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STUDIES OF DISSOLVED SPECIES AND SUSPENDED PARTICULATE MATTER IN THE FRESHWATER SYSTEMS OF SIGNY ISLAND, MARITIME ANTARCTIC

Andrew Paul Caulkett

A thesis submitted in partial requirements of the Open University for the degree of Doctorate of Philosophy

February 1998

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DECLARATION

Whilst registered as a candidate for the degree for which this submission is made I have not been registered as a candidate or enrolled student for any other award. None of the material used in this thesis has been used in submission for any other award. The vast majority of work presented in this thesis was performed by myself, but where appropriate the specific contributions of other workers have been acknowledged.

Material contained within this thesis has been accepted for publication in peer reviewed scientific journals as detailed below:

Chapter 7:

Part of Chapter 4:
Caulkett, A.P. and Ellis-Evans, J.C. (1997); Chemistry of streams of Signy Island, maritime Antarctic: Sources of major ions. Antarctic Science 9: 3-11.

Part of Chapter 6:
ABSTRACT

The freshwater lakes and streams of Signy Island, maritime Antarctic were studied during two periods of field work (Jan 1992 - Mar 1993, Nov 1994 - Feb 1995). This work examined the dynamics of both dissolved and particulate phases. Due to the complex nature of catchment, stream and lake interactions only qualitative conclusions could be made.

The sources of the major dissolved ions in the streams were identified. Ions derived from precipitation and sea spray (Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Cl\(^-\), NH\(_4\)^+\), NO\(_3^-\), Mn\(^{2+}\)) were supplied to the streams as a pulse at the beginning of the season. Areas of permanent ice were an important source of NO\(_3^-\). Dissolved reactive silica, Ca\(^{2+}\), and Mg\(^{2+}\) were derived from crustal weathering. Whilst ortho-phosphate (o-P) and Mn\(^{2+}\) were products of crustal weathering, these ions were released as a pulse probably related to thawing of the fellfield soils.

Geochemical cycles in a seasonally ice-covered lake were studied. It was demonstrated that ice-cover and the onset of inflow have profound influences on the chemistry of the lake. At the onset of inflow it was demonstrated that oxygen can penetrate deep into the lake without disruption of the stratification and this caused the rapid oxidation of Fe\(^{2+}\). It was shown that there was a dynamic link between the inorganic forms of nitrogen (NH\(_4\)^+\), NO\(_3^-\), NO\(_2^-\)).

The suspended particulate material (SPM) in the lake was examined using an electron microscope and the affects of ice-cover on SPM were identified. The endogenic particulates formed on oxidation of Fe\(^{2+}\) were examined in detail and it was demonstrated that this
process exerts controls on the concentrations of the o-P and Ca$^{2+}$ in the lake waters.

These conclusions were discussed in the context of nutrient limitation of the lake and the retreat of areas of permanent ice and snow at Signy Island.

KEYWORDS: Antarctic, lakes, streams, geochemical cycles, suspended particulate matter, electron microscope
ACKNOWLEDGEMENTS

I would like to thank everybody who contributed in any way to my success in this venture. However, special thanks are due to the individuals, groups and organisations listed below without regard to importance:

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The British Antarctic Survey.


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Dr. Mark Brandon (Oceanographer, British Antarctic Survey), for discussions regarding turbidity currents.

Mike Gardiner (Department of Geography, University of Bristol), for useful discussions and snowmelt modelling.
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<tr>
<td>DRSi</td>
<td>Dissolved Reactive Silica</td>
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<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray analysis</td>
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<tr>
<td>Group I</td>
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<td>o-P</td>
<td>Contracted form of ortho-phosphate</td>
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<td>SEM</td>
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<td>SPM</td>
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CHAPTER 1: INTRODUCTION

1.1 THE ANTARCTIC ENVIRONMENT

Antarctica is the highest continent in the world with an average height in excess of 2000m (Laws 1989). The Antarctic ice sheet contains an estimated 75% of the Earth's freshwater (Laws 1989), the melting of which would cause sea-level to rise by an estimated 60m (Laws 1989). Fortunately, despite current trends of atmospheric warming (Doake and Vaughan 1991) it remains the coldest continent; the lowest temperature recorded at the Earth's surface (-89.6°C, Phillpot 1985) was at the Pole of Inaccessibility. Arguably, it is one of the harshest environments on Earth and the absence of free water, which is essential to life, makes the ice cap virtually sterile. However, at the fringes of the continent and on the surrounding islands, where the climate is milder, free water is found; here organisms adapted to the highly seasonal climate can survive.

On the basis of climatological and biological characteristics, the Antarctic can be divided into three zones (Lewis Smith 1984):

1. sub-Antarctic: the mean daily temperature is above freezing for six to twelve months of the year and precipitation is in excess of 900mm per year. Both vascular and non-vascular plants are found in the region and the indigenous fauna includes molluscs, spiders, insects and land birds.

2. maritime Antarctic: the mean daily temperatures exceed 0°C for one to four months during summer and in winter mean temperatures rarely fall below -15°C. The majority of
Figure 1.1: The Antarctic continent and surrounding islands.
the vegetation are lichens and mosses, whilst terrestrial fauna chiefly consists of nematodes, springtails and mites. Copepods are found in the freshwater lakes. The maritime Antarctic can be further sub-divided: the southern zone receives less than 350mm per year of precipitation whilst the northern zone receives 350-500mm per year, mostly as rainfall in the summer. The South Orkney Islands (Figure 1.1) are typical of the northern zone of the maritime Antarctic.

3. continental Antarctic: the precipitation in this area is very low and the flora and fauna are very sparse. It can be sub-divided into three areas. The coastal region, including the Dry Valleys of Southern Victoria Land and the east coast of the Antarctic Peninsula, has mean winter temperatures below -20°C, whilst summer temperatures may exceed 0°C for one month. The slope region has mean monthly temperatures below -5°C whereas the plateau region has mean monthly temperatures less than -15°C.

1.2 LIMNOLOGICAL STUDIES IN THE ANTARCTIC

High latitude freshwater systems are biologically simpler than the temperate systems found at temperate lower latitudes (Heywood 1977) and the lakes of the Antarctic have a smaller biological component than Arctic lakes (Heywood 1977): the study of Antarctic freshwater systems may more readily yield insights into geochemical processes (Heywood 1977). The isolation and harshness of the Antarctic environment maintains the biological simplicity of its freshwater systems and exhibits a gradation of environments in which to study limnological processes.

Streams are limited to the regions of the Antarctic where the mean daily temperature in the summer exceeds 0°C but lakes can be found in all regions. The lakes of the plateau and slope zones of continental Antarctica are either lenses of freshwater contained within the ice
Heywood (1977) divided the lakes of the coastal region into two groups: coastal lakes e.g. Vestfold Hills and lakes of the Antarctic oases e.g. Dry Valleys, Southern Victoria Land. The Antarctic oases are areas of the continent that are permanently devoid of snow cover whilst entirely surrounded by snow and ice (Laws 1989). These areas are maintained ice-free by katabatic winds from the polar plateau, low precipitation levels and the ability of the exposed rock to absorb considerable amounts of solar radiation. The lakes and ponds of the Dry Valleys (Figure 1.1) have been extensively studied (e.g. Matsumoto 1993) and found to be a wide range of sizes, depths and salinities. Under the temperature regime experienced by the Dry Valley areas, it is the deeper and more saline lakes which do not freeze solid (Heywood 1977); these are permanently ice-covered and often meromictic. Many of the lakes described in the literature (e.g. Canfield and Green 1985; Green et al. 1993) have no outflow. Input to the lakes is derived from the meltwater of glaciers and the flow regime mimics the pattern of solar radiation through the summer (Vincent 1988). Studies of the streams in this area have covered both geochemical (e.g. De Mora et al. 1991) and biological aspects (e.g. Howard-Williams et al. 1989). Studies of coastal lakes are less abundant (Heywood 1977); they are subject to a less extreme temperature regime and receive more precipitation than the inland systems (Heywood 1970) but in common with the lakes of the Dry Valleys, are rarely ice-free and are relatively saline (Heywood 1970).

The maritime Antarctic region of Lewis Smith (1984) is characterised by significant quantities of precipitation and a period of one to four months when mean daily temperatures are positive. All the lakes and pools contain freshwater (Heywood 1977). The depth to
which these freeze during winter is governed by the insulating properties of any overlying snow, which reduces heat loss and eventually limits the maximum thickness of ice-cover. Conversely, it is the reflection of solar radiation by snow cover on the lakes that prevents re-warming and prolongs the period of ice cover, although many of the lakes do become ice-free for as long as four months (Heywood 1977). 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). In comparison to the streams of continental Antarctica, those of the maritime Antarctic have received little attention (Hawes 1989). Much of the current published research on the freshwater systems of the maritime Antarctic has been carried out by the British Antarctic Survey on Signy Island in the South Orkneys (Figures 1.1, 1.2).

The freshwater systems of the sub-Antarctic are relatively unstudied (Laws 1989). They are more complex than lakes at higher latitudes with substantially more vegetated catchments and the aquatic vegetation can be relatively rich.

The maritime Antarctic freshwater ecosystem provides a compromise between the more complex systems of the sub-Antarctic and the simpler, but often brackish and permanently ice-covered, lakes of the continent. In this environment it should be possible to gain an understanding of geochemical processes in the context of more temperate systems.

1.3 SIGNY ISLAND

Signy Island lies within the South Orkney Islands on the Scotia Arc (Figure 1.2). It is roughly triangular and approximately 7km long by 5km at its widest point. It has a permanent ice-cap from which two glaciers, the McLeod and the Orwell, extend to the sea.
Although the highest point on the island is only 279m above sea level, the terrain of the island is rugged. From the central region of high ground a series of radiating ridges divide the low-lying coastal areas into six catchments (Heywood 1967a). The geology is metamorphic with most of the bedrock comprising of quartz-mica-schists. There are a few outcrops of marble and amphibolites (Matthews and Maling 1967). Soil development is poor, being mainly derived from undifferentiated glacial deposits and frost-shattered weathered bedrock, but beneath the moss carpets which cover areas of the island some primitive soils are evident (Lewis Smith 1972). The principal mode of weathering on Signy Island is by freeze-thaw action; chemical weathering is limited (Hall 1986, 1990). The mineral soils have a low organic content and are commonly sorted into polygons and stripes by the action of freeze-thaw processes (Chambers 1967). Many researchers have used the term "fellfield" when referring to the soils of Signy Island (e.g. Davey 1991; Arnold 1995).

The climate is typical of the maritime Antarctic zone; average precipitation, falling as snow or rain, is 400mm (water equivalent) per year (Greenfield 1992). Mean winter temperatures rarely drop below -15°C and in the summer, a period of about four months, daily mean temperatures exceed 0°C (Lewis Smith 1984). The island experiences predominantly west to north-west winds with a mean annual wind speed of 6ms\(^{-1}\) (approximately 11 knots, Heywood et al. 1980) and the high degree of cloud cover reduces incident sunshine to 30% of the maximum predicted at this latitude (Heywood 1984).

The ice-cap is currently in a period of retreat; this is attributed to increasing mean annual air temperatures (Lewis Smith 1990) and is consistent with other sites in the maritime Antarctic (Fowbert and Lewis Smith 1994). The reduction of ice-cover for the island has been calculated at 35% (by ground survey) between 1949 and 1989 (Lewis Smith 1990).
Figure 1.2: The South Orkney Islands and detail of Signy Island.
The terrestrial vegetation is dominated by mosses, lichens and algae (Lewis Smith 1972), the mosses occasionally forming thick carpets. The terrestrial fauna is entirely invertebrate (e.g. springtails, mites, nematodes) and is found in the vegetation and fellfield soils (Tilbrook 1967). Both bacteria and fungi have been found in the fellfield soils (Bailey and Wynn-Williams 1981). Gulls, skuas (Catharacta lombergi), three species of penguins and several species of petrel nest on the island during the summer. Elephant seals (Mirounga leonina) have been present on the island since records began (Laws 1956), hauling out in the short summer period to moult. Fur seals (Arctocephalus gazella) were first observed in 1948 (Laws 1973) and since then a revival in the population has led to rapidly increasing numbers of these animals on the island (Lewis Smith 1988), with over 20,000 recorded in the annual census of 1995. These animals are having a profound influence on the terrestrial vegetation (Lewis Smith 1988) and lakes (Ellis-Evans 1990) of the island and there are concerns that some control measures should be taken (Hodgson et al. 1998).

1.3.1 LIMNOLOGY AT SIGNY ISLAND

There are seventeen lakes distributed around the island (Ellis-Evans 1983). They are all freshwater systems but exhibit ionic ratios more typical of the marine environment that Heywood et al. (1979, 1980) attributed to their close proximity to the sea. All the lakes are of glacial origin and most exhibit a sub-lacustrine shelf about 1m in depth. They range from ultra-oligotrophic to eutrophic and are small (largest area 45050m², Heywood Lake) and shallow (deepest 16m, Emerald Lake). The melting of winter snow and the permanent ice-cap feeds the lakes via short, highly seasonal streams (Hawes 1988), but in some cases direct run-off from the catchment is significant (Hawes 1983a): run-off waters may be enriched by percolation through vegetation or seal enriched soils. During the short summer most of the lakes are entirely ice free for a period but freeze to a depth of 1-2m over winter.
The ice-cover isolates the lakes from inflows, outflows, gaseous exchange and wind-mixing and is an important influence on the physical and geochemical processes within. Under ice-cover, lakes may become stratified and sub-oxic or even anoxic conditions can develop in the bottom waters (Ellis-Evans 1982; Hawes 1983b), but when ice-free they are completely wind-mixed (Heywood et al. 1980). Lakes exhibiting a circulation system of this nature are classified as "cold monomictic" (Hutchinson 1957). However, the summer temperature of some of the lakes on Signy Island rises above 4°C (Heywood 1967b) and would be formally defined as dimictic (Hutchinson 1957; Heywood 1967b) although there is no summer stratification. Although paradoxical, this situation is relatively common (Lewis 1983) and is a limitation of the classification system.

Heywood et al. (1980) described the lake vegetation (phytoplankton, aquatic mosses, cyanobacterial mats and filamentous algae). Cyanobacterial mats are limited to the more oligotrophic systems and substantial moss stands are only observed in Moss Lake. The fauna is restricted to copepods, cladocerans, ostracodans, (Heywood et al. 1980), tardigrades (McInnes and Ellis-Evans 1987) and benthic protozoa (Hawthorn and Ellis-Evans 1984). No pelagic diatoms are observed, although benthic species are important (Jones and Juggins 1995).

The streams of Signy Island are predominantly fed by the melting of winter snow with a period of high discharge during the early part of the summer. As the season progresses they are increasingly derived from melting of the island's areas of permanent ice (Hawes 1988). The length of the streams is limited by the small size of the island and the longest streams are of the order of 500m (Hawes 1989). The biology of the streams of Signy Island has been studied extensively by Hawes (1988) who found filamentous algae and cyanobacterial
Heywood (1967b) 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 and Brazier 1991, Davey 1993). The only detailed study of the streams of Signy Island was the biological study carried out by Hawes (1988, 1989) who identified several consistent temporal trends in the water chemistry.

Various workers (e.g. Heywood et al. 1980) have studied the lakes of Signy Island. Sombre Lake has received a considerable amount of interest since 1974 (Ellis-Evans 1985; Gallagher 1985; Ellis-Evans and Lemon 1989; Hawes 1983a, b, 1990a, b; Bayliss 1995; Jones and Juggins 1995), when along with Heywood Lake, it was adopted by the British Antarctic Survey as a site for long term studies (e.g. Ellis-Evans 1990). Only two of these studies have examined geochemical cycling in Sombre Lake (Gallagher 1985; Ellis-Evans and Lemon 1989). These papers concentrated on iron cycling and nutrient regeneration from the anoxic sediments and little attention was paid to the particulate aspects of the cycle. Heywood (1968) and Heywood et al. (1980) carried out studies of the major ions in Sombre Lake, but there was neither a spatial aspect to this study nor was there analysis of the relationship of these ions to the nutrient cycle.

Temporal and spatial studies of both allogenic and endogenic suspended particulates in lakes can reveal insights into the mechanisms controlling the chemistry and trophic status of a lake (e.g. Sholkovitz and Copland 1982a, b; Hamilton-Taylor et al. 1984). The limited studies of suspended particulate matter (SPM) from maritime Antarctic lakes have
concentrated on aspects of nutrient cycling (Gallagher 1985; Ellis-Evans and Lemon 1989).

Since the pioneering work of Mortimer (1941, 1942), studies of the regeneration of nutrients from the anoxic lake sediments have formed a major part of the continuing investigations into lacustrine geochemical processes (e.g. Stumm 1985a). Although such studies are often of a purely chemical nature, the impetus for such research is a more holistic understanding of the interaction between chemical and biological processes in the lake (Stumm 1985b). The regeneration of nutrients is critical to the annual biological cycle of a lake, providing high concentrations of dissolved nutrients when conditions are optimum for maximum growth rates (e.g. Nürnberg and Peters 1984). Nutrient cycling is therefore an important area to study in these biologically simple Antarctic systems.

**1.4 AIMS OF THIS STUDY**

The aim of this study was to investigate the processes of nutrient regeneration in a biologically simple maritime Antarctic freshwater environment. A critical prerequisite is an understanding of the movement of dissolved ions and suspended particulate matter to the lake environment and the influence of the watershed or catchment area. The main aims:

1. To identify the sources of major ions in the streams of Signy Island and the manner in which these are delivered to the lakes (Chapters 4, 5).

2. To carry out a study of lacustrine nutrient cycling and identify any interaction with other chemical species both within the inflow and the lake (Chapters 4, 5, 7).

3. To examine the nature and influence of suspended particulate matter on nutrient cycling in a maritime Antarctic lake (Chapters 6, 7).
CHAPTER 2: STUDY SITES

The field work for this study was carried out in two periods: January 1992 to March 1993 and November 1994 to February 1995. The first concentrated on the lakes and streams of Paternoster Valley which are described in Sections 2.1 and 2.2.2, whilst in the second period a more general study of the streams of Signy Island was undertaken (Section 2.2).

This chapter describes the study sites chosen for this work and where applicable, the site codes used by other workers are given (Ellis-Evans 1983; Hawes 1988) to enable comparison.

2.1 PATERNOSTER VALLEY

Paternoster Valley (Figures 2.1, 2.3), lying in the north-east catchment of Signy Island (Heywood 1967a), runs north-eastward. The valley is bounded to the south by the high ground associated with Jane Col which carries a permanent ice field and to the east by a low ridge which separates it from Three Lakes Valley. To the west it is bounded by a rocky ridge that links Jane Col to the Robin Plateau, on the slopes of which are areas of permanent snow and ice. The exposed regolith consists mainly of undifferentiated quartz-mica-schist with some marble and garnetiferous outcrops (Matthews and Maling 1967). The valley is sparsely vegetated by lichens of numerous varieties and a few small areas of moss (notably Andreaea, Chorisodontium aciphyllum and Polytrichum alpestre, Dr. R.I. Lewis Smith, British Antarctic Survey pers. comm.), under which are small amounts of peat.
Otherwise, there is no soil development.

The valley contains three interconnected lakes (Moss, Changing and Sombre): these are fed by melting winter snow in spring and early summer, but as the summer progresses an increasing proportion of meltwater comes from the permanent snow and ice fields.

2.1.1 LAKE SITES

The lakes of Signy Island are described by Heywood et al. (1979, 1980). Of the three lakes in Paternoster Valley, Sombre Lake has received the most scientific attention (e.g. Ellis-Evans 1985; Gallagher 1985; Ellis-Evans and Lemon 1989; Hawes 1983a, b, 1990a, b) and was one of the two lakes of Signy Island chosen for detailed studies (Ellis-Evans 1990). As a large background of knowledge of this lake already existed it was chosen for detailed study in this work. To give a complete picture of Paternoster Valley, Moss Lake and Changing Lake will be briefly described, followed by a fuller account of Sombre Lake.

Moss Lake (Lake 4 of Ellis-Evans 1983) lies in a cirque at the head of the valley (Figures 2.2, 2.4). After the initial thaw, it receives meltwater throughout the summer from the snowfields of Jane Col and the areas of permanent snow on the south-western side of the cirque. The lake discharges into Changing Lake, situated to the north, by two routes: a broad, shallow, surface stream and a subterranean outflow through the moraine that forms the northern containment of the lake (Light 1976). The subterranean outflow remains active for a few weeks after inflow has frozen in early autumn: consequently the volume of the lake is reduced to less than 25% of that recorded in summer (Light 1976). The maximum depth is 10.4m (Table 2.1) during the summer but after the lake has partially drained the depth is as little as 4m (Light 1976). This is the only lake on Signy Island to exhibit this type
Figure 2.1: Map of Signy Island.
Figure 2.2: Paternoster Valley viewed from the high ground to the north (Robin Plateau) with Sombre Lake in the foreground.
Table 2.1: Physical properties of the lakes of Paternoster Valley (Heywood et al. 1979). ¹
Lake depth variable, see text. Residence times of Sombre Lake are reported in Table 5.4.

<table>
<thead>
<tr>
<th>LAKE</th>
<th>ALTITUDE (m)</th>
<th>VOLUME (m³)</th>
<th>DEPTH (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moss</td>
<td>48</td>
<td>52440</td>
<td>10.4 - 4.0¹</td>
</tr>
<tr>
<td>Changing</td>
<td>35</td>
<td>21800</td>
<td>5.4</td>
</tr>
<tr>
<td>Sombre</td>
<td>10</td>
<td>132600</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The subterranean outflow from Moss Lake emerges about 15m to the south of Changing Lake (Lake 3 of Ellis-Evans 1983) and continues as surface flow. The surface outflow from Moss Lake is augmented in volume before reaching Changing Lake by meltwater from the snowfield to the west; this constitutes the major stream input. The outflow from Changing Lake runs in a northerly direction to Sombre Lake. The inflow and outflow are located in close proximity and much of the inflowing waters exit without entering the main volume of the lake. In recent years, the lake has been affected by the many juvenile skuas (Catharacta lümmbergi) that congregate at the lake, with bird droppings contributing phosphate to this oligotrophic lake. The physical properties of the lake are presented in Table 2.1.

The main inflow to Sombre Lake (Lake 1 of Ellis-Evans 1983) is the outflow stream of Changing Lake (Figures 2.2, 2.4). Meltwater from the permanent snow on the slopes of Robin Peak, situated to the west, flows into the lake. However, the flow of any individual watercourse from Robin Peak only lasts a few days (J.B. Gallagher unpublished data) and although the volumes involved may be substantial, study of such short-term flow is difficult.
There is also some seepage from the areas of moss to the east of the lake but this amounts to only 2-3% of the input to the lake (Hawes 1983a). The outflow flows directly into the sea. The physical properties of the lake are presented in Table 2.1. Although the maximum depth is reported as 11.2m the deepest point found in this study was 10.9m; this point was buoyed and used as the study site.

Sombre Lake is completely wind-mixed during the ice-free period (Heywood et al. 1980). Under ice cover, the water column exhibits an inverse thermal gradient that is exceptionally stable (Hawes 1983b); circulation of water is usually small (Lerman 1979; Priddle et al. 1986) and the lake becomes stratified at this time. As a result of microbial processes operating in the sediments of the deeper parts of the lake, the bottom 1m of water becomes anoxic each winter (Ellis-Evans and Lemon 1989; Bayliss 1995). Under these conditions, redox-sensitive compounds in the sediments are reduced and the associated ions are released to the overlying water column (Gallagher 1985; Ellis-Evans and Lemon 1989). The water column remains stratified until the loss of ice cover (Hawes 1983b).

In recent years, Sombre Lake has been influenced by the increasing numbers of fur seals (Arctocephalus gazella) on Signy Island (Lewis Smith 1988) and it is clear from the long term monitoring programme (Dr. J.C. Ellis-Evans, British Antarctic Survey pers. comm.) that the trophic status of the lake has changed from oligotrophic to mesotrophic, in a similar fashion to nearby Heywood Lake (Ellis-Evans 1990).

A total of ten sediment traps (described in Section 3.5.1) were deployed in Sombre Lake (Figure 2.3). The traps at the inflow and outflow were deployed on 12/09/91. The inflow trap was sited at mid-depth in 5m of water and the outflow trap in 4.25m of water. A deep
Figure 2.3: Sombre Lake a) bathymetric map (redrawn from Heywood et al. 1979)
b) side elevation of bathymetry of Sombre Lake, indicating positions of sediment traps.

a)

b)

INFLOW

DEEP

ICE

OUTFLOW

WINTER ANOXIC ZONE

DEEP

ICE

OUTFLOW

1m

20m
spot trap at 8m below the surface was added on 17/01/92. On 06/08/92 the array of traps was extended: two traps were added at the deep spot (at 5m and 10m below the surface) and at the original inflow site a trap was placed at 1m from the bottom. A further two sites were added at the inflow; these were along a line extending from the original inflow trap to the deep spot. The first trap was sited 10m from the original site and the second one a further 10m away. At each of the sites which were in 5m of water, traps were placed at 1m from the sediment and at mid depth. All the traps remained deployed until 26/02/93.

Water samples were obtained from the deep spot of Sombre Lake at a sampling station adjacent to the deep spot sediment traps.

2.2 STREAMS

The streams of Signy Island are subject to a highly seasonal regime and typically flow for less than six months of the year (Hawes 1989). Whilst the streams draining lakes or glaciers may have substantial flows and well defined channels, the meltwater runnels which feed the lakes or larger streams often have low and erratic flow patterns (Hawes 1989). Meltwater streams are predominantly fed by winter snow in the early part of the summer, but as the season progresses are derived from melting of the island's areas of permanent ice. The streams have various lengths, flow regimes, levels of biological activity, sources and occupy a number of different catchments over the island.

The descriptions below include a code (alphabetic) for each stream. Where samples were taken from more than one site in a stream, a second code (numeric) is given for each site. The alphabetic code starts with A in Limestone Valley and proceeds clockwise around the island and thus the streams of Paternoster Valley are labelled I - L. For intra-stream sites a
lower number defines a site closer to the source of the stream \textit{i.e.} further from the sea.

2.2.1 GENERAL STREAM SITES

Nine streams were chosen to represent six catchments on Signy Island (Figure 2.4, Streams A - H). Two of the streams (A, D) were selected for more detailed studies and extra sites were chosen in these streams to investigate the changing water chemistry within the reach of the stream. All these streams were sampled at weekly intervals during the period November 1994 - February 1995.

Stream A (Site 10 of Hawes 1988), which flows east down Limestone Valley drains Jane Col and the ice cap. Limestone Valley is an area where particularly rapid deglaciation has occurred in recent years. After the initial spring melt, the stream flows within the confines of a well defined channel and although it does not flow over them there are significant marble outcrops in the valley (Matthews and Maling 1967). This was the first of the two streams chosen for more detailed studies and five sites (A1 - A5) were sampled in this stream (Figures 2.3, 2.4, 2.5).

Stream B (Site 12 of Hawes 1988) flows down Moraine Valley alongside the lateral moraine of the Orwell Glacier. The bed is rocky but with areas of sand accumulation. Meltwater from the upper reaches of the Gourlay Snow Slope and run-off from the sides of Moraine Valley feed into Stream B.

Stream C (Site 35 of Hawes 1988) is the outflow from a small pool that collects below Gneiss Hills and consists of the water flowing from the Gneiss Hills area. For most of the season it flows in a narrow channel cut through a semi-permanent snowfield.
Figure 2.4: Stream study sites on Signy Island, with inset of Paternoster Valley.
Figure 2.5: Map of Limestone Valley, displaying the course of Stream A.
Figure 2.6: Photograph of the Limestone Valley stream (Stream A).
Stream D consists of water flowing from the southern end of the ice cap. The stream is poorly defined with copious quantities of sand and silt in its bed. It flows over some marble outcrops. There is some cyanobacterial mat development around the selected site.

Stream E (Sites 26, 27 of Hawes 1988) emerges from directly under the ice cap and is consequently often very turbid (milky) with suspended sediment. It flows west, down Erratics Valley in a steep, boulder-filled channel to a plateau, where its course is highly braided and the beds are almost entirely comprised of silt and sand. The final reaches are broad and rocky. As part of the detailed study of stream chemistry five sites were sampled in this stream. However, its flow regime proved to be unreliable for unequivocal interpretation of the results.

A valley filled by a receding icefield extends from Tranquil Lake toward the ice cap: the meltwaters from this valley form Stream F. The stream forms the main inflow to Tranquil Lake.

Streams G and H, situated in the north-west catchment (Heywood 1967a) of the island, are heavily influenced by mosses (mainly Chorisodontium aciphyllum, Polytrichum alpestre, Calliergon sarmentosum, Calliergidium austrostramineum and Drepanocladius uncinitus Dr. R.I. Lewis Smith, British Antarctic Survey pers. comm.) and Giant Petrel colonies (Macronetes giganteus). Whilst the channel of Stream H is well defined, Stream G followed an ill-defined channel and at times of high flow often flowed over areas of moss or mineral fines.

Stream I flows from Jane Col to Moss Lake. The sampling site was 5-10m from the summer
snowline. In its upper reaches the stream is poorly defined and at times of low flow, the water often percolates through the regolith to emerge significantly further down the slope.

2.2.2 STREAM SITES IN PATERNOSTER VALLEY

Although eight stream sites were studied in Paternoster Valley (Streams I - L, Figure 2.4) only four sites had reliable flow patterns (Streams I, K1, K2, L). All streams were sampled once every two weeks during the spring and summer periods (January 1992 - May 1992, October 1992 - February 1993).

Stream I which was also studied in the general stream study of 1994 - 1995 was described in Section 2.2.1.

The surface stream flowing from Moss Lake to Changing Lake is rocky and follows a complex flow path. It flows over an outcrop of marble and contains cyanobacterial mats. The volume of this stream is augmented by meltwaters from the extensive snowfield to the west of Changing Lake (Figure 2.4). The sampling site (Stream J) is at the inflow to Changing Lake.

Stream K links the outflow from Changing Lake to the inflow of Sombre Lake. Site 1 (Stream K1, Figure 2.4) is the outflow from Changing Lake (Site 3 of Hawes 1988) and is rocky with cyanobacterial mats and filamentous algae (Zygnema, Mougeotia, Hawes 1988). Site 2 (Stream K2) is the inflow to Sombre Lake. The stream, whose bed consists primarily of small pebbles and sand, flows in a relatively deep (>20cm), well defined channel over flat terrain.
Stream L (Site 1 of Hawes 1988) is the outflow from Sombre Lake (Figure 2.4). It is a broad with annual, green filamentous algae (*Zygnema, Mougeotia;* Hawes 1988) and perennial cyanobacterial (*Phormidium;* Hawes 1988) mats. The bed is comprised of large rocks and small amounts of fine material.
CHAPTER 3: MATERIALS AND METHODS

3.1 INTRODUCTION

During the summer months, snow cover on Signy Island is restricted to the retreating ice-cap and all travel across the island was by foot, in which case the time taken to transport samples to the research station was one to two hours. This limited the amount of equipment and samples that could be physically carried to a single rucksack, although it was occasionally possible to depot equipment in one of a number of small field huts and then to transport it in relay to the study site.

When there was complete snow cover during the winter months it was possible to travel by skidoo. This decreased the transit time for samples (fifteen minutes) and also increased the amount of equipment that could be carried e.g. the Jiffy ice drills. Even with the increased ease of transport, careful planning of the collections was required to enable immediate transportation of the most sensitive samples (from Sombre Lake) to the research station.

These transport problems, in addition to climatic conditions compromised certain methods, especially those relating to redox chemistry. For example, many workers have recommended that filtration is carried out as soon as possible e.g. Davison and De Vitre (1992). However, due to the extremely low temperatures experienced during the winter and relatively long transit times in summer meant that this procedure had to be delayed until samples were returned to the research station.
3.2 COLLECTION OF WATER SAMPLES

3.2.1 LAKE WATER

During periods of open water a dinghy was used to reach the sampling points. Once on site, the dinghy was tied to a marker buoy and a Whale Gusher bilge pump and rigid plastic pipes (Durapipe) in 0.5m and 1m sections (Hawes 1988) were used to pump water from the required depths (0, 1.5, 5, 7, 9, 9.5, 10, 10.5m from surface). Although the method allowed the introduction of oxygen to the water samples, this was of little consequence as the lake was well mixed and fully oxygenated during periods of open water.

The formation of ice cover provided a stable platform from which to work. A petrol driven Jiffy ice drill was used to cut a 25cm diameter hole in the ice through which a syphon device (Figure 3.1), based on that of Magnuson and Stuntz (1970) and as described by Gallagher (1985), could be introduced to the water column. This system enabled sampling at a resolution of 5cm with minimum contamination by oxygen. The syphon works because the collecting bottle is below the level of water in the ice hole and is driven by the hydrostatic pressure of the water at depth. Samples were taken from depths (0, 1.5, 2.5, 5, 7, 8, 8.5, 9, 9.5, 10, 10.5, 10.75, 10.8, 10.85m from the surface) as determined by a line marked at 5cm intervals.

The Gusher pump method was used to sample the water column from the top down but when using the syphon device, it was necessary to sample from the bottom up to prevent tangling of the Tygon tubing. With both methods, care was taken to ensure that the tubing and pipes were fully flushed with water from the appropriate sampling depth before any sample was taken. Using the Gusher pump, this was achieved by first determining the number of pumping actions required to draw the volume of water contained in a single 1m
Figure 3.1: Apparatus for obtaining water samples from under ice without contamination by atmospheric oxygen. a) Detail of apparatus; B=sample bottle, T=tubing, W=weight, C=depth control line, marked at 5cm intervals. b) Apparatus deployed in ice hole.
section of pipe and then multiplying appropriately for each depth sampled. With the syphon device, a 2000ml sample bottle was filled at each depth before the sample was taken.

Three samples were collected from each depth: a 2000ml sample for general analysis, a 150ml sample for determination of pH and alkalinity and a 50ml sample in an acid washed bottle for cation analysis. Before filling, the sample bottles were washed three times with water from the sampling depth. Filling was a simple process when the pump was employed. However, using the syphon device, it was desirable to obtain the samples with minimum contamination by oxygen: the time taken to fill the sample bottle from the bottom was recorded and then the water allowed to flow continuously into the sample bottle for three times the filling period to ensure that all the oxygen had been flushed from the bottle (Magnuson and Stuntz 1970).

3.2.2 STREAM WATER
Water samples were obtained from just below the surface of streams by simply dipping the sample bottle into the stream. Where the stream was too shallow to do this the 50ml sample bottle (for cation analysis) was first used to fill the two larger bottles. Sample bottles were washed three times before filling. Three samples were collected from each site, as described above (Section 3.2.1).

3.3 ANALYSES OF WATER SAMPLES
On return to the research station, the samples for general chemical analysis and cation analysis were stored in a refrigerator at 4±1°C whilst the samples for pH and alkalinity determination were allowed to equilibrate in a constant temperature room maintained at 4±1.5 °C.
All manipulations of samples from ice covered lakes (except for pH and alkalinity) were carried out under a nitrogen atmosphere in an anaerobic cabinet, operated in accordance with the manufacturer's instructions.

Where appropriate and unless otherwise stated, the units of concentration throughout this work are moles per litre (mol l\(^{-1}\)), or a standard S.I. variation i.e. millimoles, micromoles etc.

3.3.1 pH AND ALKALINITY

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, minimising 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 low conductivity 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.

Once the pH of a sample had been measured, the alkalinity was determined in the same bottle by titration with 0.05M hydrochloric acid from a Metrohm piston burette. Three readings of pH and titrant volume were taken at approximately pH 4.5, 4.0 and 3.7. These were used to determine the actual end-point by the Gran plot method (Talling 1973).
3.3.2 NUTRIENTS

Prior to analysis, the 2000ml samples were filtered through GF/C filters to remove particulates from the water and prevent exchange of ions between the dissolved and particulate phases (Slatt 1972).

Ammonium, nitrite, nitrate, dissolved reactive silica (hereafter DRSi), ortho-phosphate (o-P in abbreviation) and ferrous (hereafter Fe$^{2+}$) ions were determined using the methods described by Mackereth et al. (1978). Chloride was determined by titration with mercuric nitrate as described by Goltermann et al. (1978). A Pye Unicam SP6-550 UV/Vis spectrophotometer, equipped with 1cm and 4cm cells and a sipper unit, was used for colorimetric determinations.

The precision and detection limits of the methods are given in Table 3.1. Precision was calculated as twice the standard deviation of ten replicate analyses of a standard solution. The detection limit was calculated as two standard deviations of ten replicate analyses of a reagent blank.

Table 3.1: Precision and detection limits of colorimetric techniques. Units are μmol l$^{-1}$.

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<tr>
<th></th>
<th>NH$_4^+$</th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
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<th>Cl$^-$</th>
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<td>LIMIT</td>
<td>0.23</td>
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<td>PRECISION</td>
<td>0.20</td>
<td>0.21</td>
<td>0.59</td>
<td>1.5</td>
<td>0.11</td>
<td>7.4</td>
</tr>
</tbody>
</table>

If the replicate analyses of a sample differed by more than the precision of the method then the analyses were repeated. The instrument was recalibrated when either a new stock
reagent was prepared or if the two routine check standards varied from their nominal values by more than the determined precision. Results determined below the detection limit are reported as zero in this work (e.g. Table 4.1, Figure 4.8 and others).

3.3.3 CATIONS

The 50ml samples for determination of cations were filtered through acid washed 0.45µm Nucleopore filters, acidified with 5ml of undiluted hydrochloric acid (AAS grade, 18M) and stored at -20°C in acid washed bottles.

An IL Video 11 aa/ae spectrophotometer (Instrumentation Laboratory, Warrington, U.K.), operated in atomic emission (AES) and atomic absorption (AAS) modes, was used to determine the concentrations of dissolved cations: sodium and potassium by AES with an air-acetylene flame and magnesium, calcium and manganese by AAS with 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, deionised water.

Due to the complex nature of the lake and stream water matrices, the technique of standard addition (Ewing 1975) was used. An acidified mixed standard was prepared such that the concentration of acid approximated to the concentration in the samples. Acidified, double distilled, deionised water was used as a blank.

When using the standard addition technique, it is impossible to give a single value for the
precision of the technique, therefore the following method was used to determine the error in each measurement. When all the samples had been analysed, three samples for each element were chosen from the sample set to represent the maximum, minimum and mean of the concentration range for that element. Each of these samples was analysed ten times and the absorbance recorded. For each sample the value of two standard deviations of the absorbance was calculated and the largest value for each element group recorded as the maximum precision of the absorbance for that element. If the maximum precision was less than the difference in the absorbance of replicate analyses for a sample, then the error was quoted as the standard error in the mean concentration of the replicates. However, if the maximum precision was greater than the difference between the replicate analyses, this was used as the difference in the replicates; the error quoted was the standard error in the mean (n=2) based on this figure. Where the standard error was greater than 5% of the result the analysis was repeated.

3.3.4 FIELD MEASUREMENTS

3.3.4.1 Water Temperature
Lake temperatures were determined using a YSI model 58 (YSI Ltd, Yellow Springs, U.S.A.) combined oxygen and temperature meter and a YSI 5700 combined oxygen and temperature probe with a submersible stirrer. Stream temperatures were measured using a YSI Model 33M combined salinity, conductivity and temperature probe. The probes were calibrated at the research station prior to use.

3.3.4.2 Dissolved Oxygen
Dissolved oxygen was determined using the YSI combined oxygen and temperature probe. In accordance with the manufacturer's instructions, calibration was performed by
suspending the probe in an oxygen saturated water sample and adjusting the read-out to 100%. Early studies of the stream environment indicated that the stream sites were oxygen saturated, as observed by Hawes (1988), therefore measurements were discontinued after 04/04/92.

3.3.4.3 Discharge of Streams

The discharge of streams was measured by salt dilution gauging (Church 1975). A YSI Model 33M conductivity probe was used to monitor the conductivity of the stream water at a site downstream of the point where a known quantity of a sodium chloride solution (10% w/v) had been introduced. Field calibration of the technique was carried out at each site by determining the change in conductance of a sample of stream water in response to the addition of three separate aliquots of the salt solution.

The method is dependent on complete horizontal mixing of the stream between the conductivity probe and the point at which the salt solution was introduced. It was unsuitable for streams of very low discharge, probably due to poor mixing. In order to record a measurable response, the conductivity probe must be deployed in a well defined channel, through which all of the discharge passes. This limited the potential of the technique on Signy Island where many of the streams are broad and ill defined.

3.4 COLLECTION AND ANALYSIS OF SNOW SAMPLES

Snow samples were obtained by using a plastic scoop and transferred to an acid washed container for transport to the research station. The snow samples were allowed to thaw slowly prior to filtration and analysis by the same methods described in Sections 3.3.2, 3.3.3. Samples of permanent ice were first hacked from the ice field with an ice axe and then
transferred to the plastic container.

3.5 COLLECTION OF SUSPENDED PARTICULATES

3.5.1 SUSPENDED PARTICULATES FROM LAKES

Settling matter in the lake water column was collected in an array of sediment traps. The sediment traps were suspended from surface buoys and maintained in position by lines stretched across the lake. In winter the buoys and cords became frozen into the ice. The traps consisted of a plastic framework holding a maximum of four plastic pots: normally two pots were deployed at each position. The pots were cylindrical, with an aspect ratio (H/W) of 2.07: a design that Gardner (1980) found to accurately collect settling particulates in flow rates up to 15cm s\(^{-1}\). Under ice cover, only density currents and turbulence due to melt water flow occur in the lake (Lerman 1979; Priddle et al. 1986): these were considered unlikely to disturb the collected material.

At intervals of ten to fifteen days, the traps were changed by carefully pulling up the trap assembly and screw lids were fitted to the pots whilst still below the surface of the water. On recovery, very little disturbance of the trapped material was observed. The pots were replaced by new pots and those retrieved were returned to the laboratory. During periods of open water this was performed from a dinghy. When the lake was ice covered, an ice drill was used to cut holes to one side of the traps and the trap was then recovered by using a jointed stick with a hook at one end to engage and retrieve the supporting line of the trap.

The total content of each pot was filtered through pre-dried (60°C) and pre-weighed 0.45μm Nucleopore filters. The filters were dried and re-weighed to calculate the rate of trapping. The dried samples were stored at -20°C. For samples obtained below ice cover,
filtration and initial drying was carried out under a nitrogen atmosphere in an anaerobic cabinet.

3.5.2 SUSPENDED PARTICULATES FROM STREAMS
In the shallow streams that are characteristic of Signy Island (Hawes 1988) there is insufficient depth of water to suspend a trap in the water column. Methods have been developed to trap material in shallow streams (Welton and Ladle 1979), but due to the proximity of the bedrock on Signy Island, it proved impossible to sink a trap into many of the stream beds.

Suspended particulates from streams were obtained by filtering the water samples which were collected for general chemical analysis (Section 3.2.2.2). The filters were then dried and re-weighed to determine the mass of material and the samples were frozen at -20°C.

Samples were also taken from the beds of streams. This was carried out by simply scooping the top 1-2cm of material into acid washed containers. These samples were stored at -20°C.

3.6 ANALYSIS OF PARTICULATE MATTER
3.6.1 ORGANIC AND INORGANIC CONTENT
A Carlo-Erba 1106 Elemental Analyser (Carlo-Erba Instrumentizone, Milan, Italy) in carbon, hydrogen and nitrogen (CHN) mode was used to analyse the particulate matter.

In the majority of cases it was not possible to remove the particulate matter from the Nucleopore filter. A cork borer was used to sub-sample an area (4mm diameter, ~12.6mm²)
of filter with the adherent particulate material. The whole sub-sample (filter and particulates) was analysed. The mass of the portion of filter included in this analysis was approximated as the mean of twenty sub-samples prepared in the same manner from twenty different blank filters. These areas of filter were analysed to demonstrate that there was little intra- or inter-filter variation in the CHN content of blank filters. The CHN content of the analysed sample was automatically corrected for the filter material by using blank filters as the reference blank. Quantitative calculations were performed by comparing peak areas from each sample to a sulphanilamide standard, which was also analysed with similar sub-samples of blank filter. All samples were analysed as replicates (n=2) and the errors are expressed as the standard error of the mean. On summation of the percentage composition the total was always less than 100%. The material unaccounted for (hereafter "residual") was attributed to the inorganic content.

Where adequate samples existed the "residual" fraction determined by the elemental analyser was compared with data obtained from ashing experiments (fraction remaining after ashing at 475°C for 24 hours). This gave a good linear correlation ($r^2=0.94$, Figure 3.2); CHN analysis allowed accurate determination of the inorganic content of samples where small quantities of material were trapped. Generally the amounts of carbon, hydrogen and nitrogen in the samples were small compared to the overall mass of the sample.

### 3.6.2 SCANNING ELECTRON MICROSCOPY

This work was performed at the British Antarctic Survey (BAS) headquarters, Cambridge on a Leica Stereoscan S360 microscope with an Oxford Analytical QX2000 energy dispersive X-ray (EDX) analyser.
Figure 3.2: Plot of percentage inorganic ("residual") content determined by CHN analyser versus percentage determined by ashing. Error bars are standard error of the mean (n=2), $r^2=0.94$, \%Residual = 1.00 \%Inorganic + 0.21.
Samples for scanning electron microscopy (SEM) were prepared by allowing the Nucleopore filter to reach room temperature in a desiccator. A small (~5mm x 5mm) piece was cut from the filter and mounted on an aluminium stub using adhesive carbon patches (Agar Scientific Ltd, Stansted, U.K.). The stubs were stored overnight in a desiccator. An Emitech K950 turbo-pumped carbon coater (Emitech, Ashford, U.K.) was used to coat the samples for X-ray analysis. Samples prepared in a similar manner, but coated with gold (Bio-Rad SC502 sputter coater; Bio-Rad, Watford, U.K.) were used to obtain the images presented in this work.

When high energy electrons collide with a sample, the atoms in the sample emit X-rays of an energy which is characteristic of that element. The EDX detector measures the energy of X-rays and thus can identify the elements in the sample. The detector used had a beryllium window which limited the technique to elements of atomic numbers greater than 10 i.e. sodium and heavier elements.

3.6.2.1 Quantitative EDX Analysis

It is possible to carry out quantitative X-ray analysis on either flat, polished surfaces where scattering of X-rays is minimised, or small, single particles. The technique relies on the use of Oxford Analytical's ZAF-4 software which corrects for the effects of atomic number, absorbance and secondary fluorescence. Quantitative calculations are performed by comparison of peaks with pre-stored standards. On summation of the percentage composition the total was always less than 100%; this was due to the presence of elements lighter than sodium in the samples and was known as the "unanalysed" fraction. Only particles which were larger than the excitation volume of the electron beam could be reliably analysed using this technique: the diameter of the excitation volume in iron was calculated
to be 1.4μm (Friel 1986).

3.6.2.2 Semi-Quantitative EDX Analysis

Limited amounts of material were collected in the sediment traps and it was not possible to reliably apply the sequential extraction techniques used by other workers (Green et al. 1993; Tessier et al. 1979). Furthermore, Martin et al. (1987) suggested that the results of sequential extractions are very subjective and that microprobe techniques could be developed instead, as demonstrated by Mudroch (1984). In the work presented here, the X-ray detector was used to analyse the gross composition of the material collected in the sediment traps. A standardised, relatively large area of filter (~0.9mm²) was analysed and the X-ray counts for each element of interest were integrated. The integrated counts for an element are proportional to the number of atoms of that element in the surface layers of the particles in the area of analysis. Although the electron beam scanned a standardised area of filter, certain areas of the filter may be devoid of particles and as the Nucleopore filter is organic, returned no X-ray signal: a correction factor was required.

Aluminium, after oxygen and silicon, is the third most common element in the Earth's crust (8.1%, Weast and Astle 1982) and it is present in most rocks found at the Earth's surface. Unlike silicon, aluminium is not involved in biological cycles (Stabel 1985) and was the reference element chosen by Sholkovitz and Copland (1982a) in their freshwater studies. To calibrate for varying coverage of the filter, a ratio of the counts for individual elements to the counts for aluminium was calculated:

$$F(E) = \frac{\Sigma(X - \text{ray counts for } E)}{\Sigma(X - \text{ray counts for Al})}$$

where E = an element of interest and F(E) = EDX fraction of E in sample

Equation 3.1
Data obtained in this fashion can be compared to that for other filters where the area of analysis, magnification and specimen geometry are the same. The data presented are the means of five areas selected at random on each filter.

3.6.3 IMAGE ANALYSIS

Computerised image analysis systems can analyse images at higher levels of precision and reproducibility than are possible manually (Meese and Tomich 1992). In addition to simply counting and measuring all the artifacts in an image, the computer can perform routines to improve distorted or fuzzy images, separate touching objects and identify objects based on size and shape (Bjørnsen 1986; Wynn-Williams 1988, 1990).

A Solitaire Plus image analysis system (Seescan, Cambridge, U.K.) was used to identify, measure and count a specific type of particle recovered from the sediment traps (described in Chapter 7). A number of the particles in question were first examined by SEM and identified by X-ray analysis. The particles were measured using a SEM software routine that determines the distance between two cursor points on the screen. These data were used to establish a series of identification criteria for the image analysis system. These criteria were tested using a series of SEM micrographs where the aggregates had again been independently identified with the X-ray analyser. The identification criteria were slightly modified so that the image analysis counts varied from the manual counts by less than 3%.

In practice, some editing of the SEM images was required on the image analysis equipment to remove structures that could, after processing, be confused with the particles in question e.g. diatoms, structures distorted by contrast etc. In such cases variation between different processings of the same image was less than 1%.
Figure 3.3: Plot of number of particles counted by the Seescan image analysis system against number of particles counted manually. Error bars are the standard error in the mean (n=10), $r^2 > 0.86$, Seescan = 1.60 Manual + 10.
For numbers of particles counted by the Seescan system plotted against a manual count performed live on the SEM, a good linear regression ($r^2 > 0.86$) was obtained, but the gradient was not 1 and the line did not pass through the origin (Figure 3.3). This suggests a systematic error in the Seescan results, the manual count or both; either the Seescan had erroneously identified other particles or the observer had not examined all particles on the filter. However, the results obtained by image analysis were representative of the number of particles present.
CHAPTER 4: STREAM CHEMISTRY

4.1 INTRODUCTION

Dissolved and particulate species are transported by streams from the fellfield environment to the lakes and ultimately, from the lakes into the sea. To elucidate the factors affecting the dissolved and particulate species in streams it is necessary to identify the influence of the catchment and the sources of dissolved ions. This information, when applied to the inflows and outflows of Sombre Lake, will enable a better interpretation of the influence of an inflow stream on a lake and of the lake on its outflow.

Compared to the streams of continental Antarctica (described in Section 1.2), the streams of the maritime Antarctic have received comparatively little attention (Hawes 1989). Heywood (1967b) carried out 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 and Brazier 1991; Davey 1993). To date, no substantial study of the chemistry of maritime Antarctic streams has been performed.

By studying the streams of Signy Island at different levels of intensity it should be possible to identify the various controls on stream chemistry. To achieve this, two programmes were undertaken in the 1994 - 1995 austral summer. The first, to identify catchment controls on stream chemistry, involved a weekly study of the streams in six different catchments. The second programme, to identify controls on the concentrations of dissolved ions in stream
water and the sources of the dissolved ions, examined the variation of concentrations of
dissolved ions with respect to time and distance. The conclusions of this programme were
applied to the data collected during 1991 - 1992 and 1992 - 1993 summers for the inflow
and outflow of Sombre Lake to investigate the influence of both the inflowing water on the
lake and the lake on the outflowing water.

4.2 METHODOLOGY
The methods and techniques employed to obtain and analyse stream water samples have
been described in Chapter 3. The method of Mackereth et al. (1978) was used for DRSi
analysis but for samples with significant concentrations of suspended matter, very low
concentrations of DRSi were detected, even after filtering. The method is subject to
interference by various ions (Mackereth et al. 1978), but in this situation only Fe$^{2+}$ and the
heteropoly acids of phosphorus are possible sources of interference. To eliminate a potential
methodological problem, filtered samples were spiked with aliquots of a standard solution
and the concentration of DRSi determined. Concentrations measured in the spiked samples
were the sum of the sample concentration and the standard concentration, indicating that
the method was working correctly and that the low DRSi results were admissible.

4.3 SNOW CHEMISTRY
A comprehensive study of snow chemistry and its impingement on stream chemistry would
constitute a major study beyond the scope of this initial work, but some data on snow
chemistry was collected to complement the study of solute dynamics in streams. Snow
samples were collected on three occasions during the 1994 - 1995 summer: before the thaw
commenced, during the thaw and toward the end of the summer. On each date five samples
were taken and the results are the mean of the data from these (Table 4.1a). The samples
Table 4.1: Snow chemistry data for Limestone Valley.

Table 4.1a: Concentrations are µmol l⁻¹ and the error is the standard error (n=5). Zero indicates below detection limit.

<table>
<thead>
<tr>
<th>ION</th>
<th>04/11/94 BEFORE THAW</th>
<th>28/11/94 DURING THAW</th>
<th>02/01/95 ICE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRSi</td>
<td>0.091±0.024</td>
<td>0.57±0.31</td>
<td>0.35±0.11</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>17±4.1</td>
<td>2.8±1.1</td>
<td>1.4±0.73</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0</td>
<td>0.022±0.018</td>
<td>0.029±0.0080</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.13±0.016</td>
<td>0</td>
<td>8.1±0.20</td>
</tr>
<tr>
<td>o-P</td>
<td>0.12±0.032</td>
<td>0.13±0.053</td>
<td>0.24±0.030</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>350±13</td>
<td>44±4.4</td>
<td>50±9.1</td>
</tr>
<tr>
<td>Na⁺</td>
<td>280±11</td>
<td>54±14</td>
<td>48±9.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>49±0.40</td>
<td>6.3±1.4</td>
<td>3.6±0.90</td>
</tr>
<tr>
<td>K⁺</td>
<td>15±0.20</td>
<td>8.3±3.9</td>
<td>4.0±0.50</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>45±2.3</td>
<td>8.2±3.2</td>
<td>5.1±0.30</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0</td>
<td>0.40±0.30</td>
<td>0</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0</td>
<td>17±7.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.1b: Concentration ratios with respect to sodium for snow chemistry data.

<table>
<thead>
<tr>
<th>SOURCE / ION</th>
<th>Cl⁻</th>
<th>Na⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine Ions</td>
<td>1.2</td>
<td>1.0</td>
<td>0.11</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>Snow, before thaw</td>
<td>1.3</td>
<td>1.0</td>
<td>0.18</td>
<td>0.054</td>
<td>0.16</td>
</tr>
<tr>
<td>Snow, during thaw</td>
<td>0.81</td>
<td>1.0</td>
<td>0.12</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Ice</td>
<td>1.1</td>
<td>1.0</td>
<td>0.075</td>
<td>0.083</td>
<td>0.11</td>
</tr>
</tbody>
</table>
were obtained from the top of Limestone Valley (Figure 2.5) and were collected and analysed using the methods outlined in Section 3.4.

There is little data available on the snow chemistry of Signy Island and in a location with high levels of precipitation and significant inter-annual variation such as the maritime Antarctic, a comprehensive study would be required to produce truly meaningful results. Greenfield (1992) published data on the concentration range of inorganic nitrogen in glacier ice on Signy Island and the data presented here (Table 4.1a) fall within that range. The ionic ratios (Table 4.1b) support the views of other workers (Heywood et al. 1980; Arnold 1995) that when no sea-ice is present, the whole of Signy Island is subject to precipitation with solute concentrations typical of the marine environment. Whilst chloride is more commonly chosen as a reference element, sodium was chosen here to facilitate comparison with data presented later (Table 4.2), where a chloride concentration of zero is reported.

4.4 GENERAL SURVEY OF THE STREAMS OF SIGNY ISLAND

Section 2.2 describes the nine streams selected for the general survey. Two streams (A, E) were chosen for more detailed study and samples were taken at several sites along the reach of the stream. Of the two, only Limestone Valley (Stream A) displayed any consistent spatial trends along its reach: this will be discussed in Section 4.5.

4.4.1 COMPARISON OF CATCHMENTS

Nine streams were studied in six catchments around Signy Island. The time-series data for each catchment were averaged to give a mean concentration for each ion over the season (Table 4.2). These results were examined to identify any differences or trends between catchments. No statistically significant differences between catchments were identified.
(Student's t-test), but considering the large standard deviations created by averaging the season's data, this was hardly surprising. With the exception of Stream D, a Gibbs plot (Gibbs 1970) confirmed the similarity of streams in different catchments. The majority of the streams studied were in a cluster situated toward the marine end of the rock-marine arm of the plot (Figure 4.1). Although Eilers et al. (1992) claimed that the Gibbs plot is of low applicability to minor lakes and streams, it is clearly a useful tool to show the similarity of lakes and streams of an area, as illustrated in the case of Signy Island.

Whilst no statistically significant differences were found between the catchments for individual determinants, visual examination of the data from Table 4.2 suggested that Stream D displayed lower concentrations of sodium, potassium, magnesium, calcium, chloride and nitrate. This is consistent with the position of Stream D on the Gibbs plot (Figure 4.1). 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, Group II, chloride and nitrate ions in the snowpack originate from the marine environment (Heywood et al. 1980); Stream D would be expected to exhibit the lowest concentrations of these ions. Furthermore, examination of the concentration ratios (Table 4.2b) reveals that the waters of Stream D are enriched in potassium and calcium when compared to the other streams. This point will be discussed again in Section 4.5.8.

4.4.2 TEMPORAL VARIATIONS

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

In general, the concentrations of sodium, chloride and DRSi were high at the beginning of
Table 4.2a: Mean data for streams studied in the general survey. ALKA=alkalinity. Units are μmol l$^{-1}$. Error is standard error in the mean. Zero indicates below detection limit. (A; n=10, B; n=10, C; n=7; D; n=7, E; n=7, F; n=9, G; n=9, H; n=9, I; n=8).

<table>
<thead>
<tr>
<th>pH</th>
<th>ALKA</th>
<th>NH$_4^+$</th>
<th>NO$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.6±0.2</td>
<td>69±11</td>
<td>1.2±0.70</td>
</tr>
<tr>
<td>B</td>
<td>8.1±0.2</td>
<td>160±11</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>6.9±0.1</td>
<td>120±25</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>6.3±0.1</td>
<td>27±5.0</td>
<td>3.4±2.4</td>
</tr>
<tr>
<td>E</td>
<td>6.9±0.1</td>
<td>69±21</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>6.4±0.1</td>
<td>32±3.0</td>
<td>0.79±0.56</td>
</tr>
<tr>
<td>G</td>
<td>7.2±0.1</td>
<td>220±25</td>
<td>0.54±0.33</td>
</tr>
<tr>
<td>H</td>
<td>7.2±0.1</td>
<td>230±14</td>
<td>0.003±0.0020</td>
</tr>
<tr>
<td>I</td>
<td>6.9±0.1</td>
<td>120±17</td>
<td>0.32±0.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cl</th>
<th>Na$^+$</th>
<th>Mg$^{2+}$</th>
<th>K$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>550±140</td>
<td>460±120</td>
<td>60±13</td>
</tr>
<tr>
<td>B</td>
<td>540±53</td>
<td>350±40</td>
<td>59±9.8</td>
</tr>
<tr>
<td>C</td>
<td>510±79</td>
<td>400±65</td>
<td>60±13</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>4.0±2.6</td>
<td>0.40±0.40</td>
</tr>
<tr>
<td>E</td>
<td>340±0.0</td>
<td>280±0.0</td>
<td>49±0.0</td>
</tr>
<tr>
<td>F</td>
<td>420±78</td>
<td>330±60</td>
<td>41±8.4</td>
</tr>
<tr>
<td>G</td>
<td>670±36</td>
<td>510±17</td>
<td>64±4.1</td>
</tr>
<tr>
<td>H</td>
<td>690±33</td>
<td>530±63</td>
<td>69±8.9</td>
</tr>
<tr>
<td>I</td>
<td>470±120</td>
<td>390±65</td>
<td>54±9.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>o-P</th>
<th>DRSi</th>
<th>NO$_3^-$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.13±0.015</td>
<td>2.4±0.78</td>
<td>3.2±1.1</td>
</tr>
<tr>
<td>B</td>
<td>0.18±0.025</td>
<td>8.8±2.1</td>
<td>3.2±1.1</td>
</tr>
<tr>
<td>C</td>
<td>0.11±0.012</td>
<td>5.8±0.81</td>
<td>22±5.3</td>
</tr>
<tr>
<td>D</td>
<td>0.10±0.0060</td>
<td>2.9±0.84</td>
<td>0.0062±0.0</td>
</tr>
<tr>
<td>E</td>
<td>0.15±0.0</td>
<td>2.5±1.2</td>
<td>4.8±0.82</td>
</tr>
<tr>
<td>F</td>
<td>0.11±0.020</td>
<td>1.3±0.50</td>
<td>7.8±2.1</td>
</tr>
<tr>
<td>G</td>
<td>0.14±0.020</td>
<td>9.7±0.91</td>
<td>7.8±2.1</td>
</tr>
<tr>
<td>H</td>
<td>0.21±0.036</td>
<td>11±0.96</td>
<td>1400±13</td>
</tr>
<tr>
<td>I</td>
<td>0.13±0.015</td>
<td>4.6±0.41</td>
<td>8.7±1.4</td>
</tr>
</tbody>
</table>
Table 4.2b: Concentration ratios with respect to sodium for the general stream survey.

<table>
<thead>
<tr>
<th>Source / Ion</th>
<th>Cl⁻</th>
<th>Na⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine Ions</td>
<td>1.2</td>
<td>1.0</td>
<td>0.11</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>Stream A</td>
<td>1.2</td>
<td>1.0</td>
<td>0.13</td>
<td>0.030</td>
<td>0.085</td>
</tr>
<tr>
<td>B</td>
<td>1.5</td>
<td>1.0</td>
<td>0.17</td>
<td>0.060</td>
<td>0.18</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>1.0</td>
<td>0.15</td>
<td>0.048</td>
<td>0.11</td>
</tr>
<tr>
<td>D</td>
<td>0.0</td>
<td>1.0</td>
<td>0.10</td>
<td>0.85</td>
<td>6.5</td>
</tr>
<tr>
<td>E</td>
<td>1.2</td>
<td>1.0</td>
<td>0.18</td>
<td>0.054</td>
<td>0.16</td>
</tr>
<tr>
<td>F</td>
<td>1.3</td>
<td>1.0</td>
<td>0.12</td>
<td>0.036</td>
<td>0.13</td>
</tr>
<tr>
<td>G</td>
<td>1.3</td>
<td>1.0</td>
<td>0.13</td>
<td>0.055</td>
<td>0.13</td>
</tr>
<tr>
<td>H</td>
<td>1.3</td>
<td>1.0</td>
<td>0.13</td>
<td>0.038</td>
<td>0.15</td>
</tr>
<tr>
<td>I</td>
<td>1.2</td>
<td>1.0</td>
<td>0.14</td>
<td>0.028</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 4.1: Stream compositions from various catchments of Signy Island after Gibbs (1970).
the spring and decreased with time (Figures 4.2a, b, c): this is consistent with these ions arising from the rapid melting of the winter snowpack, as observed by Johannessen and Henriksen (1978). The proximity of sea has a significant effect on the precipitation at Signy Island; this accounts for the behaviour of sodium and chloride ions and is reflected in the snow chemistry data (Table 4.1). Precipitation is not a major source of DRSi and other factors, which will be discussed later, influence the concentration.

Samples of suspended particulate matter (SPM) from the streams were collected using the method described in Section 3.5.2. During the period of maximum flow when the snow was melting most rapidly, the SPM consisted initially of small rock elastics. After the initial melt pulse, the nature of the SPM changed and was composed of extremely fine particles, making the water turbid (milky) and very slow to filter. The concentration of SPM in the streams increased with time during this phase (Figure 4.2d). Water samples were filtered through GF/C filters and analysis of these particles by SEM and X-ray microanalysis proved difficult due the presence of fibres from the filter itself.

4.5 LIMESTONE VALLEY (Stream A): RESULTS AND DISCUSSION

Of the two streams studied in detail during the 1994 - 1995 austral summer, Limestone Valley had the most consistent flow regime and the best defined course. Five sites were chosen throughout its reach (Figure 2.5) and these were sampled at weekly intervals to provide data on the temporal and spatial changes of concentrations of dissolved ions. This stream exhibited the temporal trends observed in the general survey and lay within the general cluster of streams on the Gibbs plot (Figure 4.1): it can therefore be considered representative of the streams of Signy Island and suitable for more detailed study.
Figure 4.2: Time-series data for three catchments of Signy Island. a) Na⁺, b) Cl⁻, c) DRSi, d) SPM.
4.5.1 LIMESTONE VALLEY: FLOW REGIME

Fortunately, Signy Island had experienced very low temperatures during the 1994 winter and the thaw had not commenced 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 that could be sampled was at the bottom of the valley (Site 5, Figure 2.5). 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 (11/11/94 - 03/02/95).

During the 1994 - 1995 summer, the conductivity meter used for the dilution gauging experiment developed a fault that was impossible to repair during the field season, consequently the rate of discharge of the Limestone Valley stream could not be measured directly.

Hawes (1989) demonstrated that the depth of the stream waters in a well-defined channel on Signy was roughly correlated with discharge. The depth of stream waters at two sites (Sites 4, 5) in Limestone Valley were therefore measured to the nearest centimetre (Figure 4.3). This study demonstrated that initial melting of the winter snowpack was rapid i.e. 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.

4.5.2 LIMESTONE VALLEY: pH AND ALKALINITY

The waters at the top of the valley were slightly more acidic (Figure 4.4a). pH values increased at all sites downstream and although they followed the same temporal trend, this was more complex than a simple monotonic increase or decrease. Alkalinity (Figure 4.4b)
Figure 4.3: Depth of water in the Limestone Valley stream (Stream A).
4.5.3 LIMESTONE VALLEY: ORTHO-PHOSPHATE

The ortho-phosphate data were very variable (Figure 4.4c) with no simple trends apparent. Elevated concentrations were observed at all sites on 27/12/94. Prior to this date, the concentrations of ortho-phosphate were similar but with no apparent trend. After the peak (27/12/94) the concentrations fell dramatically then increased steadily with time.

In general, the concentration determined at Site 5 was always lower than at Site 4. This was attributed to a large area of cyanobacterial mat (principally *Phormidium autumnale*, Dr. K. Gapp, Warwick University *pers. comm.*) located between these two sites (see Figure 2.5). Similar mats elsewhere have been shown to be efficient scavengers of soluble phosphorus (Canfield and Green 1985; Howard-Williams *et al.* 1986).

4.5.4 LIMESTONE VALLEY: CHLORIDE, GROUP I AND GROUP II IONS

The Group I, Group II and chloride ion concentrations followed similar trends consistent with those observed elsewhere on Signy Island (Section 4.4.2). These were characterised by initial high concentrations that decreased rapidly in the early part of the summer (Figure 4.5). Only the concentration of calcium displayed any variation with respect to position (Figure 4.5d): in general, the concentrations of calcium increased with distance from the source.

4.5.5 LIMESTONE VALLEY: INORGANIC NITROGEN

Ammonium concentrations (Figure 4.6a) followed a pattern similar to those observed for
Figure 4.4: Values of a) pH, b) alkalinity, c) o-P in Limestone Valley.

- Site 1
- Site 2
- Site 3
- Site 4
- Site 5

**a**

![pH graph]

**b**

![alkalinity graph]

**c**

![o-P graph]

**Axis Labels**
- **Y-axis:** ALKALINITY (µmol l⁻¹)
- **X-axis:** Time (Nov to Feb)

**Legend:**
- Site 1
- Site 2
- Site 3
- Site 4
- Site 5
the Group I and Group II metal ions: this consisted of an initial pulse of ammonium ions which decayed rapidly to concentrations that showed little variation with time. This was consistent with the snow chemistry data (Table 4.1) and no spatial trend was identified.

Concentrations of nitrite (Figure 4.6b) were very variable with no obvious temporal or spatial trends in the data. On closer examination, an initial pulse of waters with elevated concentrations of nitrite, followed by a period of low concentration and then a rise again toward the end of the season, was suggested.

Nitrate concentrations (Figure 4.6c) were low at the beginning of the season, increased rapidly then declined to a low level through December. There was a significant peak on 02/01/95 at all the sites. A spatial trend also existed with higher concentrations being regularly found at sites lower in the valley.

4.5.6 LIMESTONE VALLEY: DRSi AND SUSPENDED MATTER

DRSi concentrations (Figure 4.7a) decreased as the summer progressed but increased with distance downstream. This was consistent with other streams on the island.

In common with Streams E and I (Figures 2.3, 4.2c), the concentration of SPM in the Limestone Valley stream increased with time (Figure 4.7b). In the pulse associated with the spring thaw the SPM consisted of larger particles (rock clastics), but as the summer progressed, greater concentrations of fine suspended matter were collected. The increase in SPM was inversely associated with DRSi at the end of the season and a good correlation was obtained at each site ($r^2 > 0.81, r < -0.90, n=6$).
Figure 4.5: Concentrations of Group I, Group II and chloride ions in Limestone Valley. a) Na\(^+\), b) K\(^+\), c) Mg\(^{2+}\), d) Ca\(^{2+}\), e) Cl\(^-\).
Figure 4.6: Concentrations of a) NH$_4^+$, b) NO$_2^-$, c) NO$_3^-$ in Limestone Valley.
4.5.7 LIMESTONE VALLEY: MANGANESE AND IRON
In highly oxygenated waters significant dissolved concentrations of Fe$^{2+}$ and Mn$^{2+}$ are unlikely (Stumm and Morgan 1981). Although only trace concentrations of Mn$^{2+}$ were detected in snow samples (Table 4.1), there is some evidence to suggest that this ion was deposited with winter snow. The concentration of Mn$^{2+}$ in the stream was higher at the beginning of the study period (Figure 4.8a) and decayed with time in a similar manner to the chloride ion. Additionally, a peak of Mn$^{2+}$ was detected on 27/12/94, which was coincident with an ortho-phosphate peak (Section 4.5.3, Figure 4.4c) and is discussed further in Section 4.5.8. Some Fe$^{2+}$ was detected (Figure 4.8b) but the concentrations were very variable.

4.5.8 LIMESTONE VALLEY: DISCUSSION
In general, no inter-catchment variation of stream chemistry was identified in the various systems studied, but 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.

In the absence of quantitative discharge data it is not possible to carry out a complete analysis of the flux of the ions studied. The stream-depth curve (Figure 4.3) indicates that maximum discharge occurred in the first three weeks of the study and was caused by the rapid melting of winter snow; those ions with high concentrations during this period will exhibit fluxes higher than at any other times in the season. Additionally, during the period when stream depth was relatively stable, it is assumed that greater concentrations of a
Figure 4.7: Concentrations of a) DRSi, b) SPM in Limestone Valley.

- Site 1
- Site 2
- Site 3
- Site 4
- Site 5
Figure 4.8: Concentrations of a) Mn$^{2+}$, b) Fe$^{2+}$ in Limestone Valley. These results appear erratic because many are reported as below the detection limit i.e. as zero.
dissolved ion are indicative of a higher flux of the ion in question.

Table 4.3 summarises the results of this study into temporal and spatial trends. Six categories were chosen, each of which relates to the source of an ion or processes affecting it.

Table 4.3: Summary of the trends in the measured concentrations for ions dissolved in Limestone Valley stream (Stream A) data.

<table>
<thead>
<tr>
<th>TREND</th>
<th>IONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Increase with distance from source</td>
<td>Alkalinity, DRSi, Ca^{2+}, NO_{3}^{-}</td>
</tr>
<tr>
<td>2. Increase with time</td>
<td>SPM</td>
</tr>
<tr>
<td>3. Decrease with time</td>
<td>DRSi</td>
</tr>
<tr>
<td>4. Pulse of highly concentrated waters, followed by rapid decay to steady concentrations</td>
<td>Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, NH_{4}^{+}, Mn^{2+}, (NO_{2}^{-})</td>
</tr>
<tr>
<td>5. Complex pattern (described in text)</td>
<td>o-P, Mn^{2+}</td>
</tr>
<tr>
<td>6. No apparent trend</td>
<td>Fe^{2+}, NO_{2}^{-}</td>
</tr>
</tbody>
</table>

If the only source of water for the Limestone Valley stream was at its emergence from the snow at the head of the valley, then spatial changes (Trend 1, Table 4.3) could be wholly attributed to seepage from the regolith and exchanges of dissolved ions with the stream bed. However, the permanent ice and snow fields to the north and south of the valley (Figure 2.5) also contributed water to the main stream. Meltwater from the snowfield (to the north)
consisted solely of general surface run-off with no defined channels and inputs from the ice-cap (to the south) were comprised of small erratic waterfalls from the cliff edge, which followed tortuous paths through the 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.

Nitrate concentrations in the fellfield soils of Signy Island are very low (Allen *et al.* 1967; Arnold 1995), therefore nitrate is not derived from a crustal source. The data from Stream D and that from other workers (Heywood *et al.* 1980; Arnold 1995) suggest that some of the nitrate, which was found in the pre-thaw snow sample (Table 4.1), is derived from the marine environment. Nitrate is very soluble and would be flushed from the snowpack at the same time as chloride ions (Trend 4, Table 4.3), 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. Nitrate was not detected in the snow sample taken during the thaw (Table 4.1) and it is possible that the initial pulse of nitrate ions from the melting of snowpack was missed in this study of Limestone Valley. After the chloride pulse, concentrations of nitrate in the stream increased (*cf* Figures 4.5e, 4.6c) and a trend of increasing concentrations of nitrate with distance from the source was noted. The release of nitrate ions from the melting of permanent ice would account for these observations. A similar conclusion was reached by Canfield and Green (1985) for the Onyx River, continental Antarctica. The snow chemistry data (Table 4.1) supports this hypothesis and Greenfield (1992) observed that nitrate was supplied to Jane Col from both ice melt and precipitation. Claridge and Campbell (1967) suggested that the predominant source of nitrate in areas of permanent ice, not only in the Antarctic but world wide, was from precipitation.
The decline of nitrate concentrations toward the end of the summer could be explained by either a reduced rate of melting as temperatures became cooler or if nitrate was only found in the top few centimetres of ice, as observed by Howard-Williams et al. (1989) for continental sites. In the work presented here, the variation of concentration of ions with respect to depth in permanent ice was not investigated and consequently it is not possible to differentiate between the two explanations i.e. the high concentration of nitrate recorded on 27/12/94 could be due to a change in the rate of melting or the melting of an ice layer that was rich in this ion. Such features would be specific to the melt profile of any individual season.

In contrast to nitrate, the other ions with Trend 1 characteristics (Table 4.3) 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 4.1). Limestone Valley contains outcrops of marble (Matthews and Maling 1967), the dissolution of which would increase the concentrations of calcium and carbonate ions in solution. This would explain the increasing concentrations of calcium and alkalinity with distance. Further evidence for this is shown by the waters of Stream D, which lie at the "rock dominated" end of the Gibbs plot envelope (Figure 4.1) and were enriched in calcium with respect to the other streams of the island (Table 4.2b).

The concentrations of DRSi in the streams decreased with time (Trend 3, Table 4.3). A significant statistical correlation between data sets is insufficient to imply a causal relationship: a possible explanation of the negative correlation between the DRSi and SPM data (Figure 4.7) is by adsorption to particulates. Holland (1978) discussed the evidence for the adsorption of DRSi to suspended clays (not present in large quantities in Signy waters)
which may control the concentration in marine waters; he concluded that this mechanism was insufficient to control the concentrations of dissolved DRSi. Nevertheless, in the streams of Signy Island, adsorption to particulates may be a significant control mechanism.

Examination of the snow data reveals that some ions (NH$_4^+$, NO$_3^-$, Cl$^-$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) had higher concentrations in the pre-thaw sample than in the post-thaw sample: these ions were flushed from the snowpack early during the thaw and appear as a pulse of concentrated waters as observed by Tranter et al. (1987). This temporal trend is typical of Trend 4 (Table 4.3) and in fact the ions listed above show this trend.

Ortho-phosphate exhibited a complex pattern described in Section 4.5.3 (Trend 5, Table 4.3). No trends were apparent until a sudden release of this ion into the watercourse during late December after which increasing concentrations with time were noted. This is consistent with the snow chemistry data (where no change in concentration of ortho-phosphate was observed, Table 4.1), suggesting that there was a reservoir of ortho-phosphate available for release into the stream at a specific point in the season (27/12/94). Davey (1993) presented data that indicate a sudden release of ortho-phosphate to streams at another maritime Antarctic location, but he observed no subsequent temporal trend.

The concentrations of ortho-phosphate in soil water solutions increase after freezing events (Ron Vaz et al. 1994) and Arnold (1995) has reported increased concentrations of ortho-phosphate in the soils of Signy Island after the 1990 winter. Numerous workers (e.g. Arnold 1995) have observed the formation of an ice layer at the base of the Signy snow pack and which effectively seals the fellfield soils (Appleby et al. 1995). Once the ice layer has thawed weathering products can be flushed from the soils. As the thaw depth increases ions
can be flushed from deeper zones where weathering may be less advanced (e.g. Cornwell 1992); this could account for the increasing concentrations with time.

In the Dry Valleys of continental Antarctica, Weand et al. (1977) observed that ortho-phosphate was derived from over-winter weathering processes in the streambed. The majority of ortho-phosphate produced in this manner was leached from the streambed in the first two weeks of flow. Compared to the soils of the maritime Antarctic, those of the Dry Valleys are arid (Campbell and Claridge 1987); thawing of the soils would not release a sufficient volume of water to transport ortho-phosphate to the stream system. Consequently, Weand et al. (1977) did not observe a pulse of ortho-phosphate ions later in the season.

Manganese, listed in the Trend 4 group (Table 4.3), was characterised by a pulse of more concentrated waters at the beginning of the season. Manganese also exhibited a peak on 27/12/94 (Figure 4.8a), coincident with the ortho-phosphate peak which was attributed to by the thawing of groundwater. The solubility of manganese is controlled by its oxidation state: these observations suggest that a change in redox conditions is associated with this release.

This discussion has elucidated the sources of dissolved ions in the stream system of Limestone Valley and these are summarised in Table 4.4.

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). In the maritime Antarctic, the melting of winter snowpack is the source of the initial pulse of meltwater (Hawes 1988); melting of the more permanent ice occurs as the season progresses. Despite these huge differences between maritime and continental terrestrial systems, Sources 2, 3 and 4 (Table 4.4) are common to both systems (c.f. Canfield and Green 1985, Green and Canfield 1984, Green et al. 1988). The Dry Valleys receive very little precipitation so Source 1 (Table 4.4) for Signy Island has no direct comparison, but it is generally accepted that at least the sodium and chloride ions in the streams of the Dry Valleys are derived from aeolian deposits of marine salts (Green et al. 1988).

Table 4.4: Sources of dissolved ions in the waters of the Limestone Valley stream (Stream A).

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>IONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Winter snow</td>
<td>Na⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺, NH₄⁺, NO₂⁻</td>
</tr>
<tr>
<td>2. Permanent ice</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>3. Crustal</td>
<td>Alkalinity, DRSi, Ca²⁺</td>
</tr>
<tr>
<td>4. Crustal - released by ground thaw and changing redox conditions.</td>
<td>o-P, Mn²⁺</td>
</tr>
</tbody>
</table>

4.6 INFLOW AND OUTFLOW OF SOMBRE LAKE: RESULTS AND DISCUSSION

The Limestone Valley system is simple in that the stream does not have the complicating presence of a lake, but many of the streams of Signy Island do enter and flow from lakes.
To enable the study of a more complex system, Sombre Lake which has a single main inflow (Stream K2) and a single outflow (Stream L) (Figure 2.4) was chosen.

Deployment at Signy Island did not occur until January in the 1991 - 1992 summer and it was therefore not possible to collect data for the full range of determinants prior to this date, but data for pH, alkalinity, ortho-phosphate and ammonium over this period were supplied by Dr. J.C. Ellis-Evans (British Antarctic Survey) for whom the field work and laboratory analyses were performed by Mr. M.O. Chalmers (British Antarctic Survey).

Samples for metal ion analysis were acidified and stored at -20°C for transport to the U.K. and analysis by AES/AAS (Section 3.3.3). Unfortunately samples taken during the 1991 - 1992 summer were damaged in transit to the U.K. and no data are available.

4.6.1 INFLOW AND OUTFLOW: FLOW REGIME

Water was first heard running beneath the winter snow cover in the region of the inflow and outflow on 01/11/91 and 23/10/92 in the respective summers. By digging down to the flowing water, it was possible to obtain a sample from the "stream" but no measurements of the discharge could be made due to the complex flow paths. Even after the stream had cut a channel through the snowpack it continued to flow over a bed of ice until 26/11/92, the implications of which are discussed in Section 6.3.1.

The discharge data for the inflow and outflow of Sombre Lake are presented in Figure 4.9; in general these were in balance, as observed by Hawes (1983a). During the 1992 - 1993 summer, a clear peak in the discharge data indicates the period of most rapid melting of snow in the catchment. In the 1991 - 1992 summer, regular sampling did not
Figure 4.9: Discharge data for inflow and outflow of Sombre Lake. Errors are the standard error in the mean (n=3).
commence until 20/01/92, at which time the peak discharge had already occurred. It is possible to predict from data presented in Chapter 6 that the period of peak discharge was between 18/12/91 and 07/01/92.

The streams were frozen on 19/05/92. Before this date, they became clogged with snow beneath which the water flowed as a trickle. The last samples before the winter period were obtained on 16/05/92. The streams continued to flow after the final sample was collected on 11/02/93.

4.6.2 INFLOW AND OUTFLOW: pH AND ALKALINITY

The pH of inflow and outflow waters of Sombre Lake was similar (Figure 4.10a) and no simple temporal trends were observed in either summer. This is consistent with the observations made in Limestone Valley.

The alkalinity of inflow and outflow waters of Sombre Lake were similar (Figure 4.10b). Contrary to the observations made in Limestone Valley, a general trend of increasing alkalinity with time was observed in both streams.

4.6.3 INFLOW AND OUTFLOW: ORTHO-PHOSPHATE

Where significant differences existed between the concentrations of ortho-phosphate in the inflow and outflow, it was the outflow that exhibited the higher concentrations (Figure 4.10c). At the beginning of the summer outflow, concentrations were low but higher than the inflow. This preceded a pulse of higher concentration waters, after which the ortho-phosphate in the outflow decreased rapidly to values similar to the inflow. These data suggest that the inflow achieves maximum concentration at approximately the same time as
Figure 4.10: Concentrations of a) pH, b) alkalinity, c) o-P and d) DRSi in the inflow and outflow of Sombre Lake.
the outflow.

A pulsed release of ortho-phosphate was observed in Limestone Valley (Sections 4.5.3, 4.5.8) which was associated with ground thaw and a change in redox conditions; the pulsed behaviour seen in the inflowing waters can certainly be attributed to a similar mechanism. However, the pulsed form of the outflow data may be complicated by the presence of the lake.

### 4.6.4 INFLOW AND OUTFLOW: DRSi AND SUSPENDED MATTER

The concentration of DRSi in the inflow and outflow (Figure 4.10d) displayed a trend of increasing concentration with time for both summers; this was more pronounced for the 1991 - 1992 austral summer. This is contrary to the observations made in the 1994 - 1995 austral summer described above (Sections 4.4.2, 4.5.6).

In both the 1991 - 1992 and 1992 - 1993 summers the DRSi concentration of the inflow was higher than that of the outflow and this situation persisted throughout the period of flow. The differences between inflow and outflow concentrations were greater for the 1991 - 1992 summer than the 1992 - 1993 summer.

SPM was only observed in the waters of Sombre Lake inflow during the period of peak flow, when the material collected consisted of rock elastics. At no other time were measurable quantities of SPM observed in Sombre Lake inflow. Fine particulates, similar to those observed in Limestone Valley and the other streams studied in the 1994 - 1995 summer, were not found in Sombre Lake inflow. No SPM was collected from the Sombre Lake outflow at any time: this may be due to a methodological error, the importance of
which is discussed in Chapter 6.

4.6.5 INFLOW AND OUTFLOW: GROUP I, GROUP II AND CHLORIDE IONS

The inflow data for sodium, potassium and chloride (Figures 4.11a, b, e) in the 1992 - 1993 austral summer displayed an initial high concentration which decreased rapidly to achieve a steady value later in the season. Where data were available (chloride only), the concentrations determined in the inflow during the initial pulse were greater than those of the outflow. This behaviour is consistent with that observed in Limestone Valley.

Magnesium (Figure 4.11c) exhibited a trend similar to that observed in Limestone Valley, but after the initial snow-melt was complete concentrations increased with time. The concentrations in the inflow and outflow were similar.

The calcium concentration in the outflow remained relatively constant and lower than that of the inflow. Neither the inflow nor the outflow data exhibited a pulse of high concentrations associated with the thawing of winter snowpack.

4.6.6 INFLOW AND OUTFLOW: INORGANIC NITROGEN

The concentrations of ammonium in the inflow displayed an initial pulse of high concentration followed by a rapid decline: this is somewhat masked in Figure 4.12a by the higher concentrations observed in the outflow at the beginning of the summer season. The outflow data also showed an initial pulse of higher concentrations of ammonium that declined rapidly. At the end of the 1991 - 1992 summer the concentration of ammonium in the outflow waters began to increase. The general trend of a pulse of high concentration waters at the beginning of the season was consistent with the observations made in
Figure 4.11: Concentrations of Group I, Group II and chloride ions in the inflow and outflow of Sombre Lake. a) Na\(^+\), b) K\(^+\), c) Mg\(^{2+}\), d) Ca\(^{2+}\), e) Cl\(^-\).
Limestone Valley.

Concentrations of nitrite in the outflow waters were normally higher than in the inflow (Figure 4.12b). For the 1992 - 1993 summer, inflow and outflow concentrations were high at the beginning of the flow period and decreased with time.

Concentrations of nitrate in the inflow and outflow of Sombre Lake were similar for the 1991 - 1992 summer and decreased with time (Figure 4.12c), but for the 1992 - 1993 summer levels were generally higher at the outflow than the inflow. In the 1992 - 1993 summer, concentrations of nitrate in both the inflow and outflow decreased with time to reach a minimum at the end of December, before beginning to rise again.

The Limestone Valley system exhibited temporal and spatial trends of nitrate concentrations that suggested this ion was derived from permanent ice cover (Section 4.5.8). The temporal trend was complex and specific to that year. However, decreasing concentrations of nitrate were observed towards the end of the summer and were consistent with the data for the inflows and outflows of Sombre Lake.

4.6.7 INFLOW AND OUTFLOW: MANGANESE AND IRON

Mn$^{2+}$ was detected on one occasion in the outflow of Sombre Lake, but never in the inflow (Figure 4.13a). The occurrence of Mn$^{2+}$ in the outflow of Sombre Lake was coincident with the peak concentrations of ortho-phosphate (Figure 4.10c). The elevated concentrations of ortho-phosphate and Mn$^{2+}$ in the Limestone Valley stream were associated with ground thaw and changing redox conditions (Section 4.5.8). The data from Sombre Lake outflow supports the hypothesis made in Section 4.5.8 that the pulses of Mn$^{2+}$ and ortho-phosphate
Figure 4.12: Concentrations of a) NH$_4^+$, b) NO$_2^-$, c) NO$_3^-$ in the inflow and outflow of Sombre Lake.
Figure 4.13: Concentrations of a) Mn$^{2+}$ and b) Fe$^{2+}$ in the inflow and outflow of Sombre Lake.
are related.

No detectable concentrations of \( \text{Fe}^{2+} \) ions were found in the inflow or outflow of Sombre Lake (Figure 4.13b).

4.6.8 INFLOW AND OUTFLOW: DISCUSSION

Sections 4.6.1 - 4.6.7 outlined the form of the data for the inflow and outflow of Sombre Lake. Where the trends were consistent with those of Limestone Valley (Table 4.3), this has been noted. Of more interest are those features of the data which differ from the Limestone Valley system and as these did not fall neatly into a single category, it was useful to devise a classification system (Table 4.5).

Table 4.5 defines a method of classifying the differences between Limestone Valley and Sombre Lake systems and is based on a two tier approach. Later, it will also be used to assess the influence of Sombre Lake on its outflow (Chapter 5).

The first tier of classification determined the relative concentrations of a substance in the inflow and outflow and there are three possible cases: (1) the concentration in the inflow and outflow are approximately equal, (2) the concentration of the inflowing water is greater than the outflowing water and (3) the outflowing water is more concentrated than the inflowing water. The second tier of classification relates the differences between the temporal trends in the Limestone Valley and Sombre Lake systems, for which there were five possible cases. In the simplest scenario, the inflow and outflow exhibited the same temporal trends as Limestone Valley, whereas in other situations the inflow and / or outflow did not display such similarities. The cases described by the conditions outlined in Table 4.5
Table 4.5: Classification of trends observed in Sombre Lake inflow and outflow (Streams K2, L). Symbols; IF = inflow trend, OF = outflow trend, LV = trend observed in Limestone Valley (see Table 4.3), [IF] = concentration of inflow waters. Operators; = similar, <> dissimilar, > greater than.

<table>
<thead>
<tr>
<th>CLASS</th>
<th>CONCENTRATION</th>
<th>TEMPORAL</th>
<th>Ions / COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TREND</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>[IF]=[OF]</td>
<td>IF=LV OF=IF</td>
<td>pH, K⁺, Fe²⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IF=LV OF&lt;&gt;IF</td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td>1.3</td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
<td>Alkalinity, Mg²⁺</td>
</tr>
<tr>
<td></td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td></td>
<td>IF&lt;&gt;LV OF=LV</td>
<td></td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td>2.1</td>
<td>[IF]&gt;[OF]</td>
<td>IF=LV OF=IF</td>
<td>Na⁺, Cl⁻</td>
</tr>
<tr>
<td>2.2</td>
<td>IF=LV OF&lt;&gt;IF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
<td>DRSi</td>
</tr>
<tr>
<td>2.4</td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>2.5</td>
<td>IF&lt;&gt;LV OF=LV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>[IF]&lt;[OF]</td>
<td>IF=LV OF=IF</td>
<td>NO₂⁻, NO₃⁻, o-P</td>
</tr>
<tr>
<td>3.2</td>
<td>IF=LV OF&lt;&gt;IF</td>
<td></td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>3.3</td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>IF&lt;&gt;LV OF=LV</td>
<td></td>
<td>Mn²⁺</td>
</tr>
</tbody>
</table>

81
are exhaustive and for the situation where the inflow and outflow concentrations were equal, certain combinations of temporal trends in the inflow and outflow made no logical sense (Table 4.5, Classes 1.2, 1.4, 1.5). For these cases no class number has been entered in Table 4.5 and the entry "ILLOGICAL" has been entered in the comments column.

In the majority of cases the temporal trends of the inflow and outflow of Sombre Lake were similar and there were only three exceptions (Ca$^{2+}$, NH$_4^+$, Mn$^{2+}$) which will be discussed below. As the discharge of the inflow and the outflow were approximately in balance (Section 4.6.1), the differences in concentration will act as a approximate guide to mass-balance of the lake.

Whilst the inflow and outflow were active, but the lake remained ice covered, the concentrations in the outflow responded rapidly to changes on the inflow (e.g. Cl$^-$, NH$_4^+$ Figures 4.11e, 4.12a) and similar trends would be expected for the Group I and Group II metal ions if the data were available. This feature of the data is caused by peculiarities in the hydraulic residence time of Sombre Lake and will be discussed in Chapter 5.

Class 1.1 (pH, K$^+$, Fe$^{2+}$) defines a system exactly the same as the Limestone Valley system: the determinants exhibit the same temporal trends observed in Limestone Valley and the concentration of these ions in the outflow is the same as in the inflow. In fact, no Fe$^{2+}$ was detected in either the inflow or outflow of Sombre Lake.

Class 1.3 behaviour (alkalinity, Mg$^{2+}$) is a case where the inflow and outflow of Sombre Lake do not exhibit the trends of Limestone Valley but are similar to each other. As the concentrations of the inflow and the outflow are comparable, Sombre Lake has no influence
on the concentrations of these ions in the outflow. Examination of the alkalinity and magnesium data for the outflow of Changing Lake (Figure 4.14a, b) revealed a similar trend of increasing concentration with time. These data suggest that a process occurring further up the Paternoster Valley catchment was responsible for the observed trend.

Class 2.1 defines a system where the inflowing and outflowing waters exhibit the same temporal trend as Limestone Valley, but the lake either acted as a sink for the ion or diluted the ion and the outflowing waters were less concentrated than the inflowing waters. The ions exhibiting this behaviour (Na⁺, Cl⁻) can be considered conservative (Jenkin et al. 1994) and will not precipitate under the conditions existing in the lake. The waters of the lake must therefore be less concentrated than the inflowing waters and are, in effect, diluting the inflowing waters. With knowledge of the concentrations of these ions in the waters of Sombre Lake, it should be possible to predict the dilution factor; this is discussed later in the context of lake waters (Chapter 5). To be strictly correct, the ions in this class should actually belong to Class 2.1 during the initial melt pulse and then Class 1.1 for the remainder of the season, but to sub-classify a group of elements further would become too complex and the simple system proposed in Table 4.5 will be adhered to.

Class 2.3 (DRSi) is similar to Class 1.3, except Sombre Lake was either diluting the inflow or acting as a sink for DRSi. Concentrations in the outflow increased with time at the same rate as those observed in the inflow, suggesting that Sombre Lake is simply diluting the inflow waters. These data will be discussed further in Chapter 5. A similar trend of increasing DRSi concentrations through the season was observed further up the Paternoster Valley catchment (Figure 4.14c), which is contrary to the temporal trend seen in the 1994 - 1995 study. However, at the time of the Limestone Valley study, a trend of decreasing
Figure 4.14: Concentrations in outflow from Changing Lake of a) Alkalinity b) $\text{Mg}^{2+}$, c) $\text{DRSi}$, d) $\text{Ca}^{2+}$, e) $\text{NH}_4^+$. 
concentrations of DRSi with time was also observed in the Paternoster Valley catchment (Figure 4.2d, Stream I). This suggests that the trends in the DRSi data in Paternoster Valley are not specific to the catchment and that some other factor may be causing the observed pattern.

In Section 4.5.8 the decreasing concentrations of DRSi were linked to increasing concentrations of fine SPM in the waters of the Limestone Valley stream. In the 1991 - 1992 and 1992 - 1993 summers SPM was only observed in the streams at periods of peak flow, when it consisted of rock elastics; fine SPM similar to that reported for the 1994 - 1995 summer was not observed. Hawes (1988) presented data showing that DRSi concentrations increased with time. Extrapolation of data over five seasons would imply that the "normal" trend was one of increasing concentrations with time and that the 1994 - 1995 summer was unusual. If this were the case then the DRSi data for Sombre Lake system could be re-classified as Class 2.1.

Calcium exhibited Class 2.4 behaviour. Increasing concentrations with time were observed in the inflow whilst concentrations in the outflow were relatively constant, either the waters of Sombre Lake contained lower levels of calcium with respect to the inflow and were diluting the inflowing waters or Sombre Lake was also acting as a sink for calcium. As the outflowing concentration would increase at the same rate as the inflow if dilution were occurring, Sombre Lake in this case must be acting as a sink for calcium. In the outflow from Changing Lake, alkalinity, magnesium and calcium concentrations increased with time (Figures 4.14a, b, d) suggesting that processes further up Paternoster Valley were causing the observed deviation from the Limestone Valley trend. The surface inflow stream to Changing Lake flows over an area of marble outcrops; this could constitute a source of
calcium, magnesium and carbonate ions which would increase the concentrations of these ions in the inflow stream and possibly the outflow stream of Changing Lake. Furthermore, these observations retrospectively support the conclusion that calcium and alkalinity were derived from crustal weathering (Section 4.5.8).

Class 3.1 defines a system where the temporal trends exhibited by the ions are similar to those observed in Limestone Valley but the concentration of the ions was greater in the outflow than the inflow. This indicates that the lake was acting as a source of the ions in question (NO$_2^-$, NO$_3^-$, o-P$^-$) i.e. the lake waters were more concentrated than the inflowing waters. Again, with knowledge of the lake chemistry it should be possible to predict the increase in concentration (Chapter 5).

Ammonium (NH$_4^+$) exhibited Class 3.2 behaviour where the inflowing waters displayed a trend similar to that observed in Limestone Valley: a pulsed input which is characteristic of an ion being derived from the snowpack. At the outflow, ammonium displayed a pulse in early summer and increasing concentrations later in the season. Additionally, during the initial summer pulse, the outflow concentrations were greater than those of the inflow. These observations are indicative of a system in which the lake waters were more concentrated than the inflowing waters at the beginning of the summer but later in the season, a process occurred in the lake which increased the concentration of ammonium in the lake waters. This process may be the generation of ammonia by anaerobic activity of bacteria in the sediments of Sombre Lake, described by Ellis-Evans (1982). The inflow to Sombre Lake flows from the outflow of Changing Lake (Section 2.1.1). If the above processes occurred in Changing Lake, then the inflow of Sombre Lake would have similar temporal trends to those observed in the outflow. Ammonium concentrations in the outflow
from Changing Lake are consistent with snowpack being the primary source of these ions (Figure 4.14e) suggesting that there was little or no ammonia production in Changing Lake. Long term data for Changing Lake indicate relatively little anaerobic activity and coring studies suggest only shallow sediment deposits dominated by aerobic processes (Dr. J.C. Ellis-Evans, British Antarctic Survey *pers. comm.*).

In Limestone Valley, Mn$^{2+}$ exhibited an initial pulse associated with snowmelt; this was not observed in the Sombre Lake streams. Mn$^{2+}$ concentrations in Sombre Lake outflow exhibited a mid-season pulse that was coincident with the pulse of ortho-phosphate in the Sombre Lake streams. A similar observation was made in Limestone Valley (Section 4.5.8). Consequently, Mn$^{2+}$ could be placed in different classes at different times in the season. However, to maintain the simplicity of the classification system it will be placed in Class 3.5 as a mid-season pulse was not observed in the inflow.

This discussion of the properties of the inflow and outflow of Sombre Lake has been restricted to a classification of the temporal behaviour and the relative concentrations of determinants in the inflow and outflow of Sombre Lake (Table 4.5). More extensive discussion of these results and observations are presented in Chapter 5.

**4.7 SUMMARY**

A general study of the streams of Signy Island was undertaken to identify the sources of dissolved ions and the effect of temporal trends on the concentrations of dissolved ions. Conclusions from the general study were applied to the inflow and outflow streams of Sombre Lake; a full discussion of the influence of Sombre Lake on the stream system will be presented in the context of the lake chemistry in Chapter 5. However, the following
general conclusions can be made from these two studies:

1. In general, stream chemistry in six different catchments of Signy Island was similar. However, there is some evidence that the concentrations of marine-derived ions in streams decreased with increasing distance from the sea.

2. Sodium, potassium, magnesium, calcium, chloride, ammonium and nitrite ions were primarily derived from thawing of the winter snowpack. In addition some Mn$^{2+}$ was released from the snowpack.

3. Nitrate was derived from areas of permanent ice.

4. DRSi, calcium, carbonate and magnesium were derived from crustal weathering.

5. Ortho-phosphate and Mn$^{2+}$ were derived from crustal weathering but were released as a pulse, probably related to thawing of the fellfield soils.

6. In comparison with the inflow, reduced concentrations of sodium, potassium, magnesium, calcium and chloride were observed in Sombre Lake outflow; the waters of Sombre Lake diluted these ions.

7. Increased concentrations of nitrite and ortho-phosphate were observed in Sombre Lake outflow waters when compared to inflowing waters; Sombre Lake acted as a source of these ions.

8. Processes occurring in Sombre Lake increased the concentration of ammonium in the outflowing waters with respect to the inflowing waters.

9. Reduced concentrations of DRSi and calcium were observed in Sombre Lake outflow when compared to inflowing waters; Sombre Lake either diluted or acted as a sink for these ions.
10. Fe\textsuperscript{2+} was not detected in the inflow or outflow of Sombre Lake. However, a pulse of Mn\textsuperscript{2+} was observed in Sombre inflow that was consistent with the release of this ion on thawing of the fellfield soils.

Chapter 5 presents data on the soluble chemistry of Sombre Lake and further discussion of points 6 - 10 will be made in Section 5.3.4.2.
CHAPTER 5: CHEMISTRY OF SOMBRE LAKE

5.1 INTRODUCTION

The transport of dissolved and particulate species from the fellside to the lake by streams on Signy Island was discussed in Chapter 4. This chapter examines the soluble chemistry of Sombre Lake and its interaction with the inflowing and outflowing water.

Sombre Lake, described in Section 2.1.1, has received a considerable amount of interest since 1974 (Ellis-Evans 1985; Gallagher 1985; Ellis-Evans and Lemon 1989; Hawes 1983a, b, 1990a, b; Bayliss 1995; Jones and Juggins 1995), when along with Heywood Lake, it was adopted by the British Antarctic Survey as a site for long term studies (e.g. Ellis-Evans 1990). Only two of these works have concentrated on geochemical cycling in Sombre Lake (Gallagher 1985; Ellis-Evans and Lemon 1989) and whilst these papers considered aspects of iron cycling and nutrient regeneration from the anoxic sediments, little attention was paid to the particulate aspects of the cycle. Heywood (1967b, 1968) and Heywood et al. (1980) carried out some studies of the major ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻) in Sombre Lake, but there was no spatial aspect to these studies. In 1967 Heywood observed that the formation of ice caused the concentrations of conservative ions in the underlying water-body to increase (Heywood 1967b). This phenomenon caused by the exclusion of dissolved ions from the ice matrix is known as the "ice-exclusion effect".

Despite the early work of Heywood (1967b), recognition of the ice-exclusion effect is
generally attributed to Welch (1974) but it was Barica (1977) who presented a model predicting the increases in the concentrations of conservative ions during ice formation. Barica's model calculates a concentration factor based on the ratio of the volume of ice to the volume of the underlying water-body, assuming that virtually all solutes are excluded from the ice matrix. Heywood (1968) demonstrated that on freezing, 99% of solutes were excluded from the ice on Sombre Lake and therefore, Barica's (1977) model is applicable to Sombre Lake.

Whilst this work concentrates on the chemical and physical processes in Sombre Lake the biological cycle is closely linked to the nutrient cycling (see page 130). Hawes (1983a) described a spring algal bloom facilitated by high concentrations of nutrients and increasing amounts of light. Despite low concentrations of nutrients a smaller peak of algal productivity occurs in the summer but the biomass falls rapidly with the onset of ice cover. Ellis-Evans (1985) reported changes to the bacterial populations under winter conditions which have a profound influence on nutrient cycling in Sombre Lake (see page 130).

Chapter 4 of this work presented the first detailed study of the inflow and outflow of Sombre Lake. With this knowledge, it is possible to demonstrate the influence of the inflowing stream waters on the lake and to explain the source of dissolved ions in the outflow.

Field work for this study commenced in January 1992, but equipment problems delayed the start of water sampling until April 1992. Data for the period prior to April 1992 was kindly supplied by Dr. J.C. Ellis-Evans (British Antarctic Survey) and the field work and laboratory analyses for this period were performed by Mr. M.O. Chalmers (British Antarctic
Survey).

5.2 RESULTS AND DISCUSSION

5.2.1 SEASONAL REGIME

Sombre Lake was ice covered and the inflow and outflow were already flowing when this study commenced. Thereafter, regular observations were made of ice cover, ice depth, snow depth and the activity of the inflow and outflow.

Figure 5.1 clearly indicates the period of ice cover. The ice and snow measurements were made at the deep spot. Although the onset of ice cover for the 1992 winter was deemed to be the day when it was first possible to walk to the deep spot on the lake (24/03/92, 5cm of ice), ice formation was actually observed on 02/03/92 and complete cover (3cm) on 22/03/97 (Table 5.1). Similarly, the loss of ice cover was defined as the last day that it was possible to walk to the deep spot: the final ice break up (22/12/92) occurred within six days of the last measurement.

The ice melted in a consistent manner for the two periods observed (austral springs 1991-1992 and 1992-1993). Melting occurred first at the inflow and outflow and then along the east bank of the lake where there is a sub-lacustrine shelf (Heywood et al. 1979); this is consistent with Hutchinson's (1957) observation that thawing usually starts in shallow water. Areas of ice disintegrated to their constituent vertically orientated crystals as described by Welch (1991) and triggered the rapid disappearance of ice cover. The solid outer boundaries of such areas either melted or broke away as rafts and the columnar ice was destroyed in a matter of days by wind action (Hobbie 1973). On the west bank, where there are no shallow waters and shade is provided by Robin Peak, a small raft of ice
Figure 5.1: Ice cover and other seasonal factors affecting Sombre Lake. Areas identified by letters: snow (S), ice (I), granular opaque ice (G).
Table 5.1: Seasonal events affecting Sombre Lake. (Tabulated data from Figure 5.1).

<table>
<thead>
<tr>
<th>DATE</th>
<th>EVENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/11/91</td>
<td>Inflow and outflow started.</td>
</tr>
<tr>
<td>21/12/91</td>
<td>Ice cover broken.</td>
</tr>
<tr>
<td>05/02/92</td>
<td>Open water.</td>
</tr>
<tr>
<td>02/03/92</td>
<td>Ice formation started.</td>
</tr>
<tr>
<td>22/03/92</td>
<td>Complete ice cover (~3cm).</td>
</tr>
<tr>
<td>24/03/92</td>
<td>Possible to walk to deep spot (ice ~5cm).</td>
</tr>
<tr>
<td>19/05/92</td>
<td>Inflow and outflow stopped.</td>
</tr>
<tr>
<td>02/08/92</td>
<td>Mini-thaw event.</td>
</tr>
<tr>
<td>23/10/92</td>
<td>Inflow and outflow started.</td>
</tr>
<tr>
<td>27/10/92 - 26/11/92</td>
<td>Iron precipitates observed (see Chapter 7).</td>
</tr>
<tr>
<td>04/12/92</td>
<td>Ice cover broken.</td>
</tr>
<tr>
<td>16/12/92</td>
<td>Last day possible to walk to deep spot.</td>
</tr>
<tr>
<td>22/12/92</td>
<td>Open water.</td>
</tr>
</tbody>
</table>
Table 5.2: Dates on which Sombre Lake water column was profiled. The column SYMBOL refers to the symbol (a-j) associated with the profile in Figures 5.2-5.17.

<table>
<thead>
<tr>
<th>MONTH</th>
<th>DATE PROFILED</th>
<th>SYMBOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>09/05/92</td>
<td>a</td>
</tr>
<tr>
<td>June</td>
<td>13/06/92</td>
<td>b</td>
</tr>
<tr>
<td>July</td>
<td>30/07/92</td>
<td>c</td>
</tr>
<tr>
<td>August</td>
<td>24/08/92</td>
<td>d</td>
</tr>
<tr>
<td>September</td>
<td>22/09/92</td>
<td>e</td>
</tr>
<tr>
<td>October</td>
<td>19/10/92</td>
<td>f</td>
</tr>
<tr>
<td>November</td>
<td>28/11/92</td>
<td>g</td>
</tr>
<tr>
<td>December</td>
<td>22/12/92</td>
<td>h</td>
</tr>
<tr>
<td>January</td>
<td>26/01/93</td>
<td>i</td>
</tr>
<tr>
<td>February</td>
<td>17/02/93</td>
<td>j</td>
</tr>
</tbody>
</table>

The ice that formed at the beginning of the 1992 winter was clear "sheet" ice (Hutchinson 1957); with snow accumulation a layer of opaque ice, formed from frozen snow, developed on the surface. This opaque ice was above the level of the water in the ice hole (Figure 5.1, area G).

Ice thickness was not uniform across the lake. Regular measurements performed at the
sediment trap sites (Figure 2.3) indicate that for most of the winter, the ice was thicker in the region of the inflow, whilst at the outflow the thickness was similar to that of the deep spot. In general, the ice at the inflow was approximately 20cm thicker than at the deep spot. The volume of Moss Lake shrinks by 75% during winter, the water draining through a subterranean outflow (Light 1976) and these waters flow onto the frozen surface of Changing Lake. Light (1976) was unable to account for all the water lost from Moss Lake with increased depth of ice on Changing Lake and he speculated that it may flow down onto Sombre Lake (see map of Paternoster Valley, Figure 2.4). This could explain the observed differences in ice thickness on Sombre Lake.

Figure 5.1 indicates the periods of time when the inflow and outflow streams were active (see Chapter 4). It is clear that the streams continued to flow for some time after the formation of ice cover (until 19/05/92) and recommenced before loss of ice cover (23/10/92). The other seasonal feature noted is the mini-thaw event that was observed in 1992 and corresponds with earlier studies of various workers (e.g. Hawes 1988; Davey 1991; Convey 1992; Arnold 1995). To enable comparison of data with the seasonal information a copy of Figure 5.1 is supplied on acetate (inside back cover); this can be used as a template to overlay the graphs which cover the whole period of study (January 1991 - March 1993).

5.2.2 DEPTH PROFILES OF SOMBRE LAKE

5.2.2.1 Temperature

During the periods of open water the water column was isothermal (Figure 5.2): under ice cover, the depth-temperature profile exhibited an inverse thermal stratification, typical of the cold monomictic system described by Hutchinson (1957). Throughout the period of ice
Figure 5.2: Depth-temperature profile a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92\(^1\), g) November 92, h) December 92, i) January 93, j) February 93. \(^1\) No temperature measurements were made in October (see Section 5.2.2.1).
cover, the water immediately below the ice layer remained at a lower temperature than the water in the main body of the lake, creating an inverse gradient. This was attributed to conduction through the ice, but Heywood (1968) also suggested that the bottom waters may be warmed by heat released from the sediments, as described by Catalan (1992) for a mountain lake. The lowest water temperatures were recorded prior to and just after the formation of ice i.e. when the ice was at its thinnest.

Comparison of the temperature profiles for June, July and August suggest that an unusual event occurred between the sampling dates in June and July. The water at the bottom of the lake was warmer (approximately 1°C) in July than in June or August. The effects of a minor thaw (meltwater overlying the ice on all lakes) were recorded on 02/08/92 (Table 5.1). The thaw itself must have occurred a few days earlier but the meteorological data from the research station showed no evidence of elevated temperatures prior to this event. Under similar circumstances, Davey (1991) observed no elevated temperatures in micro-met data recorded at his sampling sites on Signy Island. Application of a snow melt model (Tarboton et al. 1995) to the meteorological data from the research station predicted a minor melt event for 23 - 28 July 1992. The water profile for July was not obtained until 28/07/92 and therefore it could have been influenced by this minor thaw. Furthermore, other depth profiles (O$_2$, Alkalinity, pH, Mn$^{2+}$, Fe$^{2+}$, o-P, Figures 5.3 - 5.5, 5.13 - 5.15) for July exhibited disturbed profiles when compared to June and August. These observations would imply that as a result of the thaw, a flow event occurred.

Warmer water, containing more dissolved oxygen, was introduced to the bottom waters and influenced the concentrations of certain species (Alkalinity, pH, DRSi, Mn$^{2+}$, Fe$^{2+}$, o-P). There are two possible explanations for this flow event. Firstly, meltwater from outside the
lake environment may have found its way beneath the ice-cover and entered the water body. However, meltwater would be at 0°C and would not cause the increased temperatures observed in Sombre Lake during July. The alternative and more likely explanation, is that warming of the water in the shallow shelf area of Sombre Lake, as observed by Heywood (1967b) and Hobbie (1973), may promote instability in the water column causing the warmer, more oxygenated water to flow down the side of the lake as a density current. Evidence presented below (Section 5.2.3.1) supports the second explanation.

Unfortunately, due to irreparable damage to the temperature and oxygen probe no data are available for these parameters in the critical month of October. The lake became isothermal throughout the water column in November prior to loss of ice cover (22/12/92). The profiles of other determinants (e.g. oxygen, Figure 5.3) revealed that the water column remained stratified until the loss of ice cover.

5.2.2.2 Oxygen

The formation of ice cover on Sombre Lake sealed the lake from the atmosphere and prevented the exchange of gases. Microbial processes occurring in the sediments of Sombre Lake consumed oxygen from the bottom waters (Ellis-Evans 1985) leading to a pronounced clinograde (Hutchinson 1957) for dissolved oxygen (Figure 5.3). Whilst the term "anoxic" is used throughout this work to refer to the oxygen depleted bottom waters it is clear from Figure 5.3 that the waters are merely "sub-oxic"; varying from mildly sub-oxic to virtually anoxic.

The oxygen profile for July (Figure 5.3) is unusual when compared to those of June and August. A similar irregularity was observed in the temperature data (Figure 5.2) and the
Figure 5.3: Depth-concentration profile of dissolved oxygen a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92\(^1\), g) November 92, h) December 92, i) January 93, j) February 93. \(^1\) No oxygen measurements were made in October (see Section 5.2.2.1).
Figure 5.4: Depth-concentration profile for alkalinity a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
reason for this was discussed in Section 5.2.2.1.

Biological activity in the sediments and bottom waters reduced the level of dissolved oxygen, profoundly influencing the chemistry of the lake. The associated rise in concentrations of carbon dioxide and release of bicarbonate ions, adsorbed to oxidised species in the sediment, produced a concomitant increase in alkalinity (Hutchinson 1957).

5.2.2.3 pH

Increasing concentrations of carbon dioxide in the sub-oxic waters of a lake create a pH profile of increasing acidity with depth due to the reaction:

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

However, the pH profile of Sombre Lake (Figure 5.5) exhibits an acid heterograde (Hutchinson 1957), caused by increased concentrations of the bicarbonate ion in the bottom waters.

5.2.2.4 Profiles Independent of Redox Conditions

Group I (Na\(^+\), K\(^+\)), Group II (Mg\(^2+\), Ca\(^2+\)) and chloride ions exhibit no redox chemistry in the range of conditions that occur in natural aquatic systems (Buffle and De Vitre 1994). These ions can be expected to exhibit depth-concentration profiles independent of depth if sources and sinks are absent from the system. However, there is some evidence for elevated concentrations calcium in the bottom waters of Sombre Lake (Figure 5.9) and Sholkovitz (1985) has made similar observations in temperate, anoxic lakes.

The May profiles for sodium and chloride (Figures 5.6a, 5.10a) clearly illustrate elevated concentrations in the surface waters and there is also some evidence for a similar feature in
Figure 5.5: Depth profile of pH a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Figure 5.6: Depth-concentration profile for sodium a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Figure 5.7: Depth-concentration profile for potassium a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Figure 5.8: Depth-concentration profile for magnesium a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Figure 5.9: Depth-concentration profile for calcium a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Figure 5.10: Depth-concentration profile for chloride a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
the profile for potassium (Figure 5.7). This can be attributed to the ice-exclusion effect that was described in Section 5.1.

In October and November 1992, clear depth trends were observed for the Group I, Group II and chloride ions (Figures 5.6 - 5.10). In October, all ions exhibited low concentrations in the surface waters: low density water, which was relatively dilute in these ions, entered the lake at the inflow and formed a layer of moving water directly below the ice i.e. no more than 2m deep. A similar situation has been observed in Sombre Lake by Hawes (1983a) and in an Arctic lake (Rigler 1978). Also, in October, the profiles below 8m were not smooth and suggested a perturbation in the bottom waters. The profiles for November displayed a clear trend of increasing concentration with depth. These observations and the evidence for perturbation of the bottom waters will be discussed in Section 5.2.4.1.

5.2.2.5 Redox Controlled Profiles

The development of anoxic conditions in the sediment and bottom waters of Sombre Lake led to the reduction of certain redox sensitive compounds in the sediments and their release to the overlying water column. Similar observations have been made in numerous other studies (e.g. Mortimer 1941, 1942; Hutchinson 1957; Davison 1982; Sholkovitz 1985). On oxidation, Fe\(^{2+}\) forms particulate iron oxyhydroxides that can adsorb humics and other ions onto their surface (Tipping \textit{et al.} 1989). The sedimentation of the iron oxyhydroxides carries the adsorbed ions to the sediments at the end of winter; Sholkovitz and Copland (1982a) concluded that the redox chemistry of iron was "a master process" controlling the temporal and spatial distribution of other ions in the water column.

As the bottom waters became depleted of oxygen, Fe\(^{2+}\) was released from the sediment to
Figure 5.11: Depth-concentration profile for Fe$^{2+}$ a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
the overlying waters (June, Figure 5.1lb). The density current, described in Section 5.2.2.1, introduced oxygen to the bottom waters of the lake (Figure 5.3) and this disrupted the developing Fe\(^{2+}\) profile, possibly due to oxidation of the Fe\(^{2+}\).

The Fe\(^{2+}\) profile continued to develop in August and September and the ions diffused away from the anoxic zone into the upper waters of the lake (Figure 5.1ld, e). The mid-depth (2.5 - 10m) waters of Sombre Lake showed low pH values (Figure 5.5, pH < 6.5). Under such conditions, the rate of oxidation of Fe\(^{2+}\) is slower than in waters of higher pH (Stumm and Morgan 1981), promoting the stability of Fe\(^{2+}\). Gallagher (1985) observed a similar phenomenon previously in Sombre Lake.

The inflow and outflow recommenced flow on 23/10/92 and the water-column profile for October was recorded on 27/10/92. A significant decrease in the concentration of Fe\(^{2+}\), as observed in the depth-profile, implied that the removal of Fe\(^{2+}\) throughout the water column was rapid (within 4 days). This probably occurred through oxidation to the insoluble Fe\(^{3+}\) form. Simultaneously, particles were observed in the water column that could be attributed to this process (Section 6.3.2, Chapter 7). The high concentration of Fe\(^{2+}\) in the bottom waters during November was attributed to a narrow layer of anoxic water above the sediments (see Figure 5.3g). Iron oxide particulates from the water column sedimented into this zone and were immediately reduced to Fe\(^{2+}\), whilst this ion continued to be released from the sediments. These two sources of Fe\(^{2+}\) gave rise to the extremely high concentrations in the bottom waters. Linked to the redox cycle of iron, ortho-phosphate is one of the principal co-precipitants when Fe\(^{2+}\) is oxidised to its insoluble Fe\(^{3+}\) state (Buffe et al. 1989). The development of the depth-profile of ortho-phosphate ions followed that of Fe\(^{2+}\) (cf Figures 5.11, 5.12). The ortho-phosphate profile for July 1992 (Figure 5.12c) was
Figure 5.12: Depth-concentration profile for ortho-phosphate a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
affected by the density current, but unlike Fe\(^{2+}\), the concentrations of ortho-phosphate in the water column were not significantly reduced by this event. After the onset of the inflow (23/10/92), the concentration of ortho-phosphate in the water column decreased and evidence suggests that this resulted from adsorption to iron oxyhydroxides (Chapter 7). As observed for Fe\(^{2+}\), elevated concentrations of ortho-phosphate were also noted in the bottom waters in November.

In lakes which develop anoxic bottom waters during stratification, the distribution of DRSi is similar to other ions released from the sediments (Hutchinson 1957) and a comparable situation was observed in Sombre Lake (Figure 5.13). Whilst it is unlikely that DRSi concentrations are directly controlled by redox conditions, evidence is presented below that suggests Fe\(^{2+}\) may play an important role.

It is known that ammonium, produced by the anoxic respiration of bacteria, is released to the stratified waters overlying the sediment (e.g. Canfield and Green 1985); the ammonium profiles suggest that this also occurred in Sombre Lake (Figure 5.14). The depth profiles of nitrate (Figure 5.15) exhibit minimum values in the bottom waters of the lake, suggesting that nitrate was being consumed. Nitrite was only observed in the bottom waters of Sombre Lake (Figure 5.16). Comparison of the profiles for these three ions revealed an interesting feature of the data. The nitrate data for May, June and September (Figures 5.15a, b, e) clearly displayed a small peak in concentration in the 8-9m stratum (indicated by *) and it could be argued that a similar feature exists in the nitrate profile for July (Figure 5.15c). At the corresponding depths a minimum was observed in the nitrite profiles (Figure 5.16). Corresponding minima for August and September in the ammonium profiles (Figures 5.14d, e) and small inflections in the June and July data (Figures 5.14b, c) were also noted (all
Figure 5.13: Depth-concentration profile for DRSi a) May 92, b) June 92, c) July\textsuperscript{1}, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93. \textsuperscript{1} Results for July were found to be in error, and are omitted.
indicated by *). This would imply a dynamic link between these forms of inorganic nitrogen under the redox conditions existing in Sombre Lake.

The observations presented above indicate that not only is ammonium released from the sediments, but under the reducing conditions in the bottom waters of Sombre Lake, nitrate is reduced to ammonium via nitrite; this reaction is biologically mediated. This would account for the elevated concentrations of nitrite in the bottom. Ellis-Evans (1985) described a similar finding that he attributed to bacterial processes. In the region of the 8-9m stratum, where a maximal concentration of nitrate and minimal concentrations of nitrite and ammonium were noted, it appears that ammonium and nitrite were undergoing oxidation to nitrate.

Canfield and Green (1985) observed similar profiles in Lake Vanda and associated this phenomenon with nitrification. In October, after the onset of inflow (23/10/92), no nitrite was detected in the water column and ammonium was only detected below 10m. The concentrations of nitrate in the water column were dramatically reduced but a minimum persisted in the bottom waters. The elevated concentrations of ammonium and nitrate in the bottom waters of Sombre Lake in November are attributed to the narrow anoxic zone that persisted at this time and was discussed above with reference to the high concentrations of Fe$^{2+}$. At the onset of inflow, nitrate concentrations decreased rapidly as observed by Hawes (1983a). However, elevated concentrations of nitrate were detected throughout the water column in November (Figure 5.15g).

The release of Mn$^{2+}$ from the sediments is controlled by redox conditions: consequently the depth profiles for Mn$^{2+}$ (Figure 5.17) closely followed the development of the Fe$^{2+}$ profile.
Figure 5.14: Depth-concentration profile for ammonium a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93. * - see text page 113.
Figure 5.15: Depth-concentration profile for nitrate a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93. * - see text page 113.
Figure 5.16: Depth-concentration profile for nitrite a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93. * - see text page 113.
Manganese is more readily reduced than iron (Stumm and Morgan 1981) which explains its appearance (May) in the water column earlier than Fe$^{2+}$ (June). By a similar argument, Mn$^{2+}$ should diffuse higher into the water column than Fe$^{2+}$. This was not observed in June or September. If the Mn$^{2+}$ profiles for May and June (Figures 5.17a, b) are examined in detail, a curious double peak is observed with the upper peak coinciding with the depth at which formation of nitrate was postulated (Section 5.2.2.5). These findings suggest that Mn$^{2+}$ may be linked to the oxidation of ammonium to nitrate in the 8-9m stratum. The oxidation of ammonium is a microbially mediated process (Ellis-Evans 1982) and it is also known that bacteria are involved in the cycling of manganese in lakes (e.g. Chapnick et al. 1982; Sunda and Huntsman 1987). The change in the Mn$^{2+}$ depth-profiles between June and July (Figures 5.17b, c) was due to the introduction of oxygen to the bottom waters by the density current described in Section 5.2.2.1, and is consistent with the profiles for Fe$^{2+}$. The profile for Mn$^{2+}$ developed again in August and September (Figures 5.17d, e); Mn$^{2+}$ diffused up the water column in the same manner as Fe$^{2+}$ (Figure 5.11). Mn$^{2+}$, being more stable to oxidation than Fe$^{2+}$ (Stumm and Morgan 1981), remained in the water column at measurable concentrations after the onset of inflow (Figure 5.17f). Elevated concentrations of Mn$^{2+}$ persisted in the bottom waters of Sombre Lake until late December.

5.2.3 TOTAL WATER-BODY CONCENTRATIONS (TWCs)

The depth-concentration data, obtained from the analysis of water samples from various depths, were used to construct the profiles presented in Figures 5.2 - 5.17. This representation of the data is useful for most of the interpretation and discussion of the water chemistry of Sombre Lake. Subsequent integration of the data over the volume of the lake enabled a clearer picture of the processes operating in the lake to be formed.
Figure 5.17: Depth-concentration profile for manganese a) May 92, b) June 92, c) July 92, d) August 92, e) September 92, f) October 92, g) November 92, h) December 92, i) January 93, j) February 93.
Heywood et al. (1979) presented bathymetric data for Sombre Lake from which it was possible to calculate the quantity (moles) of an ion in each stratum (1m intervals), based on the concentrations measured at the deep spot and assuming no horizontal variation i.e. concentrations measured at the deep spot were consistent across the lake (Welch and Bergmann 1985). When ice free, the lake is entirely wind mixed and this assumption is clearly valid. There is also evidence (J. B. Gallagher unpublished data) from Sombre Lake, to suggest that this assumption may be applied under ice-cover to strata that are not in contact with anoxic sediments. Only the bottom 1m of Sombre Lake becomes anoxic; this forms such a small fraction of the total volume of the lake that any errors introduced are likely to be small. The total quantity of an ion in the lake was obtained by summation of the results for each stratum.

As discussed in Section 5.1, when water freezes the dissolved ions are excluded from the ice matrix (e.g. Welch 1991) and the water body of the lake becomes enriched in these excluded ions. It is a simple process to correct the volume of the water body of the lake by subtraction of a representative fraction of the volume contained in the 0-1m stratum from the total volume. For example, with ice cover to a depth of 20cm, the total volume of the lake was reduced by a value equivalent to 20% of the volume contained by 0-1m stratum. This corrected figure is the volume of the water body and division of the total quantity of an ion in the lake by the corrected volume yields the "total water-body concentration" (TWC).

Errors may exist in the calculation of TWC due to: a) the assumption that there was no horizontal variation, b) the method on which the integration was based, c) the accuracy of the bathymetric data and d) the large influence of high concentrations of ions persisting in an anoxic sump (Heaney et al. 1986). Nevertheless, data presented in Section 5.2.3.3
indicate that the TWC results are representative of plausible processes occurring in the lake.

### 5.2.3.1 TWC of Oxygen

The TWC time series (Figure 5.18a) clearly demonstrates decreasing concentrations of dissolved oxygen in Sombre Lake. Minimum TWC of oxygen was attained in late September.

In Section 5.2.2.1 it was observed that the minor thaw in late July disturbed the stratification of the lake and two mechanisms were presented for this. The first mechanism suggested that oxygenated water had entered the lake by flowing around the ice cover: if this were the case then there would be an associated increase in the TWC of oxygen between June and July. This was not observed (Figure 5.18a), adding weight to the hypothesis that a density current caused the disruption of stratification. The onset of thaw and subsequently the inflow, was a period in which there was an increase of TWC of oxygen. These data (Figure 5.18a) clearly demonstrate that in both the 1991-1992 and 1992-1993 austral summers re-oxygenation of the water column did not occur until after the loss of ice cover (05/02/92 and 22/12/92).

### 5.2.3.2 TWC of Alkalinity

The depth-alkalinity profiles (Figure 5.4) display increasing alkalinity with depth and time as would be expected in an anoxic system, but the TWC for alkalinity displayed little variation (Figure 5.18b).

### 5.2.3.3 TWCs of Ions Independent of Redox Conditions

Figure 5.19 reveals a trend of increasing TWC, rising to a maximum that was coincident
Figure 5.18: Total water body concentration (TWC) of a) dissolved oxygen, b) alkalinity. No oxygen measurements were made in October; this is indicated by the break in the line.
with the maximum ice depth. Sodium and chloride can be considered as conservative ions in aquatic systems (Jenkin et al. 1994), and the increased TWCs for these ions during winter can be accounted for by the ice-exclusion process, outlined in Section 5.1. This process would also explain the increased TWC for potassium, magnesium and calcium. The TWC for these ions reached a maximum in August, when the ice was thickest (Figure 5.1) and the water body volume was at a minimum. As the ice melted the TWCs of these ions decreased, reaching the minimum value after the loss of ice cover (22/12/92). It is probable that the TWC for these ions would remain virtually constant for the summer until the beginning of ice formation the following winter.

If TWCs for January and February 1993 are taken as typical of the ice free period (unfortunately data is not available for the ice free period of the 1991-1992 austral summer), then these values can be used to calculate a mean TWC for the ice free period. If the ratio between the ice free TWC and the maximum TWC is calculated for each ion then the result is a concentration ratio \( r_x \) for ion \( x \):

\[
r_x = \frac{W_x}{S_x}
\]  

Equation 5.1

where \( W_x \) is the maximum TWC of ion \( x \) recorded under ice and \( S_x \) is the ice free TWC of ion \( x \)

This concentration ratio \( r_x \) is the equivalent of that calculated by applying the ion-exclusion model of Barica (1977). If Barica's model is applied to Sombre Lake, assuming that the whole 0-1m stratum was frozen at maximum ice depth, then the concentration ratio is 1.2.
Figure 5.19: Total water body concentration (TWC) of a) Na$^+$, b) K$^+$, c) Mg$^{2+}$, d) Ca$^{2+}$, e) Cl$^-$.
The concentration ratio \( r_x \) was calculated for all the ions measured in Sombre Lake and the results are reported in Table 5.3. There is no information regarding the accuracy of the bathymetric data for Sombre Lake, nor is there a simple method of determining the accuracy of the model used to integrate the depth-concentration profiles. However, the concentration ratios for sodium (1.4) and chloride (1.5) are close to the value predicted by the ice-exclusion model of Barica (1977) indicating that the method used to calculate TWCs in Sombre Lake is producing realistic results. Concentration ratios calculated from the data of Heywood et al. (1980) are also presented. The values for sodium and chloride were in close agreement with the TWC ratios calculated in this work. The TWC ratios for calcium and potassium, ions which displayed depth dependent profiles, compare poorly with the unintegrated data of Heywood et al. (1980).

A TWC ratio close to that calculated for sodium and chloride indicates that increased winter concentrations of a dissolved ion can be attributed to the ice-exclusion process. Where the TWC ratio of a dissolved ion is greater than that of sodium and chloride, then a mechanism operating in the lake must be supplying excess concentrations of that ion to the water column.

5.2.3.4 TWCs of Redox Controlled Ions

The TWC for \( \text{Fe}^{2+} \) (Figure 5.20a) began to increase in August. The data indicate that TWC had started to rise in June, but at the end of July the value decreased. TWC was maximal in late September and then under the influence of the oxygen, introduced by the inflow, decreased rapidly in late October. Comparison with the TWC for ortho-phosphate (Figure 5.20b) shows close synchronisation; both curves attained a maximum value just prior to the introduction of inflow waters. Unlike \( \text{Fe}^{2+} \), the TWC value for ortho-phosphate did not fall
Table 5.3: Concentration ratios for dissolved ions in Sombre Lake. $r_x$ is the ratio between the maximum TWC of an ion and its mean TWC in the ice free period (see Equation 5.1). "Heywood ratio" is the ratio of winter and summer data from Heywood et al. (1980). n.d. = not determined. * = summer concentration reported as "trace".

<table>
<thead>
<tr>
<th>DISSOLVED ION</th>
<th>$r_x$</th>
<th>HEYWOOD RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>K$^+$</td>
<td>2.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>3.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>53</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>52</td>
<td>n.d.</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>$2 \times 10^6$</td>
<td>n.d.</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>9.0</td>
<td>*</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>4.9</td>
<td>3.5</td>
</tr>
<tr>
<td>DRSi</td>
<td>4.0</td>
<td>1.9</td>
</tr>
<tr>
<td>o-P</td>
<td>15</td>
<td>*</td>
</tr>
</tbody>
</table>
at the end of July, suggesting that any iron precipitation event occurring at that time did not involve ortho-phosphate.

The TWC curve for Mn$^{2+}$ (Figure 5.20c) is difficult to interpret. Elevated concentrations of Mn$^{2+}$ certainly survive into the latter period of ice cover, as demonstrated by the depth-concentration profiles (Figure 5.17). However, the TWC curve suggests that a maximum is attained at the end of July, which then falls rapidly. In view of the possible errors in the method of calculating TWCs, despite the supporting evidence from conservative elements, the single, grossly elevated value for July has to be interpreted cautiously.

A large peak was exhibited in the TWC time series for Fe$^{2+}$ in November (Figure 5.20a). Heaney et al. (1986) observed that extremely high concentrations of ions in a region of persistent anoxia may have a disproportionately large effect on TWC. This is exemplified by the Fe$^{2+}$ depth-profile for November (Figure 5.11g) which exhibited a very high concentration in the bottom waters relative to other depths.

The TWC for ammonium (Figure 5.21a) increased steadily throughout the period of ice cover until September, when it began to fall to its ice free value. As previously stated, it is known that the concentrations of ammonium increase in stratified waters overlying anoxic sediments due to bacterial processes. Clearly, from the form of the ammonium profiles (Figure 5.14) and the TWC ratio (Table 5.3), ammonium is being supplied to the water column in Sombre Lake during this period.

TWC for nitrate was at a maximum when ice cover commenced (Figure 5.21c) and continued at the same level until July. During this period the TWCs of other ions were
Figure 5.20: Total water body concentration (TWC) of: a) Fe$^{2+}$, b) o-P, c) Mn$^{2+}$. 
increasing due to the ice-exclusion effect e.g. sodium and chloride (Figures 5.6, 5.10); an alternative mechanism must have decreased the total quantity of nitrate ions in the lake at this time (Figure 5.21d). During the period in which the TWC of nitrate remained stable, the TWCs of nitrite and ammonium (Figures 5.21a, b) were increasing in a manner that could not be attributed to ice-exclusion (Table 5.3). The increases observed in the total quantity of ammonium are of a similar order of magnitude to the decreases observed in the total quantity of nitrate. This is illustrated by Figure 5.21d, where the TWC of nitrogen remains constant until July. This is consistent with the observations of Ellis-Evans (1985) and the data presented in Section 5.2.2.5 where it was suggested that there was a dynamic link in the bottom waters between the three inorganic forms of nitrogen ($\text{NH}_4^+$, $\text{NO}_2^-$, $\text{NO}_3^-$).

The TWCs for ammonium and nitrate decreased rapidly in August. Ellis-Evans (1985) reported that the predominance of nitrogen cycling, bacterial populations in Sombre Lake changed during the winter from nitrate fermenters ($\text{NO}_3^- \rightarrow \text{NH}_4^+$) to denitrifiers ($\text{NO}_3^- \rightarrow \text{N}$). This would explain the rapid decrease in the nitrate TWC without an associated increase for ammonium. If the rapid decrease in the TWC for ammonium was caused by adsorption to precipitating oxides, for example iron oxides, then it would be coincident with the decrease in the TWC for iron. This was not noted (cf Figures 5.20a, 5.21a) and Gallagher (1985) also observed that nitrogen dynamics were not related to iron. Growth of phytoplankton in Sombre Lake can commence under conditions of very low light as there is substantial shade adaptation (Hawes 1990b). The period of maximum growth was observed in the spring under ice cover (Hawes 1983a, 1990b). This feature of phytoplankton ecology enables the developing biomass to utilise the nutrients released from the sediments during the winter which remain in the water column at this time. Hawes (1983a), observing that the decrease in the concentrations of ammonium and nitrate in the water column was coincident
Figure 5.21: Total water body concentration (TWC) of a) NH$_4^+$, b) NO$_2^-$, c) NO$_3^-$, d) N (sum of NH$_4^+$, NO$_2^-$, NO$_3^-$).
with increasing numbers of phytoplankton, concluded that increases of biomass utilised significant amounts of the available inorganic nutrients. This would explain the dramatic decrease in the TWC for nitrate and ammonium. Phytoplankton activity would also consume significant quantities of ortho-phosphate from the water column, but it is not currently possible to assess this effect.

The TWC ratio (Table 5.3) of DRSi indicates that ice-exclusion did not account for the increased concentrations of this ion during the winter and the depth profiles (Figure 5.13) suggest that it was supplied from the sediments. The TWC value increased steadily during the period of ice cover, reached a maximum just before the streams started flowing, then rapidly decreased after the loss of ice cover when complete re-oxygenation of the lake had occurred.

The data presented (Figures 5.20, 5.22) suggests that the production of iron oxide may be implicated in the removal of DRSi ions from the water column. Additionally, it appears that DRSi was removed from the water column prior to the production of iron oxide: two mechanisms can be postulated.

Firstly, adsorption to suspended particulate matter (SPM) as observed in the Limestone Valley stream (Section 4.5.8); due to the onset of the inflow, the concentrations of SPM were increasing in the water column at this time (Section 6.3.1). The second possible mechanism is the incorporation of dissolved DRSi into the frustules of diatoms. Although biological processes occur very rapidly in the spring with the phytoplankton bloom occurring under ice-cover (Hawes 1990b), there are virtually no pelagic diatoms to be
Figure 5.22: Total water body concentration (TWC) of DRSi. The data for DRSi in July (Figure 5.13c) was found to be in error and no TWC value was calculated for July; this is indicated by the break in the line.
found in Antarctic lakes (Jones and Juggins 1995). Hutchinson (1957) suggested that the development of diatom blooms was the most important mechanism for the removal of DRSi from lake water, but for Sombre Lake it would appear that adsorption to SPM is likely to be a more important control mechanism.

5.2.4 STREAM-LAKE RELATIONSHIP

The chemistry of the streams of Signy Island was presented and discussed in Chapter 4. By using the spatial and temporal trends of dissolved ion concentrations in a relatively simple stream (Limestone Valley, Signy Island), it was possible to identify potential sources of these ions (Table 4.4). These conclusions and observations were then applied to the main inflow and outflow of Sombre Lake to elucidate the influence of the inflow on the lake and the lake on the outflow (Section 4.6). In the absence of data pertaining to the chemistry of the water column of Sombre Lake, Section 4.6 merely summarised the differences between the chemistry of the inflow and outflow of the lake (Table 4.5). The data presented in this chapter will facilitate an explanation of these observations. It will be important to refer to Table 4.5 in this Section and to this end it is reproduced below as Table 5.5.

5.2.4.1 Mixing Processes in Sombre Lake

During the thaw, Hawes (1983a) observed a current of low density meltwater flowing across the surface of Sombre Lake immediately below the ice. Data presented in Section 5.2.2.4 indicated that this process also occurred at the end of the 1992 winter. It has been generally believed that although this meltwater does not enter the body of Sombre Lake, some interchange at the interface with the lake water does occur and that re-introduction of oxygen to the bottom waters of the Sombre Lake does not take place until ice cover has been lost and the waters become completely wind mixed (Hawes 1983a, b).
Contrary to the observations of Hawes (1983b), the oxygen profile for November 1992 (Figure 5.3g) suggested that although the lake remained stratified at this time, oxygen had indeed been introduced throughout the water column. No oxygen data were available for October (Figure 5.3f) due to failure of the oxygen and temperature probe, but comparison of the Fe$^{2+}$ profiles for September and October (cf Figures 5.11e, 5.11f) revealed that the concentrations of Fe$^{2+}$ throughout the water column were significantly reduced in October. Oxidation of Fe$^{2+}$ to its insoluble Fe$^{3+}$ state proceeds rapidly under circumneutral conditions (Stumm and Morgan 1981), supporting the theory that oxygen had been introduced to the whole water column in October. Data presented in Chapter 7 confirms that the oxidation of Fe$^{2+}$ to its insoluble form occurred simultaneously throughout the water column of the lake at this time. Examination of other depth-concentration profiles presented in this chapter (NH$_4^+$, o-P, NO$_3^-$, NO$_2^-$, Figures 5.12, 5.14 - 5.16) support the occurrence of an event that altered the redox status of the lake i.e. the introduction of oxygen. Certain depth-concentration profiles (Alkalinity, pH, DRSi, Figures 5.4, 5.5, 5.13) remained unaffected by this event and an oxygen gradient persisted throughout the lake (Figure 5.3), implying that stratification of the lake was not destroyed. Therefore, the process by which oxygen was introduced to the bottom waters could not be a catastrophic mixing process. Diffusion of oxygen from the overlying layer of meltwater could occur, but this process would be relatively slow for the observed timescale and would be unlikely to account for the observed oxidation of Fe$^{2+}$ throughout the water column.

Sodium and chloride can be considered conservative ions in freshwater aquatic systems (Jenkin et al. 1994) and hence the use of these ions as tracers (e.g. Barlow and Glase 1982). For the period May to September the depth-concentration profiles for these ions (Figures
5.6, 5.10) remained relatively independent of depth and any variations could be attributed to the ion-exclusion process at the surface of the ice (Section 5.1). Examination of the depth-concentration profiles of both ions for October (Figures 5.6f, 5.10f) and November (Figures 5.6g, 5.10g) revealed profiles that were clearly dependent upon depth. In Section 5.2.2.4 it was observed that the inflowing waters, which in general, were more dilute than the lake waters with respect to sodium and chloride, flowed across the lake as a discrete current directly below the ice. This would account for the low surface concentrations of these ions observed in October. Interestingly, the depth-profiles of these ions for November (Figures 5.6g, 5.10g) displayed increased concentrations in the bottom waters. There is no evidence in the literature to suggest that these ions can be released from the sediments of the lake nor can a process that concentrates only these ions in the bottom waters of the lake be postulated. These findings imply that sodium and chloride ions were introduced to the bottom of the lake by the same mechanism that dispersed oxygen throughout the water column. Elevated concentrations of these ions were observed in Sombre inflow (Section 4.6.6, Figure 4.11a, e) on 23/10/92 and 14/11/92 and were of concentrations comparable to those observed in the bottom waters of Sombre Lake. The depth-concentration profiles for the other Group I and Group II elements exhibited similar properties.

The inflowing water, meltwater from the winter snowpack, is cold (~1°C): it would not form a density current down the side of the lake as the warmer waters at the bottom of Sombre Lake (~2°C) would be more dense (maximal density of water is at 3.94°C, Hutchinson 1957). If however, sediments from the sub-lacustrine shelf of the lake were entrained, the inflowing water could then form a current of higher density: Quadfasel et al. (1990) described such a mechanism in the marine environment. As the current flows down the side of the lake it would then lose its entrained sediments and mix with the ambient
water; this would allow plumes of water to stream into the body of Sombre Lake at various depths without disturbing the stratification of the lake (Figure 5.23). Such processes are well documented in the oceanographic literature (Smith 1975; Aagaard et al. 1981) and could also apply to Sombre Lake.

In this manner, the introduction of oxygenated water to Sombre Lake would not disturb the stratification of the lake and could explain the observations presented above. If a turbidity current is responsible for the movement of oxygen to the deeper waters of Sombre Lake, then it might be anticipated that the three sediment traps deployed at the deep spot would trap material in proportion to depth i.e. the 10m trap would collect more than the 5m trap. Evidence to support this interpretation is presented in Section 6.3.1.

In Section 5.2.2.1 a density current was proposed as a mechanism for the disruption of the depth-concentration profiles in July, whilst a turbidity current has been postulated for the introduction of oxygen to the water column after the winter. While there are similarities between the two mechanisms they have markedly different effects on the water column. Water, warmed in the shallows of Sombre Lake, becomes more dense than the deeper, colder lake water and a density current is created. This pocket of denser water then moves slowly down the side of the lake in the manner described by Hobbie (1973). The density gradient, which maintains the stratification of Sombre Lake, would be disrupted by the introduction of this warmer water causing the effects observed in Figures 5.2 and 5.3. The fast flowing waters of the inflow stream, lifting SPM from the sub-lacustrine shelf of Sombre Lake, creates a turbidity current: such a current moves faster than a density current and as it loses quantities of SPM by settlement, small amounts of water form plumes. These stream into the lake at a depth where they match the density of the ambient water as Figure
described by Quadfasel et al. (1990). The above mechanism accounts for the different effects of these two processes which are illustrated in Figure 5.23.

The turbidity current mechanism outlined here is obviously an intermittent effect. It would first introduce oxygen to the whole water column of Sombre Lake (characterised by the loss of redox sensitive ions from the water column in October) and then introduce other dissolved ions later (e.g. Group I, Group II and chloride ions). For example nitrate ions exhibited elevated concentrations in November throughout the water column and this too could be attributed to the influence of a turbidity current.

Earlier studies of Sombre Lake (Gallagher 1985; Ellis-Evans and Lemon 1989) did not examine the influence of oxygen rich inflowing waters on nutrient cycling processes: direct comparison with the observations and conclusions of this work is not possible.

5.2.4.2 Influence of Sombre Lake on its Outflow

Examination of the concentrations of ions flowing into and out of Sombre Lake (Figures 4.10 - 4.13) and consideration of the differences between the Sombre Lake system and the Limestone Valley system reveals that the temporal trend exhibited by the inflowing waters was frequently mimicked by the outflowing waters. In fact, only the trends in ammonium, Mn$^{2+}$ and calcium ions were not consistent with this observation. For the cases where the temporal trends were similar in the inflow and outflow it should be possible to explain the difference in concentration between the inflowing and outflowing waters.

A quantitative explanation of these observations would require a complex mathematical model, which is beyond the scope of this study, but it, should be possible to qualitatively
Figure 5.23: Mixing mechanisms in Sombre Lake and effects on the depth-concentration profiles of dissolved species (see text for details). Profiles are shown before and after mixing. a) Wind Mixing: Under conditions of open water the lake is completely mixed. b) Density Current: Under ice-cover warmer, denser water flows down the side of the lake and disrupts stratification. c) Low Density Inflow Water: Inflowing water flows across the surface of the lake under ice-cover; some mixing occurs with body of the lake. d) Turbidity Current: Inflowing water entrains sediment from the shelf zone; this increases its density causing flow down the side of the lake. It does not affect stratification. Symbols: $[x]_{IF}$ = concentration of ion x in inflow, $[x]_{LAKES}$ = concentration of ion x in area of lake that interacts with mixing mechanism. Vertical axis of profile indicates depth of lake.

Lake is not stratified under conditions of open water

NO INFLOWING WATER
Shallow water more concentrated than deep water e.g. $O_2$

EFFECT OF INFLOW ON PROFILE
IF $[x]_{IF} < [x]_{LAKES}$ e.g. $Cl^-$

EFFECT OF INFLOW ON PROFILE
IF $[x]_{IF} > [x]_{LAKES}$ e.g. $O_2$
explain the differences with reference to the chemistry of the lake. The discharge rates of
the inflow and outflow of Sombre Lake were approximately equal (Section 4.6.1): it is
possible to consider the relative concentrations of an ion in the inflow and outflow as a
measure of mass-balance in the lake (Section 4.6.8), as utilised by Hawes (1983a). With the
profound seasonality of the inflow and the peculiar aspects of the mixing processes, the
hydraulic residence time for Sombre Lake displays significant variations from its theoretical
value. The short residence times (Figure 5.4) account for the close synchronisation between
changes in the inflow and outflow concentrations at particular times (e.g. Cl*, NH4+). Table
5.5 summarises and classifies the observed differences in the relative concentrations of the
inflow and outflow it is a copy of Table 4.5.

Table 5.4: Residence times for Sombre Lake

<table>
<thead>
<tr>
<th>DATE</th>
<th>STATUS (see Table 5.1)</th>
<th>RESIDENCE TIME (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/01/92 - 16/03/92</td>
<td>Open water, summer flow rate</td>
<td>57</td>
</tr>
<tr>
<td>23/10/92 - 04/12/92</td>
<td>Spring flow, current of low density</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>water flowing under ice</td>
<td></td>
</tr>
<tr>
<td>05/12/92 - 13/01/93</td>
<td>Continuing high flow rates, but ice</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>cover broken</td>
<td></td>
</tr>
<tr>
<td>14/01/93 - 11/02/93</td>
<td>Open water, summer flow rate</td>
<td>55</td>
</tr>
</tbody>
</table>

The ions exhibiting Class 1.1 (pH, Fe2+, K+) and Class 1.3 (Alkalinity, Mg2+) behaviour
showed no difference in concentration between the inflow and outflow of Sombre Lake.
These ions were unaffected by the presence of the lake and their concentrations in the
inflow, lake and outflow were similar, within experimental error.
Table 5.5: This is a copy of Table 4.5. It classifies the trends observed in Sombre Lake inflow and outflow (Streams K2, L). Symbols: IF = inflow trend, OF = outflow trend, LV = trend observed in Limestone Valley (see Table 4.3), [IF] = concentration of inflow waters. Operators: = similar, <> dissimilar, > greater than.

<table>
<thead>
<tr>
<th>CLASS</th>
<th>CONCENTRATION</th>
<th>TEMPORAL</th>
<th>Ions / COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREND</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>[IF]=[OF]</td>
<td>IF=LV OF=IF</td>
<td>pH, K⁺, Fe²⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IF=LV OF&lt;&gt;IF</td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td>1.3</td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
<td>Alkalinity, Mg²⁺</td>
</tr>
<tr>
<td></td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td></td>
<td>IF&lt;&gt;LV OF=LV</td>
<td></td>
<td>ILLOGICAL</td>
</tr>
<tr>
<td>2.1</td>
<td>[IF]&gt;[OF]</td>
<td>IF=LV OF=IF</td>
<td>Na⁺, Cl⁻</td>
</tr>
<tr>
<td>2.2</td>
<td></td>
<td>IF=LV OF&lt;&gt;IF</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
<td>DRSi</td>
</tr>
<tr>
<td>2.4</td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>IF&lt;&gt;LV OF=LV</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>[IF]&lt;[OF]</td>
<td>IF=LV OF=IF</td>
<td>NO₂⁻, NO₃⁻, o-P</td>
</tr>
<tr>
<td>3.2</td>
<td></td>
<td>IF=LV OF&lt;&gt;IF</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td>IF&lt;&gt;LV OF=IF</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td></td>
<td>IF&lt;&gt;LV OF&lt;&gt;IF</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td>IF&lt;&gt;LV OF=LV</td>
<td>Mn²⁺</td>
</tr>
</tbody>
</table>

141
During the initial melt pulse, the concentration of sodium and chloride in the outflowing waters was lower than in the inflowing waters, which is the definition of Class 2.1 behaviour (Section 4.6.8). Sodium and chloride are considered to be conservative in aquatic systems (Jenkin et al. 1994) and it is unlikely that they are being consumed in the lake. The most probable explanation of the observed differences is that the concentrated inflowing waters were diluted by mixing with the less concentrated lake waters. This hypothesis is supported by the observations and conclusions made by Schindler et al. (1974) regarding the inflow and outflow of an Arctic lake.

DRSi was the only species exhibiting Class 2.3 behaviour. The temporal trends exhibited in the Sombre Lake system were different to those observed in Limestone Valley (Table 5.5). There was some evidence to suggest that the behaviour of this ion during the 1994 - 1995 summer field season was abnormal when compared to other field data (Section 4.6.8). Nevertheless, there was an observed difference between inflow and outflow concentrations with lower concentrations being observed in the outflowing waters. It could be argued that DRSi concentrations were simply diluted by the waters of Sombre Lake, as for Class 2.1; the observation that the concentration of DRSi in the inflowing and outflowing waters increases with time and in equal amounts would support this argument. However, in Section 5.2.3.4 the mechanism by which DRSi was stripped from the water column was discussed and from the data available, it appeared that DRSi was removed from the water column by adsorption to SPM in the lake.

Calcium belongs to Class 2.4 and was one of only three ions (the others being Mn$^{2+}$ and ammonium) that did not exhibit similar temporal trends in the inflow and outflow; less calcium was detected in the outflow (Table 5.5). Calcium is an important element for
biological processes (Nihlgård et al. 1994) and may be utilised by the biological processes occurring in the lake, the rate of which increase during the austral spring. It is also a co-precipitant with iron oxyhydroxides and in temperate systems has been demonstrated to be a key component of endogenic particulates (e.g. Buffle et al. 1989). These two processes probably consume a fraction of the inflowing calcium supplied to the lake, leading to the observed behaviour.

Ortho-phosphate, nitrite and nitrate belong to Class 3.1. In this class, the temporal behaviour of these ions is similar to that observed in Limestone Valley, but the concentrations determined in the outflow are greater than those determined in the inflow.

Ortho-phosphate concentrations in the lake were elevated throughout the water column during the winter period, due to redox processes occurring in the sediments. At the onset of inflow ortho-phosphate was removed from solution (Section 5.2.2.5), probably by adsorption to the oxidation products of Fe$^{2+}$ and the growth of phytoplankton. Ortho-phosphate, regenerated from the sediments during winter but not consumed by either of these two mechanisms, would be lost to the outflow during the early spring. This would increase the concentrations of this ion in the outflow relative to the inflow. It was observed that ortho-phosphate was released to the streams as a pulse related to the thawing of the basal ice layer (Section 4.5.8) and this pulse is evident in the data for the inflow and outflow of Sombre Lake (Figure 4.10c), but the peak in the outflow data was much greater than in the inflow. The lake could receive soil waters from the whole of its catchment, a larger area than available to the inflow stream, and the ortho-phosphate thus supplied would increase the concentration in the outflow stream. Unfortunately, Sombre Lake was not profiled at a temporal resolution sufficient to detect this effect.
In a similar manner to ortho-phosphate, nitrite and nitrate concentrations were elevated during the winter period and decreased rapidly at the onset of the inflow (Section 5.2.2.5). Nitrate was later introduced to the whole water column of the lake by the turbidity current mechanism proposed in Section 5.2.4.1; simultaneously nitrite was generated in the bottom waters by reduction of nitrate. The temporal trends observed in the concentrations of nitrite and nitrate in the outflow (Figure 4.13) suggest a diminishing source of these ions. This is compatible with the flushing of these ions from the lake and could occur through displacement of bottom water by the inflowing density plumes (Section 5.2.4.1).

Ammonium exhibited Class 3.2 behaviour and in common with calcium, did not exhibit similar temporal trends in the inflow and outflow (Section 4.6.8). It appears that although ammonium was not supplied to Sombre Lake, except during the initial melt pulse, ammonium was detected at the outflow until the loss of ice cover. Elevated ammonium concentrations were observed in the lake water column during the winter period, but upon the introduction of oxygen to the water column, concentrations decreased rapidly (Section 5.2.2.5): the only detectable concentrations in the lake water column after re-oxygenation were in the bottom 3m. The temporal variation of ammonium concentrations in the outflow suggests, as for nitrite and nitrate, a diminishing source of this ion and that the residual winter waters were flushed from the lake.

The behaviour of nitrite and nitrate (Class 3.1) and ammonium (Class 3.2) are consistent with the loss of inorganic nitrogen from Sombre Lake as observed by Hawes (1983b). Canfield and Green (1985) noted the egress of nutrients regenerated during the winter from Bull Lake (Dry Valleys, continental Antarctica). Other references to this lake are scarce and a detailed comparison with Sombre Lake is not possible. The flushing of these ions from the
more concentrated waters at the bottom of the lake is further evidence for the action of the turbidity current described in Section 5.2.4.1.

Based on the argument presented in Section 4.6.8, Mn\(^{2+}\) was placed in Class 3.5. The mid-season peak in the outflowing concentrations of Mn\(^{2+}\) was observed, this was coincident with the ortho-phosphate pulse. No Mn\(^{2+}\) was detected in inflow (Figure 4.13a). These observations are consistent with the theory discussed in Section 4.5.8 that Mn\(^{2+}\) and orthophosphate are released to the freshwater systems as a pulse associated with the thawing of the ice layer at the base of the Signy snowpack (Section 4.5.8). Furthermore, the observation of more Mn\(^{2+}\) in the outflow of Sombre Lake compared to the inflow is consistent with the behaviour of ortho-phosphate in these streams (discussed above). Unfortunately, this does not entirely explain the behaviour of Mn\(^{2+}\).

Fe\(^{2+}\) and Mn\(^{2+}\) were both released from the sediments under ice-cover. The retention of soluble iron released from anoxic sediments is well documented (Davison et al. 1982) and indeed it was not detected in the outflow, Mn\(^{2+}\) generated in a similar manner is normally lost from the lake (Davison et al. 1982; Pontér et al. 1992). As Mn\(^{2+}\) remained in the water column after the precipitation of iron it would be expected to be flushed from the lake, however it was only detected in the outflow in association with the ortho-phosphate peak. Both iron and manganese may have been lost from the lake in particulate form: unfortunately, there are no data available to address this question due to the methodology used to collect particulates (see Section 6.3.3).

5.2.5 SUPER-SATURATION AND PRECIPITATION

The depth-concentration profiles (Figures 5.2 - 5.17) provide information on the
development of bottom water anoxia and the associated release of ions from the sediment. Integration of the profiles to give TWC values (Figures 5.18 - 5.22) demonstrated the effects of ice-exclusion and release from the sediments on the concentration of ions in the whole water body. Increased concentrations may lead to super-saturation with respect to certain mineral phases and this was studied with the computer program SOLMINEQ88 for DOS.

For each depth and date, all the relevant data were examined using the SOLMINEQ88 software according to the documentation supplied: this identified, at each depth and date, the mineral phases which were super-saturated. Equilibrium calculations of this form can only determine whether or not the formation of a precipitate is thermodynamically possible and no inferences can be made regarding the kinetics of the reaction (Stumm and Morgan 1981).

The SOLMINEQ88 program identified that the waters of Sombre Lake were super-saturated with respect to a wide range of mineral phases, but many of these phases only figured on one date and at one depth: results of this nature were not considered relevant. Figure 5.24 is a graphical representation of the data generated by SOLMINEQ88, where super-saturation of the lake waters with respect to a particular phase was predicted for a range of dates and depths.

The water column was super-saturated with respect to manganese oxide (MnO) in August. The TWC data for manganese (Figure 5.20c) exhibited a maximum value in July, after which the TWC decreased rapidly. If the TWC calculated for manganese in July is accurate (Section 5.2.3.4), the precipitation of manganese oxide in August is a potential mechanism
Figure 5.24: Time-depth plot for super-saturation with respect to: S) siderite (FeCO₃), V) vivianite (Fe₃(PO₄)₂), M) manganese oxide (MnO) and F) iron hydroxide (Fe(OH)₃). Super-saturation was predicted for the regions below the lines.
for lowering the high concentrations of manganese.

Ferric hydroxide (Fe(OH)$_3$) was super-saturated throughout the water column for October and November. During October, oxygen was re-introduced to the lake by the inflowing waters (Sections 5.2.2.2, 5.2.3.1 and 5.2.4.1) and the depth-concentration profile for Fe$^{2+}$ (Figure 5.11) suggested that oxidation and precipitation of this ion had occurred throughout the water column at this time. This occurs via the formation of iron hydroxide (Fe(OH)$_3$) primary particles (Von Gunten and Schneider 1991): the calculations of SOLMINEQ88 and the field observations appear to be consistent in this case. This process also accounts for the falling concentrations of ortho-phosphate at this time (see Chapter 7).

Vivianite (Fe$_3$(PO$_4$)$_2$) and siderite (FeCO$_3$) were super-saturated over a similar period (June - December) and although the spatial resolution of these two phases is different (Figure 5.24), precipitation of both phases could occur simultaneously in the same region. Although vivianite is thermodynamically more stable than siderite, kinetics will control which mineral may precipitate.

Whilst Gallagher (1985) presented evidence for the formation of siderite (FeCO$_3$) in the bottom waters of Sombre Lake and also predicted the precipitation of vivianite (J.B. Gallagher unpublished data), the only documented examples in lacustrine systems are in the sediments (e.g. Cornwell 1983; Davison 1982). The TWC data clearly shows the precipitation of iron at the end of the winter, however during the period when vivianite and siderite formation are predicted the data are inconclusive. To confirm whether the mineral phases discussed in this section do precipitate it is necessary to examine the SPM from Sombre Lake. These data and observations are presented in Chapter 6.
5.3 SUMMARY

The water column of Sombre Lake was sampled on a monthly basis. The samples were analysed in order to identify the chemical processes occurring in the lake. Additionally, field observations were made of various physical parameters, these were important in understanding the soluble chemistry of the lake and will be relevant to the particulate chemistry which is examined in the following chapters. The main conclusions and findings of this chapter can be summarised:

1. Sombre Lake is subject to a highly seasonal regime, with stratification and bottom water anoxia developing under ice cover.

2. Reduction of iron and manganese compounds occurs in the sediments. The reduced species and associated adsorbed ions are released to the overlying water column.

3. The depth-concentration profiles were integrated to give values for the whole lake (total water-body concentration, TWC). The TWC values for the conservative ions were consistent with the values predicted by the ice-exclusion model of Barica (1977).

4. The depth-concentration profiles and TWC data suggest that the cycles of nitrate, nitrite and ammonium were related and much of the ammonium produced could be accounted for by nitrate reduction. The loss of ammonium from the water column is not linked to the oxidation and precipitation of iron. The data suggest that there may be a link between Mn$^{2+}$ ions and the oxidation of ammonium and nitrite ions to nitrate at the redox boundary.
5. The depth-concentration profiles of Sombre Lake suggest that oxygen was transported deep into the lake prior to the loss of ice cover and the onset of wind mixing. A turbidity current is believed to be the cause.

6. Fe\(^{2+}\) ions diffused a long way up the water column and appear to have been oxidised and precipitated at the end of the winter at the onset of the inflow. This was consistent with solubility calculations. Ortho-phosphate ions, which were also released from the sediment, appeared to be precipitated simultaneously with iron.

7. The loss of DRSi was linked to the oxidation of Fe\(^{2+}\) and adsorption to the surface of SPM.

8. Sombre Lake appears to lose inorganic nitrogen during the flushing of the winter water. Significant quantities of ortho-phosphate were supplied to the lake by ground thaw but were rapidly flushed from the lake.

9. The precipitation of iron hydroxide, manganese oxide, siderite and vivianite were predicted. This will be re-examined with respect to the particulate data in Chapters 6 and 7.
CHAPTER 6: SUSPENDED PARTICULATES FROM SOMBRE LAKE

6.1 INTRODUCTION

Dissolved ions and suspended particulate matter (SPM) are transported by streams from the fellside to the lake. The general dynamics of the stream environment on Signy Island were presented in Chapter 4 and the soluble chemistry of Sombre Lake was discussed in Chapter 5: SPM in Sombre Lake was found to play an important role in regulating the concentrations of some dissolved ions. The SPM will be discussed in detail in this chapter.

In the lake environment, particles may undergo chemical change and either be incorporated into the sediments or flushed from the lake. Temporal and spatial studies of both allogenic and endogenic suspended particulates in lakes can provide detailed insights into the mechanisms that control the chemistry and trophic status of a lake.

There have been extensive studies of suspended particulates from temperate lakes concentrating on various aspects of the subject. Suspended particulates of endogenic or allogenic origin (e.g. Stabel 1985) act as a vehicle for the regulation of trace elements (e.g. Sigg 1994) and can aid understanding of biogeochemical cycling (e.g. Sholkovitz and Copland 1982a; Hamilton-Taylor et al. 1984; Buffle et al. 1989). There have been few studies of the horizontal variations of SPM in lakes or the general dynamics of allogenic material (Bloesch and Uehlinger 1986). Studies of SPM in Sombre Lake are facilitated by the small biological component of polar systems (Heywood 1977) and the absence of
planktonic diatoms (Jones and Juggins 1995).

Green et al. (1993) have carried out the most extensive study of suspended particulates in Antarctic lakes, concentrating on meromictic Lake Vanda in the Dry Valleys (Figure 1.1) where sediment traps were deployed for one year. This duration was necessary to collect sufficient material for analysis as sedimentation rates are low compared to temperate systems (Green et al. 1993). Their work concentrated on the transport of trace metals and although it provided valuable spatial information, there was no temporal component to their work.

The only studies of SPM from maritime Antarctic lakes have concentrated on aspects of nutrient cycling (Gallagher 1985; Ellis-Evans and Lemon 1989). This aspect of SPM from Sombre Lake will be examined briefly in this chapter and in detail in Chapter 7.

A three-dimensional array of sediment traps was deployed in Sombre Lake at the positions described in Section 2.1.1 (Figure 2.3). The material collected in the traps was analysed to identify the source of the major particulate input to Sombre Lake, investigate the influence of the transition from stream to lake on the chemistry of particulates and to determine the fate of the particles in the lake environment.

6.2 MATERIALS AND METHODS

Sediment traps were deployed at a total of ten sites in Sombre Lake, of which only three sites were used for the full period of the field study (Section 2.1.1). The data presented in this chapter are from these three traps and are representative of the trends exhibited by the other traps. The data from the seven remaining traps can be found in Appendices A and C. I
am grateful to the work of Mr. M. Smithers (British Antarctic Survey) and Mr. M.O. Chalmers (British Antarctic Survey) who were responsible for the deployment and maintenance of the sediment traps for the period December 1991 - January 1992.

The quantities of material trapped at each site were low (typically < 8.5mg), and so the samples were not suitable for analysis by either acid digestion (e.g. Hamilton-Taylor et al. 1984) or sequential extraction (e.g. Tessier et al. 1979; Green et al. 1993). Sholkovitz and Copland (1982b) successfully used X-ray fluorescence (XRF) to analyse small samples of SPM deposited on Nucleopore filters but this technique can not be used to examine specific particles. Therefore the X-ray microanalysis system (EDX) of a scanning electron microscope (SEM) was used to provide compositional data (Section 3.6.2.2), the value of which has been demonstrated by Mudroch (1984).

The samples were also too small for accurate grain size determinations using laser diffraction (P. Noon, University College of London pers. comm.). An attempt was made to develop a method of size analysis using image analysis but the reproducibility of this technique was very variable and large errors resulted. Consequently no size data are presented here. This is recognised as a limitation in carrying out a full interpretation of the results, but does not affect the validity of the overall conclusions.

6.3 RESULTS AND DISCUSSION

6.3.1 RATE OF TRAPPING

The rate of trapping (Figure 6.1) displays a clearly defined winter minima (circa 14/05/92 to 10/11/92). An increase in the rate was observed in the inflow traps after the inflow stream started (23/10/92) and also at the end of the 1991 austral winter (Figure 6.1a). The rate of
Figure 6.1: Rate of trapping a) upper and lower pots in the first inflow trap, b) 8m trap at deep spot, c) outflow. Errors are the standard error in the mean (n=2). Note the differences in the scale of (a) versus (b) and (c).
trapping in the inflow traps did not increase immediately after the onset of inflow because
the melt water was initially flowing over ice (Section 4.6.1) and hence little particulate
material was available for transportation.

Data for the upper and lower inflow traps (Figure 6.1a) followed similar trends, confirming
that the traps were unaffected by turbulence. This was also true of the three traps deployed
at the deep spot (see Appendix A).

Larger particulates were recovered from stream water samples obtained during the spring
thaw and Figure 6.2 compares the hydrograph of the Sombre main inflow with the rates of
trapping at the inflow. The peak rate of trapping coincided with the peak of the hydrograph.
This is consistent with observations made in Chapter 4 and the work of Chambers (1978).

The sampling regime employed in the 1991 - 1992 summer missed the peak discharge of
Sombre inflow (Section 4.6.1); from the trapping data shown in Figure 6.1a it would have
been predicted between 18/12/91 and 07/01/92.

On two occasions (26/11/92 and 16/12/92), the rate of trapping systematically decreased
with depth and distance from the inflow (Figures 6.2, 6.3), which is consistent with the
observations of Green et al. (1993): this occurred when the stream discharge was at a
maximum. In Figure 6.3 the rates of trapping are plotted against the logarithm of distance
from the inflow; extrapolation of the data indicates that most SPM sedimented within 33m
of the inflow, even when stream discharge was maximal. The peak rate of trapping at the
deep spot and outflow were coincident (Figures 6.1b, c) and occurred after the appearance
of open water. At the deep spot the peak rate of trapping for the 1991 - 1992 summer
Figure 6.2: Comparison of the rate of trapping of the inflow traps and the hydrograph for the main inflow to Sombre Lake. Errors are the standard error in the mean (n=2 for traps, n=3 for discharge data).
Figure 6.3: Rates of trapping for the inflow traps plotted against the logarithm of the distance from the point of inflow a) 26/11/92 b) 30/11/92.
occurred between 13/02/92 and 24/03/92 (inclusive) and covers three samples. Mean rates of trapping at each site (inflow, deep spot and outflow) were calculated for these dates (Table 6.1) and were analysed with a t-test which suggested no significant differences between rates (P=0.2). These data indicate that, after the spring pulse, the overall rate of trapping throughout the lake was similar, although this is not clear from Figure 6.1 due to the differences in scale employed. Green et al. (1993) reported decreasing rates of trapping in Lake Vanda with increasing distance from the inflow, but as Lake Vanda is permanently ice covered, there are no equivalent observations for a period of open water.

Table 6.1: Mean rate of trapping at each site for period of maximum rate of trapping at the deep spot.

<table>
<thead>
<tr>
<th>TRAP</th>
<th>MEAN RATE OF TRAPPING (mg m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(13/02/92 - 24/03/92)</td>
</tr>
<tr>
<td>INFLOW</td>
<td>333 ± 36</td>
</tr>
<tr>
<td>DEEP SPOT</td>
<td>364 ± 25</td>
</tr>
<tr>
<td>OUTFLOW</td>
<td>300 ± 33</td>
</tr>
</tbody>
</table>

The bulk of the material transported to the lake sedimented within 33m of the inflow; this fact, when associated with the mean rate data (Table 6.1), suggests that the material trapped at the deep spot during the period of open water was maintained in suspension by wind generated currents (Section 2.1.1). Additional evidence to support this hypothesis is that the peak rate of trapping at the deep spot only occurred after the disappearance of ice cover. Corroboration of this hypothesis was not possible with the 1992 - 1993 summer data because the ice cover was lost much earlier and the inflow, deep spot and outflow peaks
overlapped. The SPM, maintained in suspension and recovered from the deep spot during open water, has two possible sources a) material transported by the inflow stream b) material re-suspended from the lake bottom or c) SPM generated within the lake. It is not possible from the data presented here to differentiate between these three mechanisms.

During open water (05/02/92 - 22/03/92 and 22/12/92 - end of data), the rate of trapping at the deep spot displayed no systematic variation with depth (Figure 6.4), suggesting that the lake was subject to "continuous complete mixing" (Hilton et al. 1986) and that resuspension of sediments was not significant (Bloesch 1995). This conclusion is supported by studies of the depth profiles of physical and chemical variables within the lake (Chapter 5). Ice cover prevented wind-mixing, allowing the formation of a stable water column; consequently some systematic variation of the rate of trapping with depth was observed. During the period 26/10/92 - 26/11/92 (see inset to Figure 6.4), the deeper traps caught systematically more material ($r^2 > 0.66$, $P=0.05$, $n=6$), but on 30/11/92 more material was recovered from the shallower traps ($r^2 > 0.66$, $P=0.05$, $n=6$). No depth dependency was exhibited by the rate of trapping ($r^2 < 0.40$) on all other dates when ice was present. The observation that the deeper traps caught more material between 26/10/92 and 26/11/92 is consistent with both the turbidity current described in Section 5.2.4.1 and the formation of particulate iron during this period (Section 6.3.2).

Following the formation of ice on the lake, a significantly ($P=0.01$) increased rate of trapping was observed in the outflow trap (Figure 6.1c) on 03/04/92 and similar peaks, although not as clearly defined, occurred in the inflow and 8m deep spot traps. The rates of trapping in the inflow and deep spot traps were decreasing at this time and it was not
Figure 6.4: Bar chart of the rate of trapping at the deep spot. Prior to 12/08/92 a single trap was deployed (at 8m) and no depth dependency of rates can be inferred. Inset graph displays rate of trapping plotted against depth for 27/10/92, 10/11/92 and 26/11/92. Errors are the standard error in the mean (n=2). Ice cover and stream data are displayed to aid interpretation as the acetate template (Figure 5.1) does not apply to this scale.
possible to test the statistical significance of these peaks. A similar increased rate of trapping was also observed at the deep spot of nearby, oligotrophic Moss Lake (Figures 2.2, 2.4) after the formation of ice cover (see Appendix B).

An increased rate of trapping was observed in the inflow traps on 02/08/92 (Figure 6.1a), and this was found to be statistically significant (ANOVA, P=0.01). It could be argued that there were corresponding peaks in the 8m deep spot and outflow traps (Figures 6.1b, c), but these could not be statistically separated from background variation (P=0.1).

6.3.2 INORGANIC AND ORGANIC CONTENT OF SPM

Data for the rate of trapping of carbon (0 - 75%), nitrogen (0 - 13%) and residual (4 - 100%) fractions from selected traps are presented (Figure 6.5).

Throughout the lake the SPM was dominated by the "residual" i.e. inorganic fraction (see Section 3.6.1) and this confirms that the major particulate input to Sombre Lake was inorganic. Comparison with total rate of trapping data (compare Figures 6.1, 6.5) reveals the same general trends throughout. This further supports the interpretation of the "residual" fraction as the inorganic component.

The inorganic fraction in the deep spot traps decreased after the cessation of the inflow, but did not reach a minimum until 11/10/92 (Figure 6.6). Simultaneous minima occurred in both the inflow and outflow traps, but were not as clearly defined. After the formation of ice cover and the cessation of the inflow there was no particulate input to Sombre Lake. During the winter, the material trapped can arise from one of three sources: sedimentation of material already suspended in the water column, sedimentation of endogenic particles
Figure 6.5: Rate of trapping of carbon and nitrogen, a) inflow trap, b) deep spot trap, c) outflow trap. Solid bars below date axis indicate N, whilst open bars above the date axis indicate C. Solid bars above date axis indicate "residual" i.e. inorganic fraction.
Figure 6.6: Percentage inorganic content of a) 8m deep spot b) inflow trap.
formed in the water column and material re-suspended by density currents. Consequently the amount of inorganic SPM in the water column decreased as winter proceeded (Figures 6.5, 6.6) and reached a minimum value on 11/10/92. All the deep spot traps reached a minimum value on the same date. Simultaneous minima occurred in both the inflow and outflow traps, but were not as clearly defined. Biological activity is significantly reduced in the winter and it is possible that decaying organic matter from dead organisms can be collected in the sediment traps. This feature, along with the observation that inorganic SPM is not supplied to the lake but is sedimented through the winter, accounts for the decreasing fraction of trapped inorganic material and the concomitant increase in the organic fraction (Figure 6.6).

After 27/10/92 the inorganic fraction at the deep spot began to increase: this could have been due to allogenic material transported to the lake by the inflow which started on 23/10/92. However, no allogenic material was observed in the inflow traps until 10/11/92 (Figures 6.1a, 6.6b). The only explanations for these observations is that the SPM trapped at the deep spot between 27/10/92 and 10/11/92 was derived from endogenic processes occurring in the water column of Sombre Lake or was material transported by the turbidity current (Section 5.2.4.1).

The filters from this period (27/10/92 - 10/11/92) were examined with a SEM. It was found that the sedimented material consisted of large numbers of aggregated inorganic particles of a distinct size range and morphology. Further examination of these aggregates is reported in Chapter 7.
6.3.3 ELEMENTAL COMPOSITION OF SPM

The EDX detector used could not detect elements lighter than sodium and it would be of little use to examine particles with a major organic component. The data from the carbon and nitrogen analyses of the particulate material (Section 6.3.2) suggest that the major particulate input to Sombre Lake is inorganic, thus analysis by EDX is a valid technique.

The semi-quantitative EDX method (Section 3.6.2.2) can not give absolute figures for the percentage composition. In this method, the ratio between integrated X-ray counts for individual elements and the integrated X-ray counts of aluminium was calculated:

\[ F(E) = \frac{\Sigma \text{X-ray counts for } E}{\Sigma \text{X-ray counts for Al}} \]

where \( E \) = an element of interest and \( F(E) \) = EDX fraction of \( E \) in sample

Aluminium was chosen as it is the reference element in other studies (Sholkovitz and Copland 1982a) and is not involved in biological cycles (Stabel 1985). The data presented are the mean ratios of five areas selected at random on each filter.

The EDX results are not absolute values for composition and this makes the identification of changes in composition difficult to interpret. Therefore, in order to exaggerate changes of the composition of the SPM in the lake with respect to SPM in the stream, the EDX fraction for an element in SPM from the lake has been normalised against the EDX fraction of the element in SPM from the stream. There are two potential methods for this.
1. After Sholkovitz and Copland (1982a):

\[ E_{\text{norm}} = F_{\text{lake}}(E) - F_{\text{stream}}(E) \]

2. After Martin and Meybeck (1979):

\[ E_{\text{norm}} = \frac{F_{\text{lake}}(E)}{F_{\text{stream}}(E)} \]

where: \( E_{\text{norm}} \) is the fraction of \( E \) in the SPM from the lake normalised against the fraction of \( E \) in the SPM from the stream

Both methods have individual merits. Method 1 was ultimately used to normalise the EDX data as it caused less distortion of the temporal and spatial trends in the data and was considered more likely to show up subtle differences between the reference material and the lake SPM. The potential problem associated with Method 1 (Sholkovitz and Copland 1982a) is that the difference between two large numbers may be small compared to the errors in the original figures; to reduce possible misinterpretation of the data statistical methods were applied.

Samples of SPM obtained from Sombre Lake inflow stream during the period of peak discharge and sediment from the stream bed were analysed using EDX to determine the composition of SPM being transported to Sombre Lake (Table 6.2). The samples of material from the inflow stream were sieved to separate the \(<125\mu m\) fraction, which was then analysed using EDX. These data will be discussed later with temporal and spatial changes in the composition of SPM from Sombre Lake. Material recovered from the sediment traps was not size fractionated (Section 6.2), consequently it was considered...
Table 6.2: Elemental composition of source material as determined by EDX. These figures are ratios and are without units.

1 Unpublished data of I. Johnson determined by acid digestion and AAS. The ratio of the concentration of elements to the concentration of Al was calculated. n.d. = not determined.  
2 Al/Al=1.00 by definition.

Sombre inflow n=8 (3 samples from water samples, 5 from stream bed),  
Sombre inflow 125 μm fraction n=5 (5 samples from stream bed, wet sieved)  
Limestone Valley (Stream A, Chapter 4) n=5 (3 from water samples, 2 from stream bed)  
Johnson ratio n=5 (Samples taken from Jane Col).

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SOMBRE INFLOW</th>
<th>SOMBRE 125μm</th>
<th>LIMESTONE VALLEY</th>
<th>JOHNSON RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.05±0.00</td>
<td>0.14±0.01</td>
<td>0.05±0.00</td>
<td>0.08±0.04</td>
</tr>
<tr>
<td>Mg</td>
<td>0.27±0.04</td>
<td>0.44±0.01</td>
<td>0.36±0.02</td>
<td>0.28±0.03</td>
</tr>
<tr>
<td>Al</td>
<td>1.00±0.182</td>
<td>1.00±0.032</td>
<td>1.00±0.052</td>
<td>1.00±0.002</td>
</tr>
<tr>
<td>Si</td>
<td>2.74±0.35</td>
<td>4.01±0.11</td>
<td>2.60±0.14</td>
<td>6.31±0.31</td>
</tr>
<tr>
<td>P</td>
<td>0.05±0.01</td>
<td>0.13±0.01</td>
<td>0.05±0.01</td>
<td>n.d.</td>
</tr>
<tr>
<td>K</td>
<td>0.35±0.09</td>
<td>0.44±0.02</td>
<td>0.40±0.02</td>
<td>0.16±0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>0.22±0.04</td>
<td>0.36±0.01</td>
<td>0.29±0.02</td>
<td>0.32±0.04</td>
</tr>
<tr>
<td>Ti</td>
<td>0.12±0.02</td>
<td>0.22±0.01</td>
<td>0.12±0.01</td>
<td>0.13±0.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.04±0.01</td>
<td>0.15±0.02</td>
<td>0.05±0.01</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mn</td>
<td>0.07±0.01</td>
<td>0.13±0.02</td>
<td>0.06±0.01</td>
<td>0.01±0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>0.52±0.06</td>
<td>0.73±0.01</td>
<td>0.56±0.03</td>
<td>0.58±0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05±0.01</td>
<td>0.14±0.01</td>
<td>0.06±0.01</td>
<td>n.d.</td>
</tr>
</tbody>
</table>
inappropriate to examine any other fractions of stream material. EDX was also used to assess the composition of SPM from the stream system of Limestone Valley during the early part of the 1994 - 1995 summer for comparison (Table 6.2). Data for chemical analyses of particulates from fellfield sites of Signy Island (I. Johnson unpublished data) are included in Table 6.2. These data were obtained by the classical methods of acid digestion followed by AAS/AES and measure total element contents. A t-test comparison of these data revealed no significant differences (P=0.1), except the result for silicon. This evidence supports the semi-quantitative use of the EDX for these analyses and furthermore the results obtained were directly comparable with a classical quantitative technique.

There were no significant differences (t-test, P=0.1) between samples taken from the two streams nor from the potential source of the particulates in both streams (Johnson's data) and this suggests that no detectable chemical changes occur in the stream environment. The weathered material overlying the bedrock of Signy Island consists of undifferentiated glacial till (Matthews and Maling 1967) and so direct comparison with whole rock analyses of Storey and Meneilly (1985) is not possible. Hall (1986, 1990) concluded that the principal mode of weathering on Signy Island was by freeze-thaw and that chemical weathering was not well advanced. Therefore, individual particles are likely to have a similar composition to the rock from which they were derived.

The particulate material recovered from the sediment traps was analysed using the EDX method outlined in Section 3.6.2.2. Figures 6.7 to 6.9 display the normalised composition data (E_{norm}) for material collected from the three traps deployed for the whole study. The elements have been grouped on the basis of chemical similarities: Groups I and II (Na, K, Mg, Ca), redox sensitive and co-precipitant elements (Mn, Fe, Cu, P) and weathering
indicators (Ti, Cr). EDX data for the other seven traps deployed in Sombre Lake can be found in Appendix C.

During the period of peak input, the material trapped in the inflow traps would be expected to closely resemble the SPM of the inflow stream and $E_{\text{norm}}$ should be approximately zero. At the time of peak input (26/11/92 - 07/01/92) values of $E_{\text{norm}}$ were between 0 and 0.2 (Figure 6.7). The data presented in Table 6.2 were derived from the analysis of a number of samples (see caption of Table 6.2 for details) of particulate material from the fellfield. These were a small sample of all the particles in the Signy fellfield: if all the particles on the fellfield were examined it would be expected that there would be some variation from the mean values presented in Table 6.2. This variation is responsible for the 0 - 0.2 spread of the values of $E_{\text{norm}}$. Therefore, only deviations greater than 0.2 units from zero should be considered indicative of a change in composition of the lake SPM relative to the that of the stream. In general, deviations of $E_{\text{norm}}$ from zero were positive, except in the case of silicon for which both positive and negative deviations were observed (see Figures 6.7 - 6.9).

Silicon was the only element to exhibit negative values for its relative composition, indicating that there was less silicon in the lake SPM than in the stream SPM. The data for silicon reaches its most negative value on the same date as the inorganic fraction reached its minimum value (11/10/92, Section 6.3.2). Whether found in a particle derived from rocks or created by biological activity (e.g. diatom frustules), silica will form part of the inorganic fraction of a sample. However, there are few planktonic diatoms in the waters of Sombre Lake (Jones and Juggins 1995); the EDX fraction of silicon in the SPM can be attributed mainly to non-biogenic material.
Figure 6.7: EDX data for the shallow trap deployed at the first inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1. Error bars are the standard error in the mean (n=5).
Figure 6.8: EDX data for the 8m deep spot trap. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1. Error bars are the standard error in the mean (n=5).
Figure 6.9: EDX data for the outflow trap. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1. Error bars are the standard error in the mean (n=5).
Analyses of the EDX data for the six traps deployed at the inflow revealed no significant variation of composition with respect to position or depth (ANOVA, P=0.1). Gross chemical changes of the matrix of the particulates would not be expected, but due to changes in the pH or ionic strength, the desorption of ions from the surfaces of SPM might be anticipated (Gadde and Laitinen 1974). The traps were deployed in the lake for periods of at least ten days and it would be reasonable to expect them to reach equilibrium in that time; it is unlikely that a compositional gradient would exist across the array of traps. Furthermore, the fraction of adsorbed ions on a particle would be small compared to the total material in the particle matrix and changes in the adsorbed ions would probably be undetectable with the EDX. As there were no significant changes in composition throughout the array of inflow traps, it was considered acceptable to combine all the data for comparison with material collected in deep spot and outflow traps. This does not contradict the work of Green et al. (1993) who deployed sediment traps for a year in Lake Vanda and observed a spatial variation in adsorbed cations. In contrast to maritime Antarctic lakes, Lake Vanda is permanently stratified and the traps, deployed at different depths, experienced different conditions of pH and salinity; this promoted different equilibrium positions and a detectable variation between traps.

In general, the composition of material recovered from the deep spot trap was independent of depth and this was consistent with the observation that Sombre Lake was subject to continuous complete mixing. During the period 26/10/92 to 30/11/92, when the rate of trapping increased with depth (Figure 6.4), some of the elements displayed significant trends with depth (Fe, P, Mn, Na, Ca). In addition, the fraction of iron, phosphorus, and manganese in the SPM from the deep spot increased at this time, indicating that material of a composition different to that of the inflow was formed in the vicinity of the deep spot. The
samples collected during this period were analysed in more detail and the results are presented in Chapter 7.

Although composition showed little variation with respect to depth, there were considerable variations with position in the lake and these also displayed a temporal element. The EDX data were normalised against the SPM from the inflow stream and considerations of spatial variation were restricted to differences from the reference material. The range of values (0 - 0.2) observed for $E_{\text{norm}}$ during the period of peak input were discussed above and it was concluded that only values of $E_{\text{norm}}$ greater than 0.2 were indicative of a difference between lake SPM and stream SPM. A t-test ($P=0.01$) was used to compare the data for each sample against the condition $E_{\text{norm}}= 0.2$, the results of these analyses are summarised in Table 6.3.

Table 6.3: t-test comparison of EDX results against the condition $E_{\text{norm}}= 0.2$. IF = inflow traps, DS = deep spot traps, OF = outflow trap, stream SPM = source material (Table 6.2). Operators; = similar, <> not similar.

<table>
<thead>
<tr>
<th>DATES</th>
<th>OBSERVATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>18/12/91 - 17/05/92 (excluding 03/04/92)</td>
<td>IF = stream SPM</td>
</tr>
<tr>
<td>28/01/92 - 10/04/92 (excluding 03/04/92)</td>
<td>DS = stream SPM</td>
</tr>
<tr>
<td>05/06/92 - 26/10/92 (excluding 01/08/92)</td>
<td>IF &lt;&gt; stream SPM</td>
</tr>
<tr>
<td>30/04/92 - 14/12/92</td>
<td>DS &lt;&gt; stream SPM</td>
</tr>
<tr>
<td>10/11/92 - 26/02/93</td>
<td>IF = stream SPM</td>
</tr>
<tr>
<td>07/01/93 - 26/02/93</td>
<td>DS = stream SPM</td>
</tr>
<tr>
<td>18/12/91 - 26/11/92</td>
<td>OF &lt;&gt; stream SPM</td>
</tr>
<tr>
<td>16/12/92 - 26/02/93</td>
<td>OF = stream SPM</td>
</tr>
</tbody>
</table>
Comparison of the contents of Table 6.3 with Table 5.1 leads to the following conclusions:

1. During streamflow the material trapped at the inflow always resembled the SPM of the stream, except immediately after the formation of ice cover.

2. During open water the material trapped at the deep spot was similar to the SPM of the stream.

3. In general, under ice cover and in the absence of streamflow, neither the inflow nor deep spot material resembled the SPM of the stream.

4. The outflow trap did not present simple behaviour. Whilst still under ice cover at the end of the 1992 winter, but with the streams flowing, the material trapped at the outflow resembled the SPM from the stream.

Conclusion 1 would be expected and requires no further explanation. However, Conclusion 2 appears to contradict the observation made in Section 6.3.1 that all material would be predicted to sediment within 33m of the inflow (the deep spot is 60m from the inflow). However, this applied to ice-covered conditions whereas conclusion 2 applies to conditions of open water, when the waters of Sombre Lake are entirely wind-mixed and particles from the inflow could be maintained in suspension by energetically stronger, mixing currents.

The formation of ice cover prevents wind-mixing of the lake waters (Chapter 5) allowing the sedimentation of particles, previously maintained in suspension by wind action.

Following the formation of ice cover on Sombre Lake (22/03/92), a peak of sedimentation was observed on 03/04/92 (Section 6.3.1): the EDX data for the inflow trap (Figure 6.7) displayed a distinct peak at this time which was attributed to inorganic material (Figure 6.5).
A similar peak was present in the data for the deep spot (Figure 6.8), but at the outflow no peak was observed. Analysis of the data at this time suggests that the composition of material in the inflow and deep spot traps was similar (t-test, \( P=0.01 \)) but different to the SPM of the stream (Table 6.3). Considering the preceding discussion of wind mixing, the only plausible explanation of these observations is that the formation of ice cover allows the sedimentation of particles maintained in suspension by wind action. Particles which remain in suspension are those that sediment most slowly under the prevailing conditions. Several factors affect the rate of sedimentation including: size, shape and density. It is known that smaller or less dense particles will settle more slowly, whereas the effects of shape are less predictable (Moore 1972). The EDX analysis of the 125\( \mu \)m sample from the stream bed (Table 6.2) suggested that smaller particles in the stream SPM exhibited higher values of \( E_{\text{norm}} \) than the full range of particle sizes. In summary, a sedimentation event, which contained a larger proportion of smaller particles, would create a peak in the EDX data: such a peak was observed, supporting the wind mixing theory.

In the absence of streamflow under ice, the sedimenting material was different to the SPM of the stream (Conclusion 3). Following a similar argument to that above, the material sedimenting under ice will consist of smaller particles than if the inflow were flowing. The data from Table 6.2 predicts that this material would exhibit higher values of \( E_{\text{norm}} \). The larger particles of SPM would sediment from the water column first and as winter developed, the SPM would consist of progressively smaller particles: the value of \( E_{\text{norm}} \) would be predicted to increase and this is in agreement with the data presented (Figures 6.7-6.9).

Conclusion 4 suggests that whilst there was a current of water flowing beneath the ice,
particles from the stream were transported to the outflow sediment trap without assistance from wind mixing. For the period 30/11/92 - 16/12/92, similarities were observed in the composition of material recovered from the 5m trap at the deep spot and that from the inflow and outflow traps (ANOVA, P=0.05). The predominant elements (Na, K, Mg, Ca, Si, Ti, Fe) of the rock-forming minerals on Signy Island (Storey and Meneilly 1985) were found in similar concentrations in all the sediment traps. Relatively higher concentrations of trace elements (P, Mn, Cu) were observed at the deep spot and will be discussed in Chapter 7. These data suggest, that in common with the observations of Bergmann and Welch (1985), some of the smaller particles carried to the lake during this period were flushed straight through the lake: the particles with the largest surface areas which are more likely to be involved in sorption and desorption reactions (Hart 1982; Sigg 1994) do not sediment in the lake. Kufel (1991) has presented data that suggest that the highest concentrations of inorganic phosphorus are associated with the smallest particles. This process would thus deny a potential source of nutrients to the lake.

No SPM was recovered from the outflow of Sombre Lake (Chapter 4). In order to limit the number of samples to be returned to the U.K., the GF/C filters used to filter water samples (Section 3.3) were only retained for examination of particulate material if there was any obvious deposition. Fine SPM from Sombre outflow may have been overlooked but unfortunately this is a methodological error that can not be corrected.

On 02/08/92 a statistically significant increased rate of trapping was observed in the traps deployed at the inflow of Sombre Lake (Figure 6.1a and Appendix A). The material collected at this time was predominantly inorganic (Figures 6.5, 6.6b) and a very low value for the relative composition was recorded for this date (Figure 6.7). The t-test of the
material recovered from the inflow traps revealed no significant difference from the SPM of the inflow stream (Table 6.3). A minor thaw event has been observed annually during August on Signy Island (Hawes 1988; Davey 1991; Convey 1992; Arnold 1995) and a similar event also occurred at the beginning of August 1992 (Chapter 5). The event recorded in the SPM data for Sombre Lake was attributed to this thaw.

Data presented in Chapter 5 suggest that the thaw caused a flow event in Sombre Lake. Two explanations for this flow event were discussed in Section 5.2.2.1. The evidence supported the existence of a density current caused by warming of water in the shallows of Sombre Lake which could disturb sediment from the sub-lacustrine shelf: this material, similar to the SPM of the stream, could then be deposited in the traps deployed at the inflow.

6.3.4 PRECIPITATION OF SUPER-SATURATED MINERAL PHASES
Solubility calculations (Section 5.2.5) carried out with the aid of the SOLMINEQ88 computer program predicted that Sombre Lake was super-saturated with respect to the precipitation of manganese oxide, iron hydroxide, vivianite and siderite (Figure 5.24). Iron hydroxide precipitation was specifically predicted for October and November and the material recovered from the sediment traps during this period will be dealt with in more detail in Chapter 7 (also see Section 6.3.2). Gallagher (1985, unpublished data) also predicted the precipitation of siderite and vivianite in Sombre Lake.

Thermodynamic calculations do not predict the rate at which a precipitation reaction will occur (Stumm and Morgan 1981). Therefore, it is possible that these reactions may proceed so slowly in the Sombre Lake environment that no precipitation occurred. The only way to
identify if precipitation had occurred was to examine, with the SEM, the material recovered from the sediment traps. The depths at which super-saturation were predicted (Figure 5.24) implied that the products of a precipitation event would be found in the 8m and 10m sediment traps at the deep spot. Precipitation was predicted from June to December (Figure 5.24), but the increasing occurrence of allogenic material in the sediment traps during November precluded an effective search of the material collected for this month. A precipitation event was observed in the deep spot traps in late October (Section 6.3.2) and the analysis of the material collected will be discussed in Chapter 7; at this stage it should be noted that this material was neither vivianite nor siderite. This process of elimination reduced the number of filters to be examined down to a total of twenty-two.

The remaining filters were examined in the SEM and an attempt was made to acquire the EDX spectra of as many particles as possible. This process was very time consuming and occupied some four weeks of SEM time. In that time, no particles with X-ray spectra typical of vivianite (Fe, P) were detected. Of the constituent elements of siderite (Fe, C, O) only iron could be identified by the EDX detector: potential siderite particles would have displayed a strong signal for iron alone. No conclusive evidence was found for the formation of siderite.

This work was very labour intensive; it is possible that particles of vivianite and siderite may have been overlooked due to observer error. Image analysis (described in Section 3.6.3 and employed in Chapter 7) relies on a distinct morphology to facilitate identification of particles and would have been unsuitable for this work.
6.4 SUMMARY

SPM was collected from Sombre Lake using an array of sediment traps. The general dynamics of the SPM were studied. The composition of the SPM was examined using novel applications of CHN analysis and EDX. It is possible to summarise the conclusions as follow:

1. Input of particulates to Sombre Lake was highly seasonal.

2. The particulates were predominantly inorganic and the products of physical weathering.

3. The majority of particulates sedimented within 33m of the inflow and material recovered from the inflow traps was predominantly SPM from the inflow stream.

4. During the initial melt, whilst there was a current of moving water directly below the ice, smaller particles were flushed straight through the lake.

5. The formation of ice allows the sedimentation of particles previously maintained in suspension by wind action.

6. Signy Island was subject to a minor thaw in August. Although the lake was considered to be sealed from the atmosphere at this time, the melt influenced the lake. Particulate matter, that could not be differentiated from that of the stream and fellfield, was deposited in the sediment traps at the inflow.

7. The precipitation of vivianite and siderite was predicted in Section 5.2.3. No evidence of vivianite or siderite was found.

8. Data suggests that a precipitation event occurred at the deep spot after the onset of the inflow. The particles produced will be examined in detail in Chapter 7.
Evidence suggests that the use of an EDX detector, in the manner described in Section 3.6.2.2, can yield compositional data that are directly comparable to data obtained by more classical techniques.
CHAPTER 7: ENDOGENIC IRON PARTICULATES FROM SOMBRE LAKE

7.1 INTRODUCTION

The suspended particulate matter (SPM) of Sombre Lake was discussed in Chapter 6. After the onset of inflow and the re-introduction of oxygen to the water column, a sedimentation event occurred at the deep spot, which could not be attributed to material transported to the lake, but instead to the insoluble iron oxyhydroxides that are formed on oxidation of Fe$^{2+}$. This chapter is concerned with a detailed investigation of the particles collected during this event.

Iron oxyhydroxides have been observed and studied in some detail in temperate systems (Tipping et al. 1981, 1982, 1989; Sholkovitz and Copland 1982a; Leppard et al. 1988; Buffle et al. 1989) but no work on this subject has been undertaken in polar regions. In many of these studies electron microscopy was used to identify and classify the particulates produced, but all earlier work was based on a limited number of samples that were not spatially and temporally resolved.

7.2 MATERIALS AND METHODS

Sediment traps are non-selective and collect all sedimenting particles larger than 1µm (Davison and De Vitre 1992). The flux of sedimenting particles at the Sombre Lake deep spot was at a minimum during the period 28/09/92 - 30/11/92 and iron-rich aggregates
formed a large proportion of the trapped material.

The aggregates were examined with a scanning electron microscope (SEM) using an energy dispersive X-ray analyser (EDX) to perform quantitative, non-destructive analysis of the aggregates (Section 3.6.2.1). An image analysis system was employed to count and measure the aggregates by examining micrographs obtained from the SEM (Section 3.6.3).

7.3 RESULTS AND DISCUSSION

7.3.1 RATE OF TRAPPING

The rates of trapping for the three traps deployed at the deep spot are plotted in Figure 7.1. As discussed in Section 6.3.1, there was a clearly defined winter minimum (circa 14/05/92 to 10/11/92) for the 8m trap (Figure 7.1b). The evidence for a precipitation event at the deep spot after the onset of the inflow (23/10/92) has been discussed in Section 6.3.2 and particles of a distinctive size and morphology were collected from the deep spot traps during the period 27/10/92 - 30/11/92.

The effect of ice cover in the prevention of wind-mixing and its relevance to the rate of trapping of SPM of Sombre Lake was discussed in Chapter 6. Normally, the rate of trapping at the deep spot was independent of depth even during the winter (Section 6.3.1), but during the period 27/10/92 - 30/11/92 the rate of trapping at the deep spot was depth dependent. On 30/11/92 it decreased with depth whilst on the other dates during this period it increased with depth (Figure 6.4).

Hilton et al. (1986) have explained an increasing rate of trapping with depth in the context of a stratified lake which has overturned; in the process, large amounts of re-suspended...
Figure 7.1: Rates of trapping for the sediment traps located at the deep spot a) 5m trap, b) 8m trap, c) 10m trap. Error bars are calculated as the error in the mean (n=2).
sediment were created which were distributed throughout the water column. The data presented in Chapter 5 indicated that at this time Sombre Lake remained stratified, therefore the observation that the rate of trapping increased with depth must be due to other processes. The turbidity current, which transported oxygen into the lake without disrupting the stratification, would have also carried particulate material into the bottom waters of the lake; some of this material appeared in the deep water trap. As sediment traps integrate the collected material over the whole water column, a higher rate of trapping in the deeper traps suggests that the endogenic particulates were formed throughout the water column. The situation of 30/11/92 was complicated by the under-ice current: this was created by inflowing waters transporting allogenic particulates through the lake such that they were only deposited in the trap at 5m (Section 6.3.3).

7.3.2 STRUCTURE AND SIZE

Von Gunten and Schneider (1991) have observed that the primary particles formed on oxidation of a solution of Fe$^{2+}$ ions would aggregate. The particles trapped in Sombre Lake during the period 27/10/92 - 30/11/92 were examined with the SEM and were found to be aggregates of smaller particles (Figure 7.2). These primary particles had a mean diameter of 0.1 - 0.4μm, which was similar to the range of sizes observed by other workers (Tipping et al. 1981; Buffle et al. 1989). No gross differences in morphology with depth or time were observed (Figure 7.2).

The Seescan image analysis system (Section 3.6.3) was used to measure the aggregates and the diameter reported was the mean of thirty-six equally spaced (i.e. 10° apart) diameters (Figure 7.3). The range was 1.6 - 7μm and displayed a normal distribution for
Figure 7.2: SEM micrographs from gold coated samples: a, b) Particles from the 8m trap on 26/10/92. c) Particle from the 5m trap on 10/11/92. d) Particle from the 8m trap on 10/11/92.
Figure 7.3: Variation of aggregate diameter with depth.
all depths and dates. Examination of the diameters of the aggregates revealed no temporal variation, but an increase with depth was noted.

These data have to be interpreted with caution. The effects of filtration on particles are well documented (Davison and De Vitre 1992) and can be summarised as follows: contamination by trace components on the filter, artifacts due to storage prior to filtration and coagulation on the filter surface. Due to field conditions, it would have been difficult to filter the samples in the field; consequently some storage time was required for transportation to the research station but this was kept to a minimum (Section 3.1). As sediment traps only collect particles larger than 1\(\mu\)m diameter (Davison and De Vitre 1992), study of the primary particles (0.1 - 0.4\(\mu\)m) in these aggregates was precluded. Statements about aggregate size and morphology clearly have associated errors but the trend of increasing mean diameter with depth may well have significance. Fortunately, the interpretation of the chemical composition of the aggregates is not subject to these errors.

### 7.3.3 NUMBERS OF AGGREGATES

The image analyser was used to count the number of particles in each micrograph obtained with SEM (Figure 7.4a). These data suggest that the aggregates were formed quickly, after the onset of the inflow stream but before significant quantities of material were trapped at the deep spot (cf Figures 7.4a, 7.4b).

### 7.3.4 COMPOSITION OF AGGREGATES

The EDX system was used to quantitatively analyse (Section 3.6.2.1) samples from the four dates (26/10/92, 10/11/92, 26/11/92, 30/11/92) on which the highest numbers of aggregates were recorded on the filters (Figure 7.4a). A total of one hundred and thirty-one
Figure 7.4: Comparison of the number of aggregates trapped with the rate of trapping. 
a) Mean number of aggregates in 10 fields of view at 500x magnification. b) Data for the rate of trapping in the deep spot trap.
aggregates were analysed, comprising about ten from each depth on each date.

The EDX system employed in most of the analyses to determine the composition of the aggregates was unable to detect elements lighter than sodium. The opportunity to use a boron window EDX detector (Oxford Analytical Instruments, High Wycombe, U.K.) facilitated the analysis of a few particles (n=5) for elements lighter than sodium: this revealed that the aggregates consisted predominantly of oxygen (60-70%).

The aggregates were analysed quantitatively for a wide range of elements (Fe, P, Mg, Al, Si, S, K, Mn, Na, Ca, Cu, Cr, Ti). After oxygen, iron and phosphorus formed the major fraction of the remaining components of the aggregates (Fe 20-30%, P 5-7%). Copper, chromium and titanium were not detected and the other elements formed a small proportion of the remaining material (individually < 2%) (Figure 7.5).

The composition data were analysed for temporal variations, both as pooled data (all three depths) and for each depth: no statistically significant correlations were found. Consequently, to enable the analysis of the data with respect to depth, the compositional data for each depth could be pooled. There was a clear association between iron and phosphorus, as shown by a correlation analysis of all the aggregates (Table 7.1). Sodium and manganese were also associated with iron, but sodium and manganese were not highly correlated. These data further suggest an association between magnesium, silicon, aluminium, sulphur, and potassium whereas calcium was only associated with sodium.

Although the concentrations of iron and phosphorus varied in individual aggregates, the atomic ratio of iron to phosphorus (Fe:P) was found to be approximately constant at
Figure 7.5: Histogram of aggregate composition.
Table 7.1: Correlation matrix for composition data generated by Minitab 9.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>P</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Mn</th>
<th>Na</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.927*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.068</td>
<td>0.018</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>-0.207</td>
<td>-0.256*</td>
<td>0.732*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>-0.084</td>
<td>-0.162</td>
<td>0.734*</td>
<td>0.722*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>-0.125</td>
<td>-0.155</td>
<td>0.529*</td>
<td>0.583*</td>
<td>0.495*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-0.162</td>
<td>-0.146</td>
<td>0.283*</td>
<td>0.355*</td>
<td>0.262*</td>
<td>0.218</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-0.445*</td>
<td>-0.487*</td>
<td>0.109</td>
<td>0.354*</td>
<td>0.121</td>
<td>0.148</td>
<td>0.198</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>-0.354*</td>
<td>-0.336*</td>
<td>0.059</td>
<td>0.144</td>
<td>-0.013</td>
<td>0.208</td>
<td>0.160</td>
<td>0.183</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.164</td>
<td>0.193</td>
<td>0.176</td>
<td>0.058</td>
<td>0.000</td>
<td>0.065</td>
<td>0.084</td>
<td>0.030</td>
<td>-0.252*</td>
<td></td>
</tr>
<tr>
<td>DEPTH (m)</td>
<td>0.84</td>
<td>0.89</td>
<td>-0.35</td>
<td>0.02</td>
<td>-0.11</td>
<td>0.35</td>
<td>-0.12</td>
<td>-0.94</td>
<td>-0.92</td>
<td>1.00</td>
</tr>
<tr>
<td>SIZE¹</td>
<td>0.400</td>
<td>0.399</td>
<td>0.100</td>
<td>-0.008</td>
<td>0.092</td>
<td>0.048</td>
<td>0.024</td>
<td>-0.155</td>
<td>-0.326</td>
<td>0.230</td>
</tr>
</tbody>
</table>

¹ The correlation analysis performed on the cube of the mean diameter.
For 131 degrees of freedom, the significance levels are calculated as; 0.171 (5%), 0.223 (1%*) and 0.283 (0.1%**)
4.3:1 (Figure 7.6). This agrees with the findings of Buffle et al. (1989) who reported a ratio of 4:1 (Fe:P). It should be noted that unless otherwise stated the ratios reported in Chapter 7 are atomic ratios.

There were strong linear correlations between silicon, aluminium and magnesium. These elements can be attributed to clay-like particles either adhering to or contained within the aggregates. This view is supported by the fact that the mean Al/Si ratio was 0.51±0.03, and Mg/Si was 0.59±0.03, which are indicative of clays. A selection of filters were examined by X-ray diffraction and this confirmed the presence of clays (D. McLeod Duthie, Macaulay Land Use Research Institute, Aberdeen pers. comm.). A similar observation was made by Buffle et al. (1989) who reported an Al/Si ratio of 0.56±0.08.

Sodium was the fourth most important component of the particles from Sombre Lake (Figure 7.5). In contrast, Tipping et al. (1981) and Buffle et al. (1989) reported calcium to be the most important component after iron, phosphorus and oxygen. In comparison to a temperate environment, the rate of chemical weathering in the maritime Antarctic is relatively slow (Campbell and Claridge 1987). However, due to exposure to sea spray the cation balance in the lakes of Signy Island is more characteristic of the marine environment (Heywood et al. 1980). These factors would have caused the ratio of the concentrations of dissolved sodium to calcium to be higher compared to the non-maritime study lakes of other workers and could reasonably explain why sodium features more significantly in the aggregates from Sombre Lake than those from temperate systems (cf Tipping et al. 1981; Buffle et al. 1989).

The percentage of calcium in the aggregates increased with depth (Table 7.1, Figure 7.5),
Figure 7.6: Comparison of percentage iron and percentage phosphorus a) in individual aggregates \(n=132, r^2 > 0.86, \%P = 0.23 \%Fe + 0.27\), b) variation of iron : phosphorus atomic ratio (Fe:P) with depth.
whilst that of sodium decreased with depth. Sodium and calcium were negatively correlated (Table 7.1) and the decreasing concentrations of sodium can be accounted for by increasing concentrations of calcium. Whilst the ratio of iron to calcium in the aggregates (51.8±2.1:1) remained relatively constant (Figure 7.7), that of sodium to calcium was lower compared to the lake water (3.4±0.3 cf 5.7±0.5). These observations suggest that calcium is an important component in these aggregates. The iron to calcium ratio for particles from Sombre Lake is an order of magnitude higher than in temperate systems (Tipping et al. 1981; Buffle et al. 1989): this can be accounted for by the increased sodium to calcium ratio of maritime Sombre Lake compared to the temperate lakes of other workers (Tipping et al. 1981; Buffle et al. 1989).

Although not correlated with sodium or calcium, the concentration of manganese decreased with depth (Table 7.1, Figure 7.5): the causative process was therefore independent of the variation in sodium and calcium concentrations within the aggregates. Manganese was negatively correlated with iron and phosphorus (Table 7.1), which suggests that the process by which manganese was incorporated into the aggregates occurred less readily at depth. Tipping et al. (1981) observed manganese in the particles from Esthwaite Water but the sampling regime employed did not allow studies of the spatial variation of the particulates.

In Section 6.3.3 a semi-quantitative method of EDX analysis was used to analyse the SPM from the deep spot of Sombre Lake. Depth related trends similar to those presented here were observed. This supports both the observations presented in this chapter and the conclusion made in Chapter 6 that the semi-quantitative EDX methodology can be very useful in the analysis of certain types of samples.
Figure 7.7: Comparison of percentage iron and percentage calcium a) in individual aggregates \( n=132, r^2 > 0.86, \%\text{Ca} = 0.0187 \%\text{Fe} - 0.01 \), b) variation of iron : calcium atomic ratio (Fe:Ca) with depth.
7.3.5 DISCUSSION OF SYSTEMATIC VARIATIONS IN AGGREGATE COMPOSITION

Aggregates recovered from the deep spot sediment traps after the onset of the inflow stream have been examined. As similar aggregates were not found in the traps deployed at the inflow they were not attributable to an allogenic source. Consisting predominantly of oxygen, iron and phosphorus, they exhibited an iron to phosphorus ratio similar to the iron oxyhydroxides described by Buffle et al. (1989). This suggests that the aggregates were iron oxyhydroxides formed by the oxidation of Fe$^{2+}$ after oxygen was introduced to the lake by the inflow.

Caulkett and Ellis-Evans (1996) presented the observations and results discussed in this chapter. In the published work it was suggested that oxygen was introduced to the body of the lake by diffusion. However, subsequent analysis demonstrated that oxidation of Fe$^{2+}$ within a short timescale throughout the water column unlikely. At the time of preparing the paper, the importance of the depth-concentration profiles of the conservative elements had not been considered. Consequently, the mechanism described by Caulkett and Ellis-Evans (1996) is now considered to be incorrect.

In Section 5.2.4.1 a turbidity current that could introduce oxygen throughout the water column of Sombre Lake was discussed. This did not cause turbulent mixing of the water column and stratification of the lake remained intact. The introduction of oxygen to all depths virtually simultaneously would have caused the oxidation of Fe$^{2+}$ throughout the water column and the concomitant formation of iron oxyhydroxide particulates at all depths. This is consistent with the data presented in Section 7.3.1.
The primary particles in the aggregates were the initial oxidation products of $\text{Fe}^{2+}$ and the data presented in Section 5.2.2.5 suggest that this oxidation was rapid, occurring within four days of the introduction of oxygen to the lake. Therefore, the constituent primary particles of the aggregates were formed rapidly and would exhibit no temporal variations. This is consistent with the data presented in Sections 7.3.3 and 7.3.4. It was observed in Chapter 5 that, as in previous studies (Hawes 1983b), the lake remained stratified until the loss of ice cover (22/12/92): thus the aggregates were sedimenting through gradients of concentration and redox potential.

The concentration of $\text{Fe}^{2+}$ ions in the water column increased with depth (Figure 5.11) and on oxidation would lead to greater numbers of primary particles (Von Gunten and Schneider 1991). Consequently, aggregates with larger diameters would be formed, as observed in the data presented (Table 7.1, Figure 7.3). When present in high concentrations, primary particles may cluster together before reaching the typical size range (0.1-0.4$\mu$m, Section 7.3.2): in this situation, aggregates comprised of smaller particles would have fewer void spaces and thus a relatively greater concentration of iron and phosphorus (Table 7.1, Figure 7.6). Alternatively, the increasing percentages of these elements with depth could be caused by an artifact of the EDX analysis system. The calculated diameter of the excitation volume of the electron beam was 1.4$\mu$m (Section 3.6.2.1), only particles larger than this could be reliably analysed with quantitative EDX. With increasing diameter there would be more chance that the whole of the excitation volume was filled by the aggregate under analysis; this would increase percentages of iron and phosphorus relative to the "unanalysed fraction". As iron and phosphorus exhibited statistically significant (Table 7.1, 0.1%) correlations with size, this methodological artifact cannot be discounted. Other elements that exhibited statistically significant correlations with depth (Table 7.1, Mn, Ca, Na) did...
not have significant correlations with size of the aggregates: therefore, it is unlikely that the variations of the percentages of these elements with depth could be attributed to this methodological artifact.

The percentage of manganese in the aggregates decreased with depth (Section 7.3.4, Figure 7.5). Manganese is more readily reduced than iron (Stumm and Morgan 1981) and the dissolved oxygen profile (Figure 5.3) suggests that a redox gradient persisted in the lake until the loss of ice cover. As aggregates formed in the upper waters of the lake sedimented downwards, manganese would be reductively dissolved. Additionally, those aggregates formed in more reducing conditions at the bottom of the lake would contain less manganese. This is consistent with the findings of Davison et al. (1982) who observed the reductive dissolution of manganese particles as they sedimented into the anoxic bottom waters of Esthwaite Water. An alternative explanation of these observations might be that the absolute amount of manganese in the aggregates remains constant and the observed decrease in the percentage composition is due to a dilution effect through addition of more iron. The inverse correlation between iron and manganese (Table 7.1) reflects the increasing concentration of iron with depth whilst the concentration of manganese decreases. Iron displays a significant correlation with the size of the aggregates: if the decrease in the concentrations of manganese in the aggregates with depth was predominantly due to dilution by iron, then manganese would show a significant inverse correlation to the size of the aggregates. This was not observed making this alternative hypothesis unlikely.

The concentration of calcium in the aggregates increased with depth (Table 7.2, Figure 7.5). Increased concentrations of dissolved calcium were observed in the anoxic waters of Sombre Lake (Section 5.3.2.4, Figure 5.9) and Tipping et al. (1989) found that calcium is
adsorbed to iron aggregates. Increasing concentrations of calcium in the aggregates could be explained by adsorption from waters with increased concentrations of dissolved calcium. The correlation coefficients (Table 7.1) suggest that this probably occurs by the replacement of sodium. These observations imply an indirect link between calcium and the iron cycle as observed by Sholkovitz and Copland (1982a).

In Section 5.3.3, the total water-body concentration (TWC) was used to follow the temporal trends in the overall concentrations of dissolved ions. For all ions (except dissolved oxygen) higher concentrations were recorded under ice cover and the ratio of summer and winter TWC values was used to measure these increases (Table 5.2). Comparison of the TWC ratio with the TWC ratios of sodium and chloride identified those ions (K\(^{+}\), Ca\(^{2+}\), Mn\(^{2+}\), Fe\(^{2+}\), NH\(_{4}\)\(^{+}\), NO\(_{2}^{-}\), NO\(_{3}^{-}\), o-P, DRSi) for which the increases in concentration were in part derived from processes operating in the sediments or water column (Section 5.3.3.3). The ratio in which any two ions (x and y) are released from the sediments (\(r_R\)) may indicate the sources of the two ions. This ratio, (release ratio, \(r_R\)) can be calculated from data presented in Chapter 5 using Equation 7.1. The derivation of Equations 7.1 and 7.2 are detailed in Appendix D:

\[
\frac{r_R}{y} = \frac{\theta_x}{\theta_y} \quad \text{Equation 7.1}
\]

where:

\[
\theta_x = (r_x - 1) S_x \quad \text{Equation 7.2}
\]

and \(S_x\) is the TWC for ion x in summer and \(r_x\) is the TWC ratio for ion x as defined by Equation 5.2.
The release ratio \( r_R \) for Fe\(^{2+} \) and ortho-phosphate (Fe\(^{2+}:\text{o-P} \)) was calculated as 2. If there was an alternative source of reducible iron in the sediment then the Fe\(^{2+}:\text{o-P} \) release ratio would be greater than the Fe:P ratio in the aggregates (4.3:1): although this was not the case, it is essential for the purposes of this discussion to examine possible sources of Fe\(^{2+} \).

The precipitation of Fe\(^{2+} \) compounds were predicted in Section 5.3.5 (vivianite, Fe\(_3\)(PO\(_4\))\(_2\) and siderite, FeCO\(_3\) ) but no evidence for the precipitation of either mineral was found (Section 6.3.4). Furthermore the dissolution of these minerals would increase the Fe\(^{2+}:\text{o-P} \) release ratio \( r_R \). In the absence of evidence to the contrary, this would suggest that the Fe\(^{2+} \) released to the water column originated from the reduction of the aggregates discussed in this chapter. The release ratio of 2 must be discussed in the context of ortho-phosphate concentrations and indicates that there are alternative sources of ortho-phosphate.

Hawes (1983b) observed that phytoplankton growth occurred most rapidly under ice cover in early spring, when the maximum TWC values for Fe\(^{2+} \) and ortho-phosphate were observed. This would remove some of the "excess" ortho-phosphate from the water column, whilst the remainder would be lost to the outflow as observed in Section 5.3.4.2. The sedimentation and decomposition of phytoplankton under the anaerobic conditions present in Sombre Lake during winter, as described by Ellis-Evans (1985), could be the source for the "excess" ortho-phosphate released to the water column.

The release ratio for Fe\(^{2+} \) and calcium, calculated as 52, from Equation 7.1 is the ratio of Fe:Ca in the aggregates (Section 7.3.4). Sombre Lake water was not calculated to be supersaturated with respect to calcium mineral phases (Section 5.3.5). These observations would imply that all the calcium released to the water column during winter can be attributed to the reductive dissolution of the aggregates discussed in this chapter. This explains the
elevated concentrations of calcium seen in the bottom waters of Sombre Lake (Section 5.2.2.4).

7.4 SUMMARY
A sedimentation event was observed in Sombre Lake immediately after the onset of the inflow stream. Rate of trapping data for the sediment traps suggested that this was not due to particles transported to the lake, but to endogenic particles produced within the water column. Further analysis of these particles led to the following conclusions:

1. The particles studied were aggregates of smaller particles. The primary particles persisted in these aggregates.

2. The appearance of the aggregates coincided with the influx of meltwater flowing under the ice cover and was consistent with a rapid oxidation of the dissolved Fe$^{2+}$.

3. The aggregates consisted mainly of iron, phosphorus and oxygen. Calcium was also found but was a smaller component than in temperate systems. There was also evidence that sodium and manganese were constituents of the aggregates. Elemental ratios suggested that magnesium, silicon and aluminium were probably in the form of clay particles.

4. The concentrations of iron and phosphorus showed some variation between aggregates. The ratio of iron to phosphorus remained practically constant at 4.3:1 in all aggregates, irrespective of the depth and date of sampling. Likewise the ratio of iron to calcium remained constant at 52:1. This confirms that calcium is an important trace component of this type of particle.
5. The concentrations of iron (concomitantly phosphorus) and calcium in the aggregates increased with depth whilst the concentration of manganese decreased with depth. The water column of Sombre Lake remained stratified during this time and these observations were consistent with the aggregates sedimenting through concentration and redox gradients.

6. The ratio in which Fe$^{2+}$ and ortho-phosphate were released from the sediments was calculated as 2 compared to 4.3:1 in the aggregates. This suggested that there were alternative mechanisms supplying and removing ortho-phosphate from the water column. These were attributed to biological activity. The Fe$^{2+}$ and calcium release ratio was calculated as 52, the same as the composition ratio of the aggregates. The calcium released to the water column during winter was attributed wholly to the reductive dissolution of the aggregates.
CHAPTER 8: OVERVIEW AND SYNTHESIS

8.1 SUMMARY OF CONCLUSIONS

In this section a synthesis of the main conclusions of Chapters 4 - 7 is presented. The aim of this chapter is to discuss the implication of these points for Signy Island.

A synthesis of the principal conclusions of each chapter is presented below:

1. The freshwater systems of Signy Island were subject to a highly seasonal regime. The streams were frozen for as long as six months each year and Sombre Lake was ice covered for nine months. Sombre Lake was entirely sealed from the atmosphere for four months with the development of stratification throughout and anoxia in the deepest layers (see Chapters 4, 5).

2. Allogenic inputs to Sombre Lake only occurred whilst the inflows were flowing. The material transported by the streams to Sombre Lake consisted of both dissolved ions and suspended particulate matter (SPM) and most of the input occurred within four weeks of the stream flow commencing. This was related to the melt of winter snowpack. SPM supplied to Sombre Lake was predominantly inorganic (see Chapters 4, 6).

3. In general, stream chemistry in six different catchments of Signy Island was similar. However, there is some evidence that the concentrations of marine-derived ions in the streams were affected by distance from the sea. The ions
derived from precipitation and sea spray (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NH$_4^+$, NO$_3^-$, Mn$^{2+}$) were supplied to the streams as a pulse at the beginning of the season. Areas of permanent ice were an important source of nitrate. Calcium, DRSi, carbonate and magnesium were derived from crustal weathering. Whilst orthophosphate and Mn$^{2+}$ were products of crustal weathering, these ions were released as a pulse probably related to thawing of the fellfield soils (see Chapter 4).

4. Reduction of iron and manganese compounds occurred in the sediments of Sombre Lake and the reduced ions and associated adsorbed ions were released to the overlying water column (see Chapter 5).

5. The cycles of nitrate, nitrite and ammonium in Sombre Lake were related and much of the ammonium produced could be accounted for by nitrate reduction. The loss of ammonium from the water column was not linked to the oxidation and precipitation of Fe$^{2+}$. The phytoplankton bloom, which occurs in early spring whilst the lake was still ice covered, was probably responsible for removal of ammonium ions (see Chapter 5).

6. The loss of DRSi was linked to the oxidation of Fe$^{2+}$ and adsorption to the surface of SPM (see Chapter 5).

7. Interpretation of the depth-concentration profiles of Sombre Lake suggested that oxygen was transported deep into the lake prior to the loss of ice cover and the occurrence of wind mixing. This was attributed to the action of a turbidity current (see Chapter 5).
8. Sombre Lake appeared to lose inorganic nitrogen during the flushing of the winter water. Significant quantities of ortho-phosphate were supplied to the lake by ground thaw, but were rapidly flushed from the lake (see Chapters 4, 5).

9. During the initial melt, whilst there was a current of moving water directly below the ice, smaller particles were flushed straight through the lake (see Chapter 6).

10. Signy Island was subject to a minor thaw in August. Although the lake was considered to be sealed from the atmosphere at this time, the melt influenced the soluble chemistry of the lake: particulate matter that could not be differentiated from that of the stream and fellfield was deposited in the sediment traps at the inflow (see Chapters 5, 6).

11. Fe$^{2+}$ ions diffused a long way up the water column and at the onset of inflow were oxidised and precipitated: this was consistent with solubility calculations. Ortho-phosphate ions which were also released from the sediment were precipitated simultaneously with iron. Particles recovered from the sediment traps at this time were aggregates consisting mainly of iron, phosphorus and oxygen but calcium was also found. The ratios of iron to phosphorus and iron to calcium remained practically constant at 4.3:1 and 52:1 respectively in all aggregates, irrespective of the depth and date of sampling (see Chapters 5, 6, 7).

12. The ratio in which Fe$^{2+}$ and ortho-phosphate were released from the sediments was calculated as 2. This suggested that there were alternative mechanisms supplying and removing ortho-phosphate from the water column; these were attributed to biological activity. The Fe$^{2+}$ and calcium release ratio was calculated as 52: calcium released to the water column during winter was attributed wholly to the reductive dissolution of the aggregates (see Chapter 7).
Lewis Smith (1990) used radiocarbon dating of material from moss banks on Signy Island to postulate a series of ice-cover maps dating back to 5000 B.C. and concluded that ice-cover reached a minimum coverage between 3000 B.C. and 1 B.C. Since that time, there have been several periods of expansion and contraction which are consistent with periods of warming and cooling reported by other workers (e.g. Clapperton and Sugden 1988). From the 1950's an increase in the summer air temperatures on Signy Island (Lewis Smith 1990) have been observed; associated with this there has been a 35% reduction in the total area of permanent ice-cover on Signy Island between 1949 and 1989 (Lewis Smith 1990). Over the same time period, Appleby et al. (1995) reported the reduction of permanent ice cover in the catchment of Moss and Sombre Lakes to be 90% and 60% respectively. These observations suggest that glacial retreat on Signy Island is occurring in real time and the simple systems should prove a suitable environment in which to study the effects of deglaciation in response to local climate change (Power and Power 1995). At Cornwallis Island in the Arctic, Schindler et al. (1974) observed that a small disturbance in the catchment of oligotrophic Char Lake had a significant effect on the concentrations of dissolved ions. In the same year Welch and Kalff (1974) observed an increase in the productivity of Char Lake. In the maritime Antarctic, Ellis-Evans (1990) has reported increased concentrations of ammonium and ortho-phosphate ions in Heywood Lake, Signy Island as a response to growing populations of fur seal in its catchment.

The climate of Signy Island is predominantly a wet, maritime environment (Lewis Smith 1984) and it seems unlikely that the increased temperatures observed on Signy Island would significantly affect the amount of precipitation. The concentrations of ions supplied by snowmelt to the freshwater systems are unlikely to change greatly. Deglaciation affects two
catchment variables: the amount of ice-cover and the amount of ice-free (exposed) soil. This will decrease the quantities of ions derived from permanent ice ($\text{NO}_3^-$) whilst potentially increasing the quantities of ions supplied from crustal sources ($\text{DRSi, Ca}^{2+}, \text{Mg}^{2+}, \text{HCO}_3^-, \text{o-P, Mn}^{2+}$). Byers Peninsula, Livingston Island (South Shetland Islands, maritime Antarctic) has a similar climate to Signy Island and although it receives more winter snow (Jones et al. 1993) there are no significant, permanent ice fields in the area. Data presented by Jones et al. (1993) indicate that the lakes of the Byers Peninsula exhibit increased concentrations of $\text{DRSi}$ and reduced concentrations of nitrate ions in comparison to the lakes of Signy Island. Nitrate ions on Signy Island are not solely supplied from permanent ice but can also be derived from sea-spray and the activities of marine animals (Ellis-Evans 1990); it could be argued that in fact increased concentrations would be expected on Signy Island. In comparison with the most saline of the Byers coastal lakes, Signy lakes have significantly higher concentrations of nitrate. This is consistent with the view that permanent ice is a major source of nitrate ions in maritime Antarctic systems. With no permanent ice-cover there is a potentially larger source of $\text{DRSi}$ ions at the Byers Peninsula: this could explain the increased concentrations of this ion in the lakes although it could also be the result of the unique geology of Livingston Island (Jones et al. 1993). In comparison to Livingston Island, the concentrations of other ions derived from a crustal source on Signy Island either showed no differences in concentration ($\text{Ca}^{2+}, \text{Mg}^{2+}$) or were not determined ($\text{o-P, Mn}^{2+}$) by Jones et al. (1993). In summary, the data from Livingston Island supports the hypothesis presented above i.e. that decreasing ice-cover in the catchment will affect the concentrations of ions in a manner predictable from the conclusions of Chapter 4.

Appleby et al. (1995) have presented data implying that the retreating ice-cover has increased the amounts of inorganic particulates supplied to Sombre Lake. Furthermore, the
particulates supplied to the lake have increased in size as the percentage ice-cover in the catchment decreased (P. Noon, University College of London pers. comm.). Contrary to this view, high concentrations of very fine SPM were observed in the streams of Signy Island during the 1994 - 1995 summer season. Such a season was possibly atypical because of extensive melting of the permanent ice fields, revealing areas of soil that had not been exposed during recent history; it is likely that the unusual SPM observed in the streams could be attributed to this melt. Consequently, when an area of soil first loses its ice cover, any fine material in the regolith would be rapidly flushed into the freshwater systems.

It was observed in Chapter 6 that during the initial thaw period, whilst a current of lower density water was flowing across the surface of the lake, small particulates may be carried through the lake. Such particles are likely to have a high surface area with correspondingly large amounts of adsorbed ions (Stumm and Morgan 1981; Kufel 1991). Adsorption and desorption processes are controlled by temperature, pH and concentration; these parameters would be relatively constant in the sub-ice current and any desorbed ions would be rapidly flushed from the lake. Larger particulates would be more likely to sediment from the flowing water in their passage across the lake.

The data presented in Chapters 4 and 5 support the view of many other workers (e.g. Hawes 1989; Ellis-Evans 1985) that the freshwater systems of Signy Island are subject to a highly seasonal regime. The streams of Signy Island are frozen for as long as six months and the inflow to Sombre Lake constitutes the majority of input to the lake. Consequently, during the period that the streams and the lake are frozen, there is no input to Sombre Lake. During the study period, Sombre Lake was ice-covered for nine months of the year and was entirely sealed from the atmosphere for four months (Chapter 5). For this period the lake
can be considered a closed system. The term "closed system" can also be interpreted to mean that the lake is isolated from the external environment (e.g. Rigler 1978, Heywood 1977). In Chapters 5 and 6, it was shown that a minor thaw caused a warming of the lake waters with some circulation, which disrupted the developing stratification and anoxia. Although Sombre Lake can be considered a "closed system" for purposes of interpreting its chemistry (e.g. total water body concentration), the data clearly show that it can not be considered "isolated"; a term much used by other authors (e.g. Hobbie 1973; Hawes 1983b) when describing ice-covered Arctic and Antarctic lakes.

Data collected by the automatic meterological station at the Signy research station was used as an input file for a snow-melt model (Tarboton 1995). The model predicted a minor thaw event for the end of July 1992 (M. Gardiner, University of Bristol pers. comm.) which was consistent with field observations and data collected from Sombre Lake. Sensitivity testing of the model suggested that the observed thaw could be attributed to black-body radiation (M. Gardiner, University of Bristol pers. comm.). A minor thaw-event for July/August has been reported on Signy Island by several workers (Hawes 1988; Davey 1991; Convey 1992; Arnold 1995, W. Marshall, British Antarctic Survey pers. comm.), but this is the first attempt to identify the cause of this event. As this thaw event was apparently not related to temperature, it is unlikely to be affected by any further increases in mean annual temperature. Changes in the atmosphere of the earth (ozone depletion e.g. Farman et al. 1985, increased atmospheric carbon dioxide e.g. Delmas et al. 1980) could attenuate the power of sunlight but are considered, at present, unlikely to have a significant influence on this phenomenon (Dr. H.K. Roscoe, British Antarctic Survey pers. comm.).

The local warming reported by Lewis Smith (1990) would reduce the period of ice-cover on
Sombre Lake and a trend of diminishing periods of lake ice-cover has been observed in recent years (Laybourn-Parry et al. 1996). However, Ellis-Evans (1990) reported that the depth of ice formed on nearby Heywood Lake had not decreased over the past two decades. Unfortunately, due to the lack of maritime Antarctic stream studies, there is no comparable data set for stream flow regimes but it would seem likely that increased mean annual temperatures would lead to longer periods of stream flow. In addition to the more circumstantial evidence of decreasing ice duration (Laybourn-Parry et al. 1996) and increasing mean air temperature (Lewis Smith 1990), this hypothesis is supported both by the work of Hawes (1988) and the data presented in Chapter 4 of this work. Hawes (1988) observed the streams to be frozen from April until early December 1984, whilst in 1992 the streams were frozen from late May until mid October 1992. The onset of streamflow has a profound influence on the lake by the introduction of dissolved ions and oxygen to the water column.

During the thaw, the inflowing waters formed a current of low density water immediately below the surface of the ice: under such conditions, other workers (Rigler 1978; Hawes 1983b) have noted a minimal interaction between the inflowing waters and the water in the body of the lake. Although there was evidence for a similar current in Sombre Lake in 1992, it was also observed at this time that oxygen was introduced to the bottom waters without disruption of the stratification. Diffusional processes would be too slow to account for this and other evidence suggested that this may have occurred by the formation of a turbidity current. The introduction of oxygen to the bottom waters before the loss of ice-cover is contrary to the observations of Hawes (1983b) and studies of nutrient cycling in Sombre Lake (Gallagher 1985; Ellis-Evans and Lemon 1989) did not examine the influence of oxygen rich inflowing waters. Consequently, it was not possible to ascertain whether the
turbidity current was an isolated event, specific to the conditions of the 1992 spring, or an annual process. Nevertheless it is certain that the onset of inflow is more critical to the chemistry of the lake than the loss of ice-cover.

If the trends of decreasing periods of ice-cover and increasing periods of streamflow continue, the duration for which Sombre Lake is sealed from the atmosphere will be reduced. As a result, dissolved oxygen concentrations may not fall to the low levels observed in this and earlier studies (Gallagher 1985; Ellis-Evans 1989). This could affect the concentrations of ions regenerated from the lake sediments and water column during the winter (Fe$^{2+}$, o-P, NH$_4^+$, Mn$^{2+}$, K$^+$, Ca$^{2+}$, NO$_3^-$, DRSi).

Once the lake became ice-covered the concentration of dissolved oxygen began to decrease; concomitant with this was the reduction of nitrate to ammonium which is biologically mediated (Jones et al. 1982; Ellis-Evans 1985). The majority of the input to Sombre Lake is from snow melt and the inflow stream: as there is very little seepage from the seal damaged, moss carpet to the east of Sombre Lake (Hawes 1983a), nitrate must be supplied to Sombre Lake during the initial melt-pulse and from the retreating ice-field between Sombre and Changing Lakes (Appleby et al. 1995). The data presented in Chapters 4 and 5 suggested that the lake lost inorganic nitrogen to its outflow; consequently biological processes occurring in the lake are not limited by nitrogen at the current time. This is consistent with the observations of Hawes (1983a). The long-term data set for Sombre Lake, analogous to that of Heywood Lake (Ellis-Evans 1990), has not as yet been published, but there is evidence (Dr. J.C. Ellis-Evans, British Antarctic Survey pers. comm.) of increasing concentrations of inorganic nitrogen in recent years which could be attributed to the melting of the permanent ice-fields. If ice-retreat continues, supplies of both nitrate and derived
ammonium may be reduced.

Hawes (1983a) observed that the phytoplankton crop of Sombre Lake was limited by phosphate availability. Low concentrations of ortho-phosphate in Sombre Lake could be explained by the low yield from the catchment (Hawes 1983a) and the controlling influence of the iron cycle on the availability of ortho-phosphate released from the sediments (Gallagher 1985; Ellis-Evans and Lemon 1989). At that time, the critical ratio of iron and phosphorus (Fe:P = 4:1, Buffle et al. 1989) in natural iron oxyhydroxides was not known and it has since been shown (Chapter 7) that iron oxyhydroxides from Sombre Lake exhibit a similar ratio. Re-examination of the early iron cycling data of Gallagher (1985, unpublished data) with knowledge of the Fe:P ratio, confirmed that the conclusion of these early workers was indeed correct; the concentrations of ortho-phosphate in the water column were controlled entirely by the iron cycle. In fact, there was sufficient dissolved Fe$^{2+}$ to strip any ortho-phosphate from the water column that may have been supplied to the lake by melt-water. The situation for 1992, reported in Chapter 7, was quite different. It was found that although the concentrations of Fe$^{2+}$ released from the sediments of Sombre Lake have increased since 1985 (Gallagher 1985, unpublished data), the concentrations of ortho-phosphate in the water column could not be wholly attributed to the reduction of iron compounds in the sediments: there must be an alternative source of ortho-phosphate.

Deglaciation on Signy Island, occurring in real-time (Lewis Smith 1990; Appleby et al. 1995), has exposed greater areas of regolith and increased the availability of ortho-phosphate in the Sombre Lake catchment. The additional ortho-phosphate, which is not bound by labile iron, is available for utilisation by biological processes in the water column. Jones and Juggins (1995) demonstrated the response of benthic diatom communities to
nutrient changes in Sombre Lake. This had occurred since 1980 when, according to Hawes (1983a), ortho-phosphate was limiting and was entirely controlled by the iron cycle (Gallagher 1985). Hawes (1990a) has reported differences in species composition between the oligotrophic and eutrophic systems of Signy Island, as have other more recent workers (e.g. Laybourn-Parry et al. 1996). Since the work of Hawes, studies are currently in progress to examine these changes in the planktonic communities of Sombre Lake (Dr. H. Butler, British Antarctic Survey pers. comm.).

Changes in the nutrient status of Sombre Lake have been attributed to the current period of deglaciation on Signy Island. At nearby Heywood Lake, massive increases of ortho-phosphate and ammonium ions in the water column have been related to the activities of fur seals (Ellis-Evans 1990). In comparison with Heywood Lake, the catchment of Sombre Lake is not as heavily influenced by seals due to its more rugged nature (J.C. Ellis-Evans, British Antarctic Survey pers. comm.) but numbers in the catchment are increasing (Hodgson et al. 1998). For most of the period of open water, Sombre Lake receives very little input from groundwater seepage (Hawes 1983a; Chapter 4 this work) and therefore the summer activities of seals are unlikely to contribute nutrients to the waters. However, the thawing of the winter snowpack may flush nutrients deposited by seals during the preceding summer, into the lake.

In summary, on-going deglaciation of Paternoster Valley will continue to supply increased quantities of nutrients (NO₃⁻, o-P, DRSi) to Sombre Lake, although the proportions of these will change as the ice-cover recedes. Additionally, the activities of increasing numbers of fur seals in the Sombre Lake catchment will also augment the supply of certain nutrients (o-P, NH₄⁺, NO₃⁻) to the lake. Unfortunately, it is not possible with the data available to
differentiate between the activities of fur seals and the effects of deglaciation. The trophic status of Sombre Lake has already been altered by these two processes and will continued to be monitored by the long term study programme of the British Antarctic Survey.

8.3 SUGGESTED AREAS FOR FURTHER RESEARCH

The objective of this thesis was to examine the interactions of diverse aspects of the freshwater chemistry on Signy Island, maritime Antarctic. At the outset it was not feasible to plan for all eventualities and in some situations the data presented here are not conclusive, but are only indicative of processes which may be occurring in the freshwater ecosystems of the island. There are several areas of research that need to be pursued to prove either that the data presented here are generally representative of Signy Island or were specific to the time period during which the research was carried out.

The principal areas requiring further research are:

1. The mixing processes that occur in Sombre Lake, which are clearly more complex than had previously been recognised by polar limnologists.

2. The cryo-processes which generate ortho-phosphate and other ions over winter and their relationships to deglaciation.

3. More accurate assessments of total water body ion concentrations to monitor possible changes in patterns of nutrient cycling within Sombre Lake which is undergoing significant change at this time.

4. To use the methods applied here to examine other lacustrine systems on Signy Island and elsewhere in the maritime Antarctic and thereby establish the applicability of the conclusions made in this study to other sites.
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APPENDIX A

Figure A1: Rate of trapping data for Sombre Lake sediment traps that was not presented in Chapter 6. Rate of trapping data for a) SIF 2, b) SIF 3 and c) SDS. (see Figure 2.2 for trap positions). Presented in Chapter 7.
Rate of trapping data from a sediment trap deployed at the deep spot of Moss Lake, Paternoster Valley. This figure clearly illustrates the effect of ice-over on the rate of trapping and corroborates the observations made for Sombre Lake (Section 6.3.1).
APPENDIX C

Normalised EDX data for Sombre Lake sediment traps not presented in Chapter 6.

Figure C1: EDX data for the deep trap deployed in the first inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C2: EDX data for the shallow trap deployed in the second inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C3: EDX data for the deep trap deployed in the second inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C4: EDX data for the shallow trap deployed in the third inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C5: EDX data for the deep trap deployed in the third inflow position. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C6: EDX data for the 5m trap deployed in the deep spot. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
Figure C7: EDX data for the 10m trap deployed in the deep spot. Data are normalised against the SPM of the inflow stream using the method defined in Section 6.3.1.
APPENDIX D

The derivation of the release ratio \( r_\text{R} \) for the release of species from the sediments of Sombre Lake, as used in Chapter 7 (Equation 7.1).

The total water body concentration (TWC) of species \( x \) in winter \( (W_x) \) may be expressed as:

\[
W_x = S_x + \beta_x + \theta_x
\]

where: 
- \( S \) is the mean TWC in summer \( (\text{mol} \, \text{l}^{-1}) \)
- \( \beta \) is the increase in concentration due to ice exclusion \( (\text{mol} \, \text{l}^{-1}) \)
- \( \theta \) is the increase in concentration due to release from the sediment \( (\text{mol} \, \text{l}^{-1}) \)

It is not necessary to include a term for the stream input as there is no stream flow in winter and the summer TWC used in the calculations is the mean value for 2 months.

The term \( \beta_x \) can be defined by the equations of Barica (1977), or by using experimentally determined values for a conservative ion \( \text{e.g.} \, \text{Na}^+ \):

\[
W_{\text{Na}} = S_{\text{Na}} + \beta_{\text{Na}} + \theta_{\text{Na}}
\]

however, \( \text{Na}^+ \) is not released from the sediment:

\[
\theta_{\text{Na}} = 0
\]
and therefore:

\[ W_{Na} = S_{Na} + \beta_{Na} \]

The TWC ratio \( (r_x) \) was defined in Chapter 5:

\[ r_x = \frac{W_x}{S_x} \]  

where: \( W_x \) is the TWC for species \( x \) in winter

\( S_x \) is the mean TWC for species \( x \) in summer

Therefore for \( Na^+ \),

\[ r_{Na} S_{Na} = S_{Na} + \beta_{Na} \]

\[ \beta_{Na} = S_{Na} (r_{Na} - 1) \]

and the TWC ratio for \( Na^+ \) was determined by experiment (Table 5.2):

\[ r_{Na} = 1.4 \]

The ice exclusion effect is the same for all ions, thus for any species \( x \):

\[ \beta_x = 0.4 S_x \]

Therefore:

\[ W_x = S_x + 0.4 S_x + \theta_x \]

\[ W_x = 1.4 S_x + \theta_x \]

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Substituting for $W_x$ from Equation 5.1 and rearranging:

$$\theta_x = (r_x - 1.4) \cdot S_x$$

Equation 7.2

And the release ratio ($r_R$) for species $x$ and $y$ is:

$$r_R = \frac{\theta_x}{\theta_y}$$

Equation 7.1