approximated to the concentration in the samples. Acidified double distilled, deionized water was used as a blank.

Snow samples were collected on two occasions and ice on one occasion. On each date five samples were taken from the top of Limestone Valley (Fig. 2) and the results are the mean of the data from these five samples.

Snow samples were collected in a plastic scoop and transferred to an acid washed container for transport to the research station. The snow samples were allowed to thaw slowly before filtering and analysis by the same methods used for water samples. Samples of permanent ice were removed from the ice sheet with an ice axe before being transferred to an acid washed plastic container.

Results

Snow chemistry

A comprehensive survey of snow chemistry and how it impinged on stream chemistry would constitute a major study beyond the scope of this work. However, some data on snow chemistry were collected to complement the study of solute dynamics in streams.

The snow chemistry data presented here (Table II) supports the view that when there was no sea-ice present the whole of Signy Island was subject to precipitation, with solute concentrations typical of the marine environment.

Comparison of catchments

Nine streams were studied in six catchments around Signy Island. The time-series data for each catchment were averaged (Table III) to create a mean value for the concentration of each ion over the season. These results were examined to identify any differences or trends between catchments. No statistically significant differences between catchments were identified, but considering the large standard deviations created by averaging the season's data this was hardly

Table I. Precision and detection limits of colorimetric techniques. Units are $\mu\text{mol l}^{-1}$.

	NH_4^+	NO_2^-	NO_3^-	SiO_4^{+}	PO_4^{3-}	Cl^-
Limit	0.007	0.028	1.2	1.1	0.074	1.8
Precision	0.20	0.21	0.59	1.5	0.11	7.4

Table II. Snow chemistry data for Limestone Valley. Concentrations are $\mu\text{mol l}^{-1}$ and the error is the standard error ($n=5$). n.d. = not detected.

ion	04/11/94 before thaw	28/11/94 during thaw	02/01/95 ice
SiO_4^{4-}	n.d.	n.d.	n.d.
NH_4^+	17 ± 4.1	2.8 ± 1.1	1.4 ± 0.73
NO_3^-	n.d.	n.d.	8.1 ± 0.20
PO_4^{3-}	0.12 ± 0.032	0.13 ± 0.053	0.24 ± 0.030
Cl^-	470 ± 13	44 ± 4.4	50 ± 9.1
Na^+	280 ± 11	54 ± 14	4.8 ± 9.5
Mg^{2+}	49 ± 0.40	6.3 ± 1.4	3.6 ± 0.90
K^+	15 ± 0.20	8.3 ± 3.9	4.0 ± 0.50
Ca^{2+}	45 ± 2.3	8.2 ± 3.2	5.1 ± 0.30

surprising. With the exception of Stream D, a Gibbs plot (Gibbs 1970) confirmed the similarity of the streams in the different catchments. The majority of the streams studied were in a cluster situated toward the precipitation dominated end of the rock – precipitation arm of the Gibbs plot. Whilst no statistically significant differences (Students *t*-test) were found between the catchments for individual determinants, visual examination of these data (Table III) suggested that Stream D displayed lower concentrations of sodium, potassium, magnesium, calcium, chloride and nitrate. The ice field from which Stream D flows is arguably the most distant ice field on the island from any coastal region. The Group I (Na^+ , K^+), Group II (Mg^{2+} , Ca^{2+}), chloride and nitrate ions in the snowpack originate from the marine environment (Heywood *et al.* 1980) and therefore Stream D would be expected to exhibit the lowest concentrations of these ions.

Although there were too few data points for a statistical time-series analysis of the data collected, some trends were identified as present in all streams.

The concentrations of sodium and chloride were high at the beginning of the spring and decreased with time (Fig. 3a, b). Precipitation at Signy Island is profoundly influenced by the proximity of the sea and this accounts for the waters of the lakes and streams exhibiting ionic ratios more typical of a marine environment. Rapid melting of the winter snow releases these ions as a pulse, which then decays as the stream sources become predominantly meltwater derived from the areas of permanent ice.

Table III. Time averaged data (with standard errors) for determinants in streams studied around Signy Island. Where appropriate units are mmol l^{-1} . n.d. = not detected. ALK = Alkalinity.

	pH	ALK	NH_4^+	NO_3^-	PO_4^{3-}	SiO_4^{4-}	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
A	6.6 ± 0.2	69 ± 11	1.2 ± 0.70	3.2 ± 1.1	0.13 ± 0.015	2.4 ± 0.78	640 ± 140	460 ± 120	60 ± 13	14 ± 2.4	39 ± 4.7
B	8.1 ± 0.2	160 ± 11	n.d.	3.2 ± 1.1	0.18 ± 0.025	8.8 ± 2.10	540 ± 53	350 ± 40	59 ± 9.8	21 ± 1.8	64 ± 6.5
C	6.9 ± 0.1	120 ± 25	n.d.	22 ± 5.3	0.11 ± 0.012	5.8 ± 0.81	730 ± 79	400 ± 65	60 ± 13	19 ± 1.6	43 ± 5.7
D	6.3 ± 0.1	27 ± 5.0	3.4 ± 2.4	n.d.	n.d.	2.9 ± 0.84	n.d.	4.0 ± 2.6	0.40 ± 0.40	3.4 ± 1.4	26 ± 5.8
E	6.4 ± 0.1	69 ± 21	n.d.	4.8 ± 0.82	0.15 ± 0.0	2.5 ± 1.20	470 ± 0.0	280 ± 0.0	49 ± 0.0	15 ± 0.0	45 ± 0.0
F	6.4 ± 0.1	32 ± 3.0	0.79 ± 0.56	7.8 ± 2.1	0.11 ± 0.020	1.3 ± 0.50	580 ± 78	330 ± 60	41 ± 8.4	12 ± 1.9	42 ± 14
G	7.2 ± 0.1	220 ± 25	0.54 ± 0.33	7.8 ± 2.1	0.14 ± 0.020	9.7 ± 0.91	670 ± 36	510 ± 17	64 ± 4.1	28 ± 5.7	68 ± 7.0
H	7.2 ± 0.1	230 ± 14	n.d.	1400 ± 1300	0.21 ± 0.036	11 ± 0.96	690 ± 33	530 ± 63	69 ± 8.9	20 ± 2.4	77 ± 11
I	6.9 ± 0.1	120 ± 17	0.32 ± 0.23	8.7 ± 1.4	0.13 ± 0.015	4.6 ± 0.41	640 ± 120	390 ± 65	54 ± 9.2	11 ± 1.5	59 ± 7.0

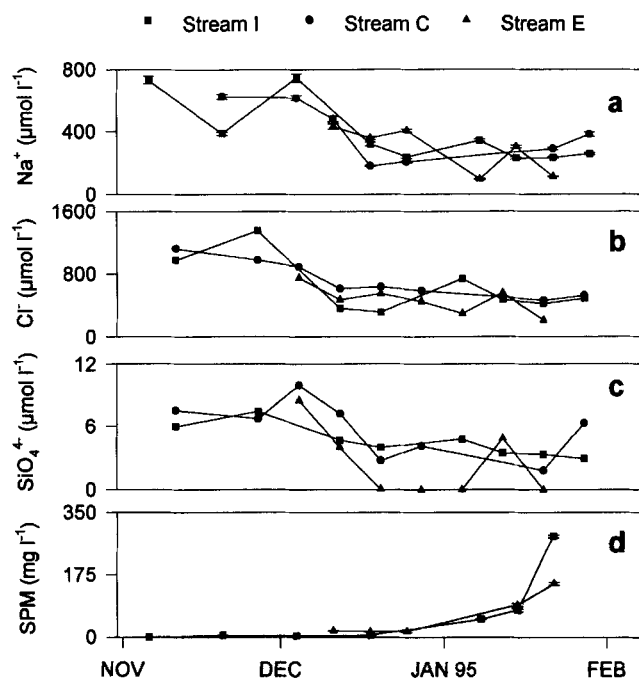


Fig. 3. Time-series data for three catchments of Signy Island. a. Na^+ , b. Cl^- , c. SiO_4^{4-} , d. SPM.

In general, the concentration of silicate in the streams of Signy Island decreased with time (Fig. 3c).

During the period of maximum flow, when the snow was melting most rapidly, the SPM consisted initially of small rock clastics. After the initial melt pulse, a trend of increasing SPM with time (Fig. 3d) was observed. This material consisted of extremely fine particles that made the waters very turbid (milky) and water samples were slow to filter.

Limestone Valley (Stream A)

Flow regime

Fortunately, Signy Island had experienced very low temperatures during the 1994 winter and the thaw had not started when the field season began. The streams started to flow within a week and the proximity of Limestone Valley to

the research station ensured that the first few days of flow were sampled. Until the stream bed lost its ice cover the only area of flow which could be sampled, was at the bottom of the valley (Site 5) and three samples were taken from this site before the other sites could be effectively sampled. The stream flowed for the full period of the study (11 November 1994–3 February 1995).

The conductivity meter used in the dilution gauging experiment developed a fault that proved impossible to repair at Signy Island. Therefore, the rate of discharge of the Limestone Valley stream could not be measured directly. However, Hawes (1988) demonstrated that the depth of the stream waters in a well-defined channel was roughly correlated with discharge. Therefore the depth of stream waters at two sites (Sites 4, 5) in Limestone Valley were measured to the nearest centimetre (Fig. 4). These data demonstrate that initial melting of the winter snowpack was rapid, occurring within three weeks of the onset of thaw. The difference in the depth of water recorded at Sites 4 and 5 can be accounted for by differences in channel morphology.

pH and alkalinity

pH displayed a spatial trend of slightly more acidic waters at the top of the valley where the waters emerged from the snow field (Fig. 5a). The pH values at all sites followed the same trend with respect to time, although this was more complex than a simple monotonic increase or decrease. Alkalinity (Fig. 5b) displayed no temporal trend, but there was, broadly, a spatial trend of increasing alkalinity with distance from the source.

• Site 4 ■ Site 5

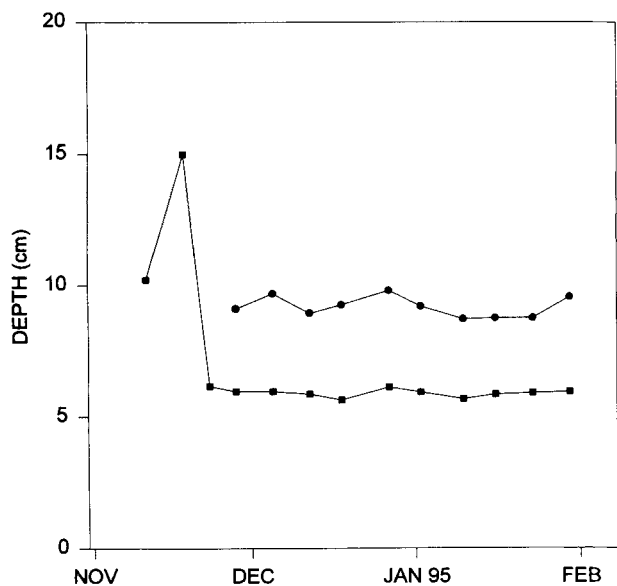


Fig. 4. Depth of water in the Limestone Valley stream (Stream A).

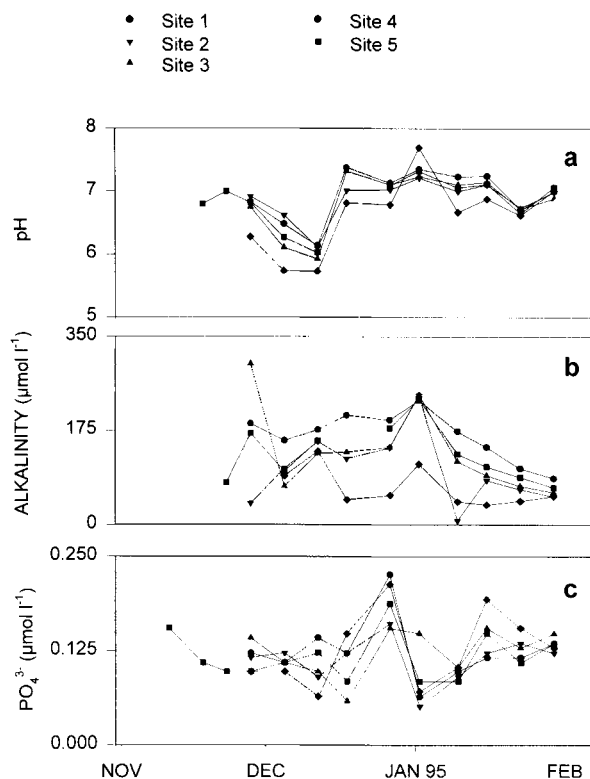


Fig. 5. Values of a. pH, b. alkalinity, c. PO₄³⁻ in Limestone Valley.

Dissolved ions

The ortho-phosphate data were very variable (Fig. 5c) with no simple trends apparent. The elevated concentrations observed at all sites on 27 December 1994 were not coincident with any other event in the data for Limestone Valley. Prior to this date the measured concentrations were similar with no apparent trend. After the peak (27 December 1994) the concentrations fell, before increasing steadily with time.

In general, the concentration determined at Site 5 was always lower than at Site 4. This was due to a large area of cyanobacterial mat (principally *Phormidium autumnale*) between these two sites, and similar mats elsewhere have been shown to be efficient scavengers of soluble phosphorus (Howard-Williams *et al.* 1986).

The Group I, Group II and chloride ion concentrations followed similar trends of initially high concentrations that decreased rapidly in the early part of the summer (Fig. 6). This was consistent with trends observed elsewhere on Signy Island. Only the concentration of calcium displayed any variation with respect to position (Fig. 6d) although this was masked by the variability of the calcium data. In general, the concentrations of calcium increased with distance from the source.

Ammonium concentrations (Fig. 7a) followed a pattern similar to those observed for the Group I and Group II metal ions: an initial pulse of ammonium ions through the system

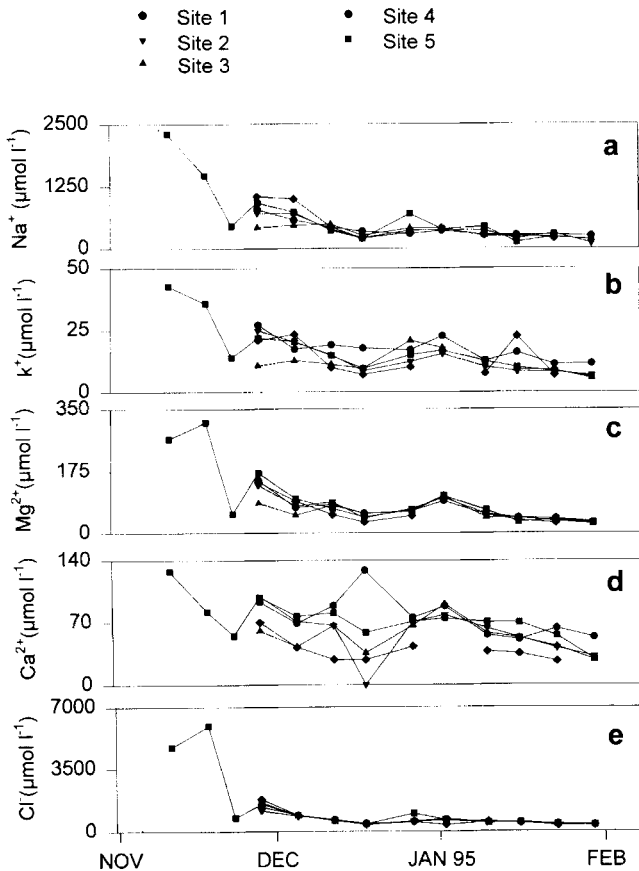


Fig. 6. Concentrations of a. Na^+ , b. K^+ , c. Mg^{2+} , d. Ca^{2+} , e. Cl^- in Limestone Valley.

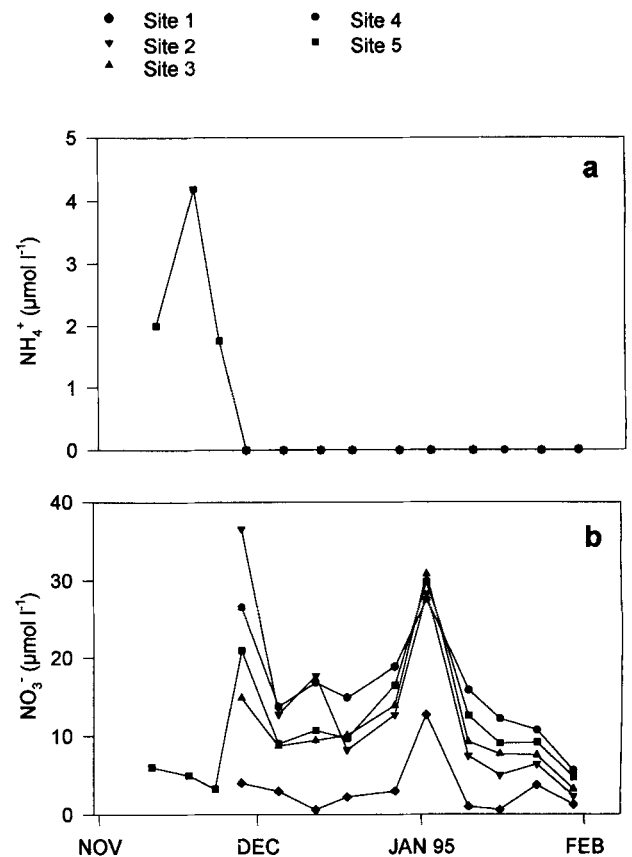


Fig. 7. Concentrations of a. NH_4^+ , b. NO_3^- in Limestone Valley.

which decayed rapidly to concentrations that showed little variation with time. This was consistent with the snow chemistry data (Table II). No spatial trend was identified in these data.

Nitrate concentrations (Fig. 7b) were low at the beginning of the season and then increased rapidly, afterwards declining to a low level through December. There was a significant peak on 2 January 1995 in the lower four sites. A spatial trend also existed with higher concentrations being regularly found at sites lower in the valley.

Dissolved silicate concentrations (Fig. 8a) decreased as the summer progressed but increased with distance downstream. This was consistent with other streams on the island.

Suspended particulate matter

In common with the other streams on the Island, the concentration of SPM in the Limestone Valley increased with time (Fig. 8b). Initially the suspended matter consisted of larger particles of rock clastics, but this was in the pulse associated with the spring thaw, as the summer progressed greater concentrations of fine suspended matter were collected on the filters. The increase of SPM was congruent with the decreasing concentrations of silicate recorded at the end of

the season and a good correlation was obtained at each site ($r < -0.90$).

Discussion

In general, no influence of catchment on stream chemistry was identified in the various systems studied. However, in the lower reaches of streams the potential for impact of marine mammals (seals), birds (penguin rookeries and nesting colonies of flighted seabirds), vegetation (mosses) and lakes was apparent. All of these situations warrant a detailed study but the stated aim of this work was to identify the sources of major ions in the streams and thus facilitate future studies into the effects of the influences mentioned above.

There are few data available on the snow chemistry of Signy Island. However, Greenfield (1992) has published data on the range of concentrations of inorganic nitrogen in glacier ice at Signy Island ($3.5\text{--}12 \text{ mmol l}^{-1}$) and the data presented here (Table II) falls within that range. Arnold (1995) presented data that supported the view of Heywood *et al.* (1980) in summer, when no sea ice was present the solute concentrations are typical of a marine environment and data presented here concur with this.

The whole of Signy Island is a sea spray zone (Heywood

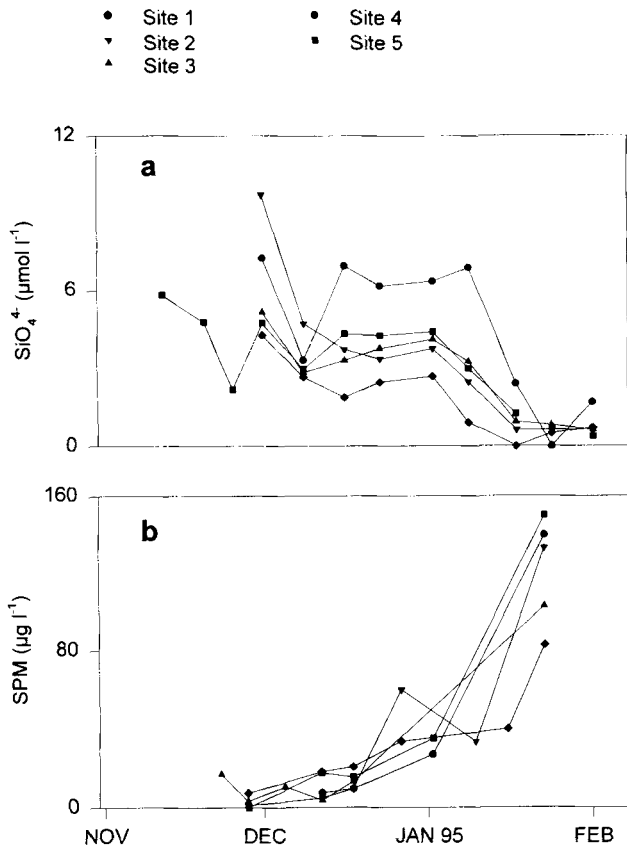


Fig. 8. Concentrations of a. silicate, b. SPM in Limestone Valley.

et al. 1980) and the concentrations of various marine derived ions in the lakes of the Island have been correlated with distance from the sea (Heywood *et al.* 1980). A similar influence was observed here, notably in Stream D which was derived from the most remote (from the sea) of Signy's permanent ice fields and displayed low concentrations of marine-derived ions. Signy Island is small and such effects would be magnified on a larger island.

In the absence of quantitative discharge data it is not possible to carry out a complete analysis of the flux of the ions studied. However, the stream–depth curve (Fig. 4) indicates that maximum discharge occurred in the first three weeks of the study and was caused by the rapid melting of winter snow. Therefore, the fluxes of ions exhibiting peak concentrations during this period will be significantly higher than at other times. Additionally, during the relative stable period of stream depth, it is assumed that greater concentrations of a dissolved ion are indicative of a higher flux of the ion in question.

Table IV summarizes the results of this study into temporal and spatial trends. If the only source of waters in Limestone Valley was the snow at the top of the valley then spatial changes (Trend 1, Table IV) could be wholly attributed to losses or gains of dissolved ions to or from the stream bed. However, the permanent ice between the stream and Jane

Table IV. Summary of the trends in the measured concentrations for ions dissolved in Limestone Valley stream (Stream A) data.

trend	ions
1. Increase with distance from source	Alkalinity, SiO_4^{4-} , Ca^{2+} , NO_3^-
2. Increase with time	SPM
3. Decrease with time	SiO_4^{4-}
4. Initial pulse, flowed by decrease with time	Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , Cl^-
5. Complex temporal and pattern (described in text)	PO_4^{3-}

Peak and the island's ice cap to the south of the valley (Fig. 2) also contribute waters to the main stream. The waters from the snowfield consisted of general surface runoff with no defined channel, whilst inputs from the ice cap consisted of small and erratic waterfalls over the cliffs that then followed complex paths through the mass of frost-shattered material at the base of the cliffs. Quantification of these inputs was therefore impractical, but inferences as to the sources of these ions can be made.

Arnold (1995) has shown that nitrate concentrations in the fellfield soils of Signy Island are very low, and therefore nitrate is not derived from a crustal source. The data from Stream D and those of other workers (Heywood *et al.* 1980, Arnold 1995) suggest that nitrate at Signy Island is instead derived from the marine environment. Nitrate was found to have relatively high concentrations in the pre-thaw snow sample (Table II). Nitrate is very soluble and would be expected to be flushed from the snowpack at the same time as chloride ions (Trend 4, Table IV). However, Tranter *et al.* (1986, 1987) have reported the preferential elution of nitrate with respect to chloride over a time period of a few hours. Therefore, it is possible that the initial pulse of nitrate ions from the melting of snowpack was missed in this study of Limestone Valley. This is consistent with no nitrate ions being detected in the snow sample taken during the thaw (Table II). After the chloride pulse, concentrations of nitrate in the stream increased (compare Figs 8c, 7e) and there was a trend of increasing concentrations of nitrate with distance from the source. These observations are consistent with nitrate ions being supplied from the melting of permanent ice. A similar conclusion was reached by Canfield & Green (1985) for the Onyx River, continental Antarctica. The snow chemistry data (Table II) also support this hypothesis and Greenfield (1992) observed that nitrate, in addition to that from precipitation, was supplied to Jane Col from ice melt.

Assuming that nitrate is supplied from melting ice then the decline of concentrations toward the end of the summer could be explained by a reduced rate of melting as temperatures became cooler or because nitrate was only found in the top few centimetres of ice as observed by Howard-Williams *et al.* (1989) for continental sites. However, in the work presented here, the variation of concentration with respect to depth in permanent ice was not investigated and, therefore it is impossible to differentiate between the two possible explanations.

In contrast to nitrate, the other ions displaying Trend 1 can all be accounted for by acquisition from crustal material in and around the stream bed, although there could be a contribution from the meltwaters of the permanent ice fields (Table II). Limestone Valley contains outcrops of marble (Mathews & Maling 1967) the dissolution of which would increase the concentrations of calcium and carbonate ions in solution. This would account for the increasing alkalinity of the stream waters with distance.

The concentrations of dissolved silicate in the streams decreased with time. The negative correlation between the silicate and SPM data (Fig. 8) indicates that Trends 2 and 3 (Table IV) are related and this is probably due to adsorption of silicate to particulates. Holland (1978) discussed the evidence that the adsorption of silicates to suspended clays may control the concentration of silicate in marine waters and concluded that this mechanism was insufficient to control the concentrations of dissolved silicates. However, in the streams of Signy Island it appears to be a significant control mechanism.

The ions that exhibit Trend 4 in the snow sample taken during the thaw (Table II) exhibited significantly reduced concentrations when compared to the pre-thaw snow sample (Table II). This suggests that these ions were derived from the melting of the winter snow and these ions are then released as a pulse as observed by Tranter *et al.* (1987).

Ortho-phosphate exhibited a complex pattern (Trend 5, Table IV). It appeared to exhibit no trends until an event that released increased amounts of the ion into the water course, after which it exhibited increasing concentrations with time. This is consistent with the snow chemistry data where the concentration of ortho-phosphate did not change between the pre-thaw and post-thaw snow samples (Table II). This suggests that there was a reservoir of ortho-phosphate available which was released into the stream at a particular point in the season. Davey (1993) presented data which indicated a sudden release of ortho-phosphate to the streams, but no temporal trend was apparent after the release.

Ortho-phosphate is generated from rocks during the winter period (Ron Vaz *et al.* 1994) and Arnold (1995) suggested that this occurred at Signy Island. This reservoir of ortho-phosphate would become available for transportation to the stream system once the primitive fellfield soils had thawed. Arnold (1995) has shown that thawing of fellfield soils does not occur until snow and ice cover has been lost *i.e.* relatively late in the summer and this could cause the observed pulse of ions.

Working in the Dry Valleys, Weand *et al.* (1977) observed that ortho-phosphate was derived from over-winter weathering processes in the stream bed. The majority of ortho-phosphate produced in this manner was leached from the stream bed in the first two weeks of flow. The soils of the Dry Valleys are arid compared to those of the maritime Antarctic (Campbell & Claridge 1987) so thawing of the soils would not release a substantial volume of water to transport ortho-phosphate

Table V. Sources of dissolved ions in the waters of the Limestone Valley stream (Stream A).

source	ions
1. Winter snow	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , NH ₄ ⁺ , Cl ⁻
2. Permanent ice	NO ₃ ⁻
3. Crustal	Alkalinity, SiO ₄ ⁴⁻ , Ca ²⁺
4. Crustal - released by ground thaw	PO ₄ ³⁻

produced by weathering processes to the stream system. This would explain why Weand *et al.* (1977) did not observe a pulse of ortho-phosphate ions later in the season.

The gross climatic differences between the maritime and continental areas of the Antarctic significantly affect the availability and sources of free water (Walton 1984). In the Dry Valleys region, where all the continental stream studies have been carried out, water is supplied by the melting of glaciers (Vincent 1988). However, in the maritime Antarctic the melting of winter snowpack is the source of the initial pulse of meltwater (Hawes 1988) followed by melting of the more permanent ice as the season progresses. Despite these huge differences between maritime and continental terrestrial systems ion Sources 2,3 and 4 (Table V) are consistent in both systems (*c.f.* Canfield & Green 1985, Green & Canfield 1984, Green *et al.* 1988). However, as the Dry Valleys receive little precipitation, Source 1 (Table V) for Signy Island has no direct comparison. The source of ions in the snow at Signy Island has been attributed to the proximity of the sea (Arnold 1995) and whilst sodium and chloride ions in the Onyx River have been attributed to aeolian deposits of marine salts (Green *et al.* 1988) it has been shown that in the nearby Alph River that rock weathering is the important source of these ions (de Mora *et al.* 1991).

Conclusions

This is part of the first detailed study of the geochemistry of the streams of the maritime Antarctic. A general study of the streams of Signy Island was undertaken to identify the effects of catchment, distance from source and time on concentrations of dissolved ions. The following conclusions can be drawn:

- Although in the majority of cases catchment did not affect the chemistry of streams, marine-derived ions were affected by distance from the sea.
- Sodium, potassium, magnesium, calcium, chloride and ammonium were primarily derived from thawing of the winter snowpack.
- Nitrate was derived from areas of permanent ice.
- Silicate, calcium, carbonate and magnesium were derived from crustal weathering.
- Ortho-phosphate was derived from crustal weathering, but was released as a pulse probably related to thawing of the fellfield soils.

Acknowledgements

We would like to thank the British Antarctic Survey for providing the funding and facilities for this work and especially the staff of Signy Station during the 1994–95 summer season for their assistance and companionship. We would also like to thank the referees whose comments significantly improved the quality of this paper.

References

- ARNOLD, R.J. 1995. *Seasonal periodicity of physical and edaphic factors, microalgae and their associated sugars and polyols in Antarctic fellfield soils*. MPhil thesis, Open University, 107pp. [Unpublished.]
- CAMPBELL, I.B. & CLARIDGE, G.G.C. 1987. *Antarctica: Soils, weathering processes and environment*. Oxford: Elsevier Science Publishers, 368pp.
- CANFIELD, D.E. & GREEN, W.J. 1985. The cycling of nutrients in a closed-basin Antarctic lake: Lake Vanda. *Biogeochemistry*, **1**, 233-256.
- DAVEY, M.C. 1993. Carbon and nitrogen dynamics in a maritime Antarctic stream. *Freshwater Biology*, **30**, 319-330.
- EWING, G.W. 1975. *Instrumental methods of chemical analysis*. London: McGraw-Hill, 560pp.
- GIBBS, R.J. 1970. Mechanisms controlling world water chemistry. *Science*, **170**, 1088-1090.
- GOLTERMANN, H.L., CLYMO, R.S. & OHNSTAD, M.A.M. 1978. *Methods for physical and chemical analysis of freshwaters*. Oxford: Blackwell Scientific Publications, 213pp.
- GREEN, W.J. & CANFIELD, D.E. 1984. Geochemistry of the Onyx River (Wright Valley, Antarctica) and its role in the chemical evolution of Lake Vanda. *Geochimica et Cosmochimica Acta*, **48**, 2457-2467.
- GREEN, W.J., ANGLE, M.P. & CHAVE, K.E. 1988. The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys. *Geochimica et Cosmochimica Acta*, **52**, 1265-1274.
- GREEN, W.J., GARDNER, T.J., FERDELMAN, T.G., ANGLE, M.P., VARNER, L.C. & NIXON, P. 1989. Geochemical processes in the Lake Fryxell Basin (Victoria Land, Antarctica). *Hydrobiologia*, **172**, 129-148.
- GREENFIELD, L.G. 1992. Precipitation nitrogen at maritime Signy Island and continental Cape Bird, Antarctica. *Polar Biology*, **11**, 649-653.
- HAWES, I. 1988. *The ecology of filamentous algae in lakes and streams of Signy Island, Antarctica*. PhD thesis, Council for National Academic Awards, 246pp. [Unpublished.]
- HAWES, I. 1989. Filamentous green algae in freshwater streams on Signy Island, Antarctica. *Hydrobiologia*, **172**, 1-18.
- HAWES, I. & BRAZIER, P. 1991. Freshwater stream ecosystems of James Ross Island, Antarctica. *Antarctic Science*, **3**, 265-271.
- HEYWOOD, R.B. 1967a. Antarctic ecosystems. The freshwater lakes of Signy Island and their fauna. *Philosophical Transactions of the Royal Society of London*, **B261**, 347-362.
- HEYWOOD, R.B. 1967b. Ecology of the fresh-water lakes of Signy Island, South Orkney Islands: I. Catchment areas, drainage systems and lake morphology. *British Antarctic Survey Bulletin*, No. 14, 25-43.
- HEYWOOD, R. B., DARTNALL, H.J.G. & PRIDDLE, J. 1980. Characteristics and classification of the lakes of Signy Island, South Orkney Islands, Antarctica. *Freshwater Biology*, **10**, 47-59.
- HOLLAND, H.D. 1978. *The Chemistry of the Atmosphere and Oceans*. 1st ed. New York: John Wiley & Sons, 351pp.
- HOWARD-WILLIAMS, C., VINCENT, C.L., BROADY, P.A. & VINCENT, W.F. 1986. Antarctic stream ecosystems: Variability in environmental properties and algal community structure. *Internationale Revue der Gesamten Hydrobiologie*, **71**, 511-544.
- HOWARD-WILLIAMS, C., PRISCU, J.C. & VINCENT, W.F. 1989. Nitrogen dynamics in two Antarctic streams. *Hydrobiologia*, **172**, 51-61.
- MACKERETH, F. J. H., HERON, J. & TALLING, J.F. 1978. *Water analysis: some revised methods for limnologists*. Kendal: Titus Wilson & Son Ltd, 120pp.
- MATHEWS, D.H. & MALING, D.H. 1967. The geology at the South Orkney Islands: I. Signy Island. Falkland Islands Dependencies Scientific Report, No 25, 32pp.
- DE MORA, S.J., WHITEHEAD, R.F. & GREGORY, M. 1991. Aqueous geochemistry of major constituents in the Alph River and tributaries in Walcott Bay, Victoria Land, Antarctica. *Antarctic Science*, **3**, 73-86.
- RON VAZ, M.D., EDWARDS, A.C., SHAND, C.A. & CRESSER, M.S. 1994. Changes in the chemistry of soil solution and acetic-acid extractable P following different types of freeze/thaw episodes. *European Journal of Soil Science*, **45**, 353-359.
- SMITH, R.I.L. 1984. Terrestrial plant biology. In LAWS, R.M., ed. *Antarctic ecology, Vol. 1*. London: Academic Press, 61-162.
- SMITH, R.I.L. 1990. Signy Island as a paradigm of biological and environmental change in Antarctic terrestrial ecosystems. In KERRY, K.R. & HEMPEL, G., eds. *Antarctic ecosystems. ecological change and conservation*. Berlin: Springer-Verlag, 32-50.
- TALLING, J.F. 1973. The application of some electrochemical methods to the measurement of photosynthesis and respiration in fresh waters. *Freshwater Biology*, **3**, 335-362.
- TRANTER, M., BRIMBLECOMBE, P., DAVIES, T.D., VINCENT, C.E., ABRAHAMS, P.W. & BLACKWOOD, I. 1986. The composition of snowfall, snowpack and meltwater in the Scottish Highlands - evidence for preferential elution. *Atmospheric Environment*, **20**, 517-525.
- TRANTER, M., DAVIES, T.D., BRIMBLECOMBE, P. & VINCENT, C.E. 1987. The composition of acidic meltwaters during snowmelt in the Scottish Highlands. *Water, Air and Soil Pollution*, **36**, 75-90.
- VINCENT, W.F. 1988. *Microbial ecosystems of Antarctica*. Cambridge: Cambridge University Press, 304pp.
- WALTON, D.W.H. 1984. The terrestrial environment. In LAWS, R.M., ed. *Antarctic ecology, Vol. 1*. London: Academic Press, 1-60.
- WEAND, B.L., HOEHN, R.C. & PARKER, B.C. 1977. Nutrient fluxes in Lake Bonney - a meromictic Antarctic lake. *Archiv für Hydrobiologie*, **80**, 519-530.