DOCTOR OF PHILOSOPHY

Dissolved organic matter in the Southern Ocean

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DISSOLVED ORGANIC MATTER IN THE SOUTHERN OCEAN

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by

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To my parents and in memory of my great-grandmother
Jane Helen Hope (1908-2000)

SUMMARY

The main objective of the present study was to investigate the spatial and temporal distribution of dissolved organic matter in coastal, oceanic waters and sea ice of the Southern Ocean.

The distribution and dynamics of dissolved and particulate organic matter were investigated in surface waters at a shelf and oceanic station off the island of South Georgia in the South Atlantic sector of the Southern Ocean during an austral spring bloom. A weak coupling was observed between bacterial and phytoplankton activity. Dissolved organic carbon and nitrogen concentrations were in a similar range at both sites. The correlation observed between particulate organic carbon and nitrogen was not found for the dissolved organic carbon and nitrogen pools.

A time series study was conducted at the Rothera Time Series site in coastal waters of the Antarctic Peninsula over four consecutive years (austral summer 1997-austral summer 2001). Distinct seasonal changes in the organic matter concentrations were discerned. Dissolved and particulate organic carbon peaked in austral summer in correspondence with greatest phytoplankton abundance and decreased to negligible values in winter. A significant interannual variation was observed, with increasing dissolved organic matter concentration and phytoplankton abundance over time.

Dissolved and particulate organic carbon distribution was investigated in profiles of first and second year winter pack ice along a transect across the Weddell Sea. The study indicates an enrichment of dissolved and particulate organic matter in second-year sea ice.

The incorporation of dissolved organic matter in brine and ice was investigated in controlled experiments in virtually abiotic conditions. Inorganic nutrients were conservatively enriched in brine in comparison to water and ice phases, consistent with the processes of sea ice formation and brine rejection. Dissolved organic carbon was also enriched in brine but was more variable and enriched in comparison to the ranges expected from purely physical dilution, suggesting a different concentration effect of dissolved organic carbon in brine in comparison to inorganic nutrients.

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ABBREVIATIONS

ACC	Antarctic Circumpolar Current
AO	Acridine Orange
BB	Bacterial Biomass
BCD	Bacterial Carbon Demand
BP	Bacterial Production
BR	Bacterial Respiration
BGE	Bacterial Growth Efficiency
CTD	Conductivity-Temperature-Depth
°C	Degrees Centigrade
CV	Coefficient of Variation
DAPI	4', 6-Diamidino-2-phenylindole
DFAA	Dissolved Free Amino Acids
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DOM	Dissolved Organic Matter
GFF	Glass Fibre Filter
HPLC	High Pressure Liquid Chromatography
HTC	High Temperature Combustion
OPA	Orto-phthaldi-aldehyde
PF	Polar Front
POC	Particulate Organic Carbon
PON	Particulate Organic Nitrogen
RRS	Royal Research Ship
RV	Research Vessel
SD	Standard Deviation
TDAA	Total Dissolved Amino Acids
TOC	Total Organic Carbon
TIN	Total Inorganic Nitrogen
TON	Total Organic Nitrogen
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

1.1 Introduction

Oceanic dissolved organic carbon (DOC) is one of the three main global reservoirs of organic carbon, comparable to the carbon stored in terrestrial plants or the soil humus and in the atmosphere in the form of carbon dioxide (750 x 10^{15} g C) (Hedges, 1987; Farrington, 1992; Siegenthaler and Sarmiento, 1993). DOC is estimated to reach 700 x 10^{15} g C or 97% of total oceanic organic carbon, the second largest pool after dissolved inorganic carbon (DIC) in oceanic waters (Ducklow and Fasham, 1992; Hansell, 2002). The export of both particulate organic carbon (POC) and DOC from the surface of the ocean (the biological pump) to depth is responsible for maintaining the vertical gradient of DIC and indirectly the level of atmospheric carbon dioxide (Hansell, 2002). Knowledge of the amount of DOC has implications on the productivity of the ocean and on the biogeochemical global carbon cycling (Hedges, 1987). The understanding of the carbon cycle needs to follow and account for production and consumption processes within different environments. In particular, the Antarctic Ocean has an important role in the use of carbon dioxide from the atmosphere through both biological and physical processes. On a global scale it contributes 15% to the oceanic primary production (Huntley et al., 1991). This introduction intends to describe some of the main factors affecting dissolved organic matter (DOM) and to highlight its importance in parts of the Southern Ocean.

1.2 Formation of Organic Matter and the Microbial Loop

In the surface layers of the oceans, autotrophic organisms synthesise organic compounds using the energy provided by sunlight, needing carbon dioxide, inorganic ions and nutrients. It is a long-standing paradigm that organic matter fixed by the autotrophs becomes available to higher trophic levels, from phytoplankton to higher predators such as fish, seabirds and marine mammals along a relatively short trophic chain. However, in the early 1970s the role of heterotrophic bacteria as decomposers

of organic matter, remineralizing inorganic nutrients, was recognised with Steele's model (1974). The seminal paper by Pomeroy (1974) highlighted the role of the microbial "loop", based on the concept that DOM, released from a number of processes (see section 1.6), is channelled to bacteria and is available to re-enter the food web through micro-heterotrophs (protozoa) consuming bacteria (see also Jumars et al., 1989; Nagata, 2000) (see Fig. 1.1).

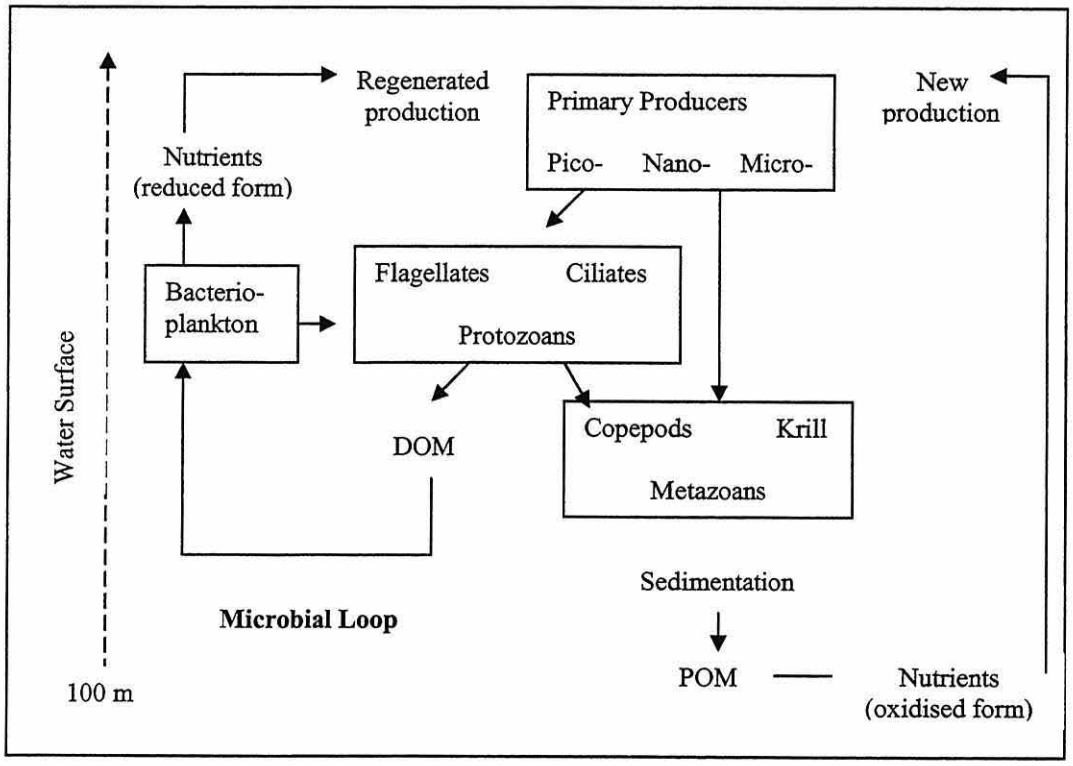

Fig. 1.1. Schematic diagram of the microbial loop in the euphotic zone illustrating the fate of dissolved and particulate organic matter. At each stage of the microbial loop food chain, regenerated inorganic nutrients are used up by phytoplankton (krill, copepods, metazoans). Adapted from Jacques (1989).

The microbial population in this sense was re-evaluated as representing a short cut to refuel the flux of organic matter along the upper trophic levels (Fig. 1.1). The significance of the microbial loop amplified into the concept of a complex microbial food web with the realisation of new trophic interactions between organisms (Azam et al., 1983; reviewed by Kirchman and Williams, 2000). Experimental investigations demonstrated mixotrophic consumption by protozoa and algae (Sherr et al., 1989; Le Fèvre et al., 1998), and the significance of viral lysis was highlighted (Proctor and Fuhrman, 1990).

1.3 Characterisation of Organic Matter

DOM has been operationally defined as the size fraction of organic matter separated from the particulate organic matter (POM) by an available nominal pore size filter used (0.2-1 μm, Strickland and Parsons, 1972). Despite small size cut-offs, the particulate form remains. This is because there is a continuum of organisms, from zooplankton down to picoplankton (0.2-2.0 μm size-range) and virioplankton (0.02-0.2 μm) (Antia et al., 1991; Fuhrman, 1999). DOM has been further classified into low molecular weight (LMW) compounds (<1000 Da[1] or 1 nm, e.g. monosaccharides, fatty acids, free and combined amino acids) and high molecular weight (HMW) or colloidal fraction (>1000 Da-500 kDa, e.g. large proteins, polysaccharides, humic and fulvic acids) (Benner et al., 1992; Guo et al., 1994; Guo and Santschi, 1997). Heterotrophic bacteria cannot utilise HMW compounds directly but have to produce hydrolytic exo-enzymes (Sundh, 1988). Both LMW and HMW fractions are produced during phytoplankton growth; however, it is argued that during the exponential growth LMW organic matter is preferentially produced while HMW compounds are released during the later decaying stages (Chróst and Faust, 1983; Passow, 2002).

The size-fractionated distinction is operational but does not take into account DOM biological, chemical and molecular composition or bioreactivity. Composition and physical size may indicate bioavailability of DOM to consumers and the diagenetic state of the DOM pool, according to the size-continuum model of Amon and Benner (1996, Fig. 1.2). The authors found that bacterial growth and respiration rates were 6 and 3 times higher respectively when using HMW rather than LMW DOC. Different molecular size fractions are found to differ in bioreactivity and consequently in their residence time in the ocean (Amon and Benner, 1994). Turnover rates of DOC compounds may vary in time scale from minutes to days (labile fraction), weeks to months (semi-labile) to years (refractory), and thus are further defined according to their lability.

[1] Dalton (Da) is the atomic weight unit corresponding to 1/12 of carbon atomic mass, i.e. 1.66×10^{-24}g

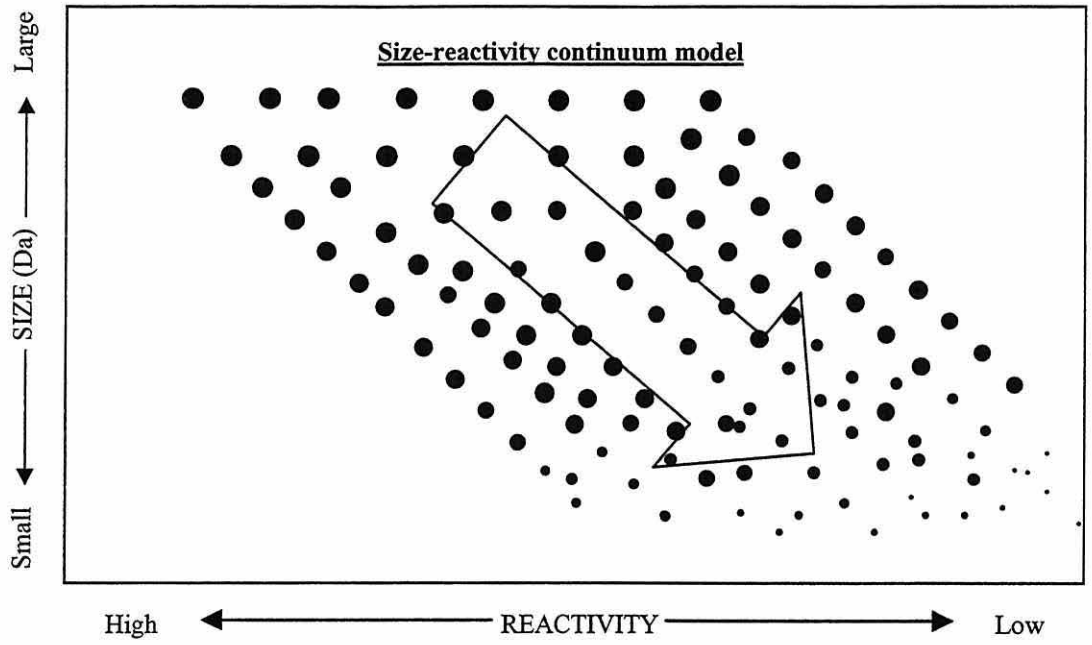

Fig. 1.2. Diagram of the model of the size-reactivity continuum. The concept implies that the macromolecules are sequentially decomposed into smaller-sized molecules and at the same time decrease in reactivity. The arrow indicates the pathway of degradation from bioreactive macromolecules to refractory micromolecules. Large dots represent particulate organic matter (POM), medium-size dots represent high molecular weight dissolved organic matter (DOM) and small dots represent low molecular weight DOM. Reactivity is measured by bacterial respiration via biological oxygen demand and production through leucine and thymidine incorporation rates. Figure adapted from Amon and Benner (1996).

Although there are data on the bulk DOC characterisation, only a relative small fraction of DOM (46-87%) has been identified at the molecular level in seawater, showing that the majority is unidentified and of low molecular weight (Mannino and Harvey, 2000; Benner, 2002). Total carbohydrates (combined and free) represent 10-25% of seawater DOC (Pakulski and Benner, 1994; Børsheim et al., 1999) and analyses have indicated that glucose is the major neutral aldose both in seawater and in phytoplankton cellular material (Mopper et al., 1980; Skoog and Benner, 1997; Biersmith and Benner, 1998). Dissolved free amino acids (DFAA) make up <10% of the DON pool and glycine is utilised for bacterial biosynthesis and remineralization and for phytoplankton cell protein synthesis, particularly under nitrogen-limitation conditions (Sharp, 1983; Tupas and Koike, 1990; Antia et al., 1991; Keil and Kirchman, 1991; Simon, 1991; Jørgensen et al., 1993; Bronk et al., 1994).

1.4 Dissolved Organic Carbon in the Marine Environment

Concentration gradients are found between surface and deep waters and between coastal and oceanic areas (Benner, 2002, examples of surface and deep waters in Table 1.1). Surface DOC concentrations in surface temperate and tropical waters are over twofold those reported at depth, due to the production of organic matter in the euphotic zone by the food web. DOC concentrations decrease at the thermocline and remain low and relatively constant (40-50 μM) at depth due to low bioreactivity (Guo et al., 1995; Chen et al., 1996; Hansell and Carlson, 1998).

Table 1.1. Concentrations of dissolved organic carbon (DOC) in surface and deep waters in a range of seas and oceans.

	Study Area	DOC (μM)	Reference
Surface Waters			
Pacific Ocean	North Pacific Subtropical Gyre	85-105	Church et al., (2002)
	North Pacific Subtropical Gyre	82	Benner et al., (1992)
	Equatorial Pacific (140° W)	70-74	Fry et al., (1996)
Atlantic Ocean	North Atlantic (Georges Bank)	72-85	Chen et al., (1996)
	North Atlantic (Georges Bank)	66-70	Fry et al., (1996)
	North Atlantic (Bermuda 32° N 64° W)	65-75	Ducklow et al., (1995)
	North Atlantic (Bermuda 32° N 64° W)	50-81	Fry et al., (1996)
	Coastal (Woods Hole Harbour)	99-105	Fry et al., (1996)
Indian Ocean	Central Indian Basin	52-191	Sardessai and de Sousa (2001)
Mediterranean Sea	North-western	75-92	Copin-Montégut and Avril (1993)
Norwegian Sea	Trondheimsfjord	78-80	Børhseim et al., (1999)
Southern Ocean	Polar Front	34-55	Kähler et al., (1997)
	Weddell Sea	45-60	Wedborg et al., (1998)
	Ross Sea	40-70	Carlson et al., (1998)
	Scotia-Weddell Sea	41-80	Cadée (1992)
	Australian Sector (56° S-144° E)	45-55	Ogawa et al., (1999)
Deep Waters			
	North Pacific Ocean	35	Bauer et al., (1992)
	North Pacific Ocean	41	Benner et al., (1992)
	North Atlantic (Georges Bank)	54-56	Chen et al., (1996)
	North Atlantic Ocean	43	Druffel et al., (1992)
	Southern Ocean	41	Druffel and Bauer (2000)
	North-western Mediterranean Sea	50-58	Copin-Montégut and Avril (1993)

DOC concentrations of 42-43 μM C have been recorded for deep waters in the North Atlantic (Bodungen and Kähler, 1994) and 35-39 μM C were observed in the older deep Pacific Ocean waters (Carlson and Ducklow, 1995). Long average residence time of 4000-6000 years, as ascertained through radiocarbon ^{14}C dating, shows the slow cycling and high refractory nature composed mostly by LMW (65%-80%) (Williams and Druffel, 1987; Malcolm, 1990; Benner et al., 1992).

While POC export is dominated by sinking, hydrodynamic processes such as diffusion and advection determine the vertical and horizontal transport of DOC, estimated to be in the order of 2 x 10^{-3} mol C m^{-2} d^{-1} (0.7 mol C m^{-2} yr^{-1}) both in the Gulf of Mexico and Sargasso Sea (Carlson et al., 1994; Guo et al., 1994). In sediment pore waters DOC is enriched by a factor of 3 to 50 (350 and 2000 μM C) in comparison to overlying seawater (40-350 μM) (Bauer et al., 1991; Chen et al., 1993; Hulth et al., 1997), indicating a considerable benthic diffusion process to the water column of refractory DOC, which over long timescales may be upwelled in surface waters.

In temporal terms, a seasonal variation in DOM has been observed in a number of geographically distinct coastal areas: from the English Channel, Californian Pacific coast, North Sea and Dutch coast to the north-western Sargasso Sea (Ducklow et al., 1995; Williams, 1995). The observations drawn are that the DOC production occurs predominantly during blooms, but is exported to the lower 100-250 m in winter, undergoing slow degradation during the rest of the year (Carlson et al., 1994). A limited number of studies have addressed the long term temporal variation in DOM in Antarctic coastal waters (Scott et al., 2000). This study intends to fill the gap in the knowledge.

1.5 Dissolved Organic Nitrogen in the Marine Environment

The nitrogen cycle is of importance to oceanic production given that the element is biolimiting to autotrophs. Dissolved inorganic nitrogen species (e.g. nitrate NO_3^-, nitrite NO_2^-, ammonium NH_4^+) assimilated by micro-organisms are transformed in structural proteins and enzymes. Typical components excreted by organisms are urea,

dissolved and combined amino acids. This nitrogen enters the biogenic cycle through assimilation and is released from the particulate form by bacterial remineralization. DON consists of a small amount of LMW organic compounds (e.g. amines, DFAA) released from organisms in comparison to the macro molecular components (>1 kDa) such as urea, humic and fulvic acids (McCarthy et al., 1997). Free amino acids have turnover times of minutes (Fuhrman, 1990). Other components of the DON pool are amino-sugars, purines, pyrimidines, peptides, polypeptides and proteins, all of which are released as decay products (e.g. purines and pyrimidines derive from the decomposition of nucleic acids), and are exuded from living cells (Newell et al., 1972). DFAA and ammonium have been outlined as important sources of energy for bacterial demand: apparently sustaining up to 90% of the nitrogen requirement of bacterioplankton and in carbon terms free amino acids sustain up to 40% of the carbon production (Keil and Kirchman, 1991; Simon, 1991; Jørgensen et al., 1993).

The total labile organic nitrogen, however, appears to represent only 10-20% of the DOM, dominated by a pool of slow cycling refractory biomacromolecules, possibly deriving from organisms structural parts, such as the mucopolysaccharide chitin or mureins and lipopolysaccharides present in bacteria cell walls (McCarthy et al., 1997). According to Hedges (1988), as referred to by Burdige and Zheng (1998), refractory DON can also be produced through abiotic condensation (i.e. geopolymerisation or humification reactions).

In the aquatic ecosystem, nitrogen gas, although inert, dominates the nitrogen reservoir, followed by the bioreactive and biolimiting inorganic nitrate ion and the less abundant nitrite and ammonium ions (Sharp, 1983). Nitrate is generally reduced in concentration in surface waters, with the exception of high latitudes and coastal and estuarine areas, whereas it increases below the euphotic zone (Sharp, 1983). Urea, although contended whether it is part of the DON reservoir, is a LMW compound found in concentrations ranging from 0 to 13 μM in surface waters, whereas amino acid concentrations vary between 20-600 nM in surface layers and 2-200 nM in deep water (Lee and Bada, 1977; Mopper and Lindroth, 1982; Jackson and Williams, 1985; Bronk, 2002). These chemical components represent only a small part of the DON pool (5-20%), which remains largely uncharacterised, despite its relevance in the nitrogen budget of oceanic waters. In addition, the vertical profiles of DON through

the water column show decreasing concentrations with depth, indicating production of DON by organisms in the euphotic zone and degradation of DON, largely by bacterial action, at depth (Jackson and Williams, 1985). DON has also been observed to be inversely proportional in concentration to nitrate in the English Channel and off Southern California (Banoub and Williams, 1972; Butler et al., 1979). Similarly, Lara et al., (1993), observed an inverse relationship between DIN and DON in the Greenland Sea (66-80° N) and typical range of DON concentrations between 2.5 and 6 μM, with the higher values found in the top 100 m and decreasing with depth. Maita and Yanada (1990) investigation in the oligotrophic North Pacific (24-49° N) found a range of DON values from 1 to 10 μM (see Table 1.2).

Table 1.2. Examples of concentrations of dissolved organic nitrogen (DON) reported for surface waters in a range of global oceans. See review by Bronk (2002).

Surface Waters	Study Area	DON (μM)	Reference
	Greenland Sea	4.5	Lara et al., (1993), Hubberten et al., (1994)
	North Pacific	8-10	Koike and Tupas (1993)
	Equatorial Atlantic	5-13	Vidal et al., (1999)
	Arctic	3.6-5.3	Wheeler et al., (1997)
Southern Ocean	Australian Sector	4.5	Ogawa et al., (1999)
	Ross Sea	2.1-6.3	Carlson et al., (2000)
	Polar Front	6.9-11	Kähler et al., (1997)

It has been estimated that 25-41% of the DIN taken up by phytoplankton by assimilatory nitrogen reduction is released as DON using the ^{15}N isotopic technique (Bronk et al., 1994; Feuerstein et al., 1997). Pujo-Pay et al., (1997) indicates levels of DON excretion of <10% of the DIN uptake from algal cultures kept in axenic conditions. DON is thus inserted into the nitrogen pool and will potentially fuel regenerated production after being oxidised by microbial populations through dissimilation and ammonification.

1.6 Sources and Sinks of Dissolved Organic Matter

During photosynthesis phytoplankton release extracellular products, such as carboxylic acids, glycolic acid, amino acids, polysaccharides, vitamins and sterols (Fogg, 1983; Malinsky-Rushansky and Legrand, 1996; Nagata, 2000). Other compounds are released, such as acrylic acid and dimethyl sulphide (DMS) as a defence mechanism in response to grazing pressure (Wolfe, 2000). The percentage of algal carbon extracellular release (PER) in relation to primary production is species-specific and varies according to the physiological state and growth-rate of phytoplankton. Healthy phytoplankton cells can release 10-15% of the total primary production (Bjørnsen 1988; Baines and Pace, 1991; Pujo-Pay et al., 1997). The amount of dissolved exudates released appears to be lower from larger algal cells than in picoeukaryotes (29%), and in oligotrophic systems the estimated percentage of algal production released is 25% in contrast to 5-10% in eutrophic systems (Sundh, 1988), suggesting a correlation of phytoplankton excretion with the nutrient conditions in oceanic waters.

Bacteria and algae also produce non-particulate dissolved exopolymer secretions (EPS) which buffer against osmotic pressure and dehydration and facilitate surface attachment to detrital particles and DOM aggregates, increasing potential DOM availability for higher consumers (Decho, 1990). EPS require large amounts of carbon, and a large proportion of the microbial secondary production (up to 62%) may be channelled into the production of these macromolecules (HMW polysaccharides, 100-300 kDa) (Decho, 1990). Phytoplankton also generate mucilage, in particular when conditions deteriorate (Passow, 2002): these are transparent exopolymer particles (TEP), which may form from colloidal substance polysaccharides released by phytoplankton and bacteria over a time scale of hours to days from initial release (Passow, 2000).

DOM can also be released as a consequence of the rupture of prey cells by the mouth parts of macrozooplankton by sloppy feeding (copepods, euphausiids) (Conover, 1966; Lampert 1978; Jumars et al., 1989; Billen and Becquevort, 1991; Strom et al., 1997). Protozoan grazers, such as ciliates and flagellates, are also known to release DOC by egesting food vacuoles (Nilsson, 1979; Nagata and Kirchman, 1992).

Peduzzi and Herndl (1992) and Hygum et al., (1997) report that herbivorous meso-zooplankton grazing enhances bacterial production and biomass. Another active release mechanisms of organic matter is excretion and the rapid diffusion of solutes from faecal material (Jumars et al., 1989; Lampitt et al., 1990).

Leakage of DOM from phytoplanktonic cell cytoplasm can also occur by autolytic or viral lysis. The former is an enzymatic process by direct action of autolytic enzymes present in the cells of organic tissues after natural death observed after the breakdown of blooms (see van Boekel et al., 1992; Agustí et al., 1998; Kirchman, 1999). In contrast, viral-induced lysis may be responsible for 10-50% bacterial and phytoplankton mortality, but results of modelling show that it can enhance bacterial production and respiration (Proctor and Fuhrman, 1990, 1991; Fuhrman, 1999).

Allochtonous DOM inputs to the marine environment occur through atmospheric, fluvial and erosion inputs. Riverine DOC concentrations are in higher range (400-800 μM) than marine waters (Amon and Benner, 1996; Mopper and Kieber, 2002). Terrigenous DOM consists of humic, fulvic acids and biopolymers representing around 0.7-2.4% of DOM with a residence time of approximately 20-130 years due to inert and refractory characteristics (Lee and Henrichs, 1993; Opsahl and Benner, 1997). However, riverine and terrigenous inputs, despite being large (0.25×10^{15} g $year^{-1}$), are considered negligible to the oceanic DOM pool (Benner, 2002; Mopper and Kieber, 2002).

Bacterial remineralization of organic matter yields energy in the form of adenosine triphospate (ATP) and involves the oxidation of carbon present in organic molecules (e.g. carbohydrates, proteins and lipids) to carbon dioxide. DOM is converted to inorganic matter through the aerobic respiratory activities of bacterial organisms in the water column. The process is important in returning inorganic carbon to the atmosphere and to re-fuel primary production. The remineralization process appears to be important in the upper parts of the water column (0-500 m), and less pronounced at depth. The assimilation of organic matter is a sink for DOM resulting in bacterial synthesis of organic compounds (bacterial production, BP) giving rise to essential proteins (e.g. valine, leucine, thymidine). Bacterial biomass is then available to

secondary consumers. BP is dependent and hence potentially correlated to phytoplankton production.

Several quantitative estimates have been made of the amount of DOC processed by bacterial plankton, operationally defined as the sum of bacterial secondary production (assimilation) and bacterial respiration (del Giorgio et al., 1997). The quantification of the carbon demand by the bacteria is debated, but it is estimated that between 5-50% of bacterial production is supported by the daily photosynthetic rate (Lancelot and Billen, 1985; Baines and Pace, 1991; Nagata, 2000; Williams, 2000).

The normal BP ratio relative to primary production (PP) is around 0.2 for the open ocean (Ducklow and Carlson, 1992). However, in the Arctic ocean the BP:PP ratios ranged from 0.7 to over 1.0 (Rich et al., 1997). In the Weddell Sea bacterial production was equal and in some instances higher than phytoplankton production in autumn (ratio of ≥1, Cota et al., 1990). The reasons behind these high bacterial productions could be the observed high concentrations, turnover and uptake rates of components of the DOM. Rich et al., (1997) found DFAA >200 nM and turnover rates of 0.23 day^{-1}. It has also been suggested that the picophytoplankton may utilise amino acids as a source of nitrogen and experiments with ^{3}H-amino acids have demonstrated such uptake by the prokaryotes in general (Li and Dickie, 1985). Similarly, Kirchman (1990) observed that in the sub-Arctic Pacific, DFAA are the most important factor in stimulating bacterial production as compared to other sources such as glucose and ammonium: bacterial growth rate was increased by addition of DFAA, whereas bacterial biomass was unchanged. However, it appears that below the mixed layer, respiration and decomposition processes do not affect the concentration of DOC, given that a poor correlation has been found between DOC and AOU (apparent oxygen utilisation) (Menzel and Ryther, 1968; Martin and Fitzwater, 1992; Wiebinga and de Baar, 1998).

Organic matter in the oceanic euphotic zone is sensitive to photo-chemical degradation, in particular by UV-A and UV-B sunlight rays (Mopper et al., 1991; Moran and Zepp, 1997; Mopper and Kieber, 2002). The process is important in view of the fact that the oxidation of 1% of seawater DOM would generate in one year a

carbon dioxide flux greater than that produced by anthropogenic fossil fuel combustion (Hedges, 2002). Photo-oxidation may also reduce the residence time of DOM (Mopper et al., 1991).

Aggregates of organic material may be physically generated by the collision and binding (coagulation) of colloidal DOM on gas bubble surfaces through adsorption in turbulent surface water conditions (Kepkay and Johnson, 1988). The colloidal fraction can aggregate further to form larger particles (>0.2 μm) and nanomolecular films, which may be aggregated into insoluble organic particles and by their shear size are potentially less available to bacterial respiratory action (Cauwet, 1981; Kepkay, 1990; Kepkay and Wells, 1992; Kepkay, 1994). However, direct experimental evidence by Kepkay and Johnson (1988) indicated that sea surface bubbling enhances microbial respiration (measured by oxygen consumption) by a factor of 4.8-11.2, showing that in fact this is a source of carbon for bacterial consumption and a mechanism for recycling DOC pool back to CO_2 in the upper water layers.

In temperate and tropical ocean surface waters the positive link between bacterial and primary production is well established (Cole et al., 1988). However, in areas of the global ocean such as the Southern Ocean, Equatorial and sub-Arctic Pacific, despite substantial quantities of inorganic nutrients, there is evidence of a low response by the primary producers and poor coupling between bacteria and primary producers. A delay in timing response between the two communities peak of activity has been observed (Cota et al., 1990; Karl et al., 1991; Karl, 1993; Lochte, 1997; Bird and Karl, 1999).

Organic matter produced by algae during a spring bloom may control microbial biomass, as it represents the main source of carbon for the microbial food web (van Boekel et al., 1992). The question whether it is organic resources that may play a role in limiting the bacterial production or it is a top-down control by protozoan grazing on bacterioplankton (Becquevort, 1997) is a subject of further testing. Recently, Pomeroy and Wiebe (2001) emphasised that multiple factors such as temperature and substrates may be interacting in limiting heterotrophic bacteria according to the environment.

1.7 The Southern Ocean

Sea ice formation in the polar environments is mostly a seasonal phenomenon on a large spatial scale with profound effects on the biogeochemical properties of the environment. Antarctic ice growth begins at the onset of austral autumn in early March, advancing in May-June and reaching its maximum extent in September. The ice cover ranges fivefold from 3-4 x 10^6 km^2 to a maximum of around 20 x 10^6 km^2 in the austral winter, representing 7% of the Earth's surface (Zwally et al., 1983; Staley and Gosink, 1999). With increasingly lower solar irradiance, increasing wind action and turbulence, seawater reaches its freezing temperature (-1.8 °C) at a salinity of approximately 35 and ice crystals start to aggregate into a solid lattice matrix. With the development of sea ice, the rejected liquid brine, containing 60 to 70% of the dissolved ions and particulate constituents of seawater, is extruded and trapped in a network of highly inter-connected channels and pockets of approximately <100 μm up to 1 cm diameter (Weeks and Ackley, 1982; Weissenberger et al., 1992). The sea ice is *per se* a system which undergoes physical and chemical changes, including increasing salinity, pH and gas concentrations. Therefore sea ice has a lower bulk salinity depending on the rate of ice formation, with salinity linearly related to speed of growth. The unstable water column during early ice formation is due to "haline" convection.

Sea ice is essentially a porous solid, characterised by inclusions of dissolved nutrients, gases, sediment and an active sea ice inhabiting (sympagic) biogenic community (Horner et al., 1992). The organisms found within sea ice include bacteria, dominating abundance, fungi, autotrophic and heterotrophic protozoa, microalgae (dominated by diatoms in terms of biomass) and a range of metazoa such as polychaetes, amphipods and euphausiids (Garrison et al., 1983; Palmisano and Garrison, 1993). The composition and distribution of the sympagic assemblages have been studied *in situ* and experimentally. However there is scope for work on determining the fate of organisms, suspended and dissolved compounds during the first stages of ice growth, in particular due to difficulty associated with the logistics of sampling. The literature reporting on the freezing periods highlights the enrichment of sea ice in terms of abiotic and biotic components. Recently, Tuschling et al., (2000) reported enhanced

phytoplankton biomass in the Laptev Sea (Arctic) in autumn sea ice in comparison to the underlying water, but a partial representation of the water species. On the other hand, Gradinger and Ikavalko (1998) described a sea ice ecosystem in which all species in the water were found in the ice.

However, the sea ice has also been characterised by the presence of DOM, consisting of an array of compounds produced by *in situ* processes, such as grazing, algal and bacterial exudation, bacterial ectoenzymatic activity, viral lysis of phytoplanktonic cells and mechanical damage (Sullivan and Palmisano, 1984; Baines and Pace, 1991; Gleitz and Thomas, 1993; Hygum et al., 1997). DOM is vital in providing the energetic substrates for the microbial community and has potential cryoprotectant properties (Krembs et al., 2001). Despite DOM being an important component of sea-ice only relatively few studies have determined concentration of DOC in polar sea ice both in the liquid brine and solid ice phases. In Arctic multi-year sea ice core profiles, typical DOC concentrations of 50-100 μM have been recorded (Thomas et al., 1995); however >600 μM DOC was observed in the bottom ice of one sea ice core, despite no correlation with chlorophyll *a* concentration (<2 $\mu g\ l^{-1}$). DOC concentrations (50-200 μM) in bottom layers of first-year sea ice in the Canadian sub-Arctic exceeded those in the underlying seawater and were strongly correlated to bacterial abundance and production (Bunch and Harland, 1990). In ice cores from the Antarctic perennial pack ice DOC concentrations in brine have been measured up to 2000 μM, despite a relatively low biological activity (Thomas et al., 1998, 2001). DOC concentrations in platelet ice from a Weddell Sea coastal inlet have been observed in the 100-200 μM range, double the open water values measured in the area (Thomas et al., 2001).

The studies in the literature show variability in the quantity of DOC, which may depend on a variety of factors, such as mode of ice formation, ice age and the sympagic communities associated. However, the common indications are that DOC is enriched relative to the open water and is actively produced and consumed within sea ice. In particular the lower ice layers, next to the ice-water interface, seem the most productive and DOM-enriched sites, replenished by nutrients from the underlying water and by gravity-driven brine draining from the upper layers. Upon melting this has been shown to act as an important inoculum of DOM into the water column

available for uptake and growth by both bacteria and phytoplankton (see Brandini and Baumann, 1997; Kähler et al., 1997).

Few data are available for individual DOC substrate classes distribution within sea ice. Thomas et al., (2001) recorded a high variability of total dissolved carbohydrate contribution averaging around 35% of the DOC pool, with maximum values of 99%. Recently Amon et al., (2001) reported a DOC concentration of 112 µM from an Arctic ice floe inhabited by algae, observing that neutral sugars and free amino acids contributed to 21% of total DOC (glucose being the dominant free aldose) and were in concentrations higher than ambient seawater levels. Herborg et al., (2001) indicated that total carbohydrates contribute up to 30% to DOC in Weddell Sea ice cores, dominated by monosaccharides.

No investigation has been conducted to study the effects of ice formation and growth on dissolved organic constituents contained in surface seawater and distribution within the formed ice matrix. Experimental work and analyses of field samples have shown that the initial concentration and distribution of inorganic nutrients within sea ice cores are determined by the salinity of the ice and that nutrients are proportional to the brine salts rejected, showing conservative behaviour (Clarke and Ackley, 1984; Cota et al., 1987; Garrison et al., 1990). However, the mode of ice formation, whether under turbulent or calm conditions, may drive the process of incorporation. On one hand, Weissenberger et al., (1992) stated that planktonic organisms may not be incorporated efficiently under slow, quiet thermodynamic ice growth. On the other hand, Garrison et al., (1983) and Gleitz and Thomas (1993) have shown that phytoplantkonic organisms are physically enriched in sea ice. Parallel questions have arisen on mechanisms of DOM inclusion into the sea ice during initial ice formation during the autumn freezing phase. Is it a conservative mechanism, purely driven by physical dilution processes or is it due to biological processes? Is it scavenged like microalgae or is it actively produced within the ice? One of the major problems hindering such investigations is to separate biological influences from the physical and chemical processes, as well as being able to follow temporal developments. Laboratory controlled production of sea ice (Grossmann and Gleitz 1993; Weissenberger and Grossmann, 1998; Haas et al., 1999) can thus be a useful tool to study and monitor such processes.

1.8 Thesis Objectives

The main objective of this thesis is to determine organic matter spatial and temporal distribution using a broad spectrum of measurements from key environments of the Southern Ocean in coastal and oceanic waters and in the sea ice ecosystem. Another aim is to propose factors and/or mechanisms which may control the distribution of DOC.

Specifically in coastal waters the objectives were:

i) To determine the spatial distribution and biogeochemical cycling of DOC and POC in surface open and coastal water profiles at the island of South Georgia in response to an austral bloom.

ii) To investigate the seasonal variations and characterise the long-term trends in the interannual variations of DOC and POC in coastal waters of the western Antarctic Peninsula using unique records of these variables.

In sea ice the objectives were:

i) To characterise the spatial distribution of DOC in first- and second-year winter to early spring Weddell Sea pack ice and propose factors affecting variations in concentrations.

ii) To determine whether DOC behaves conservatively or non-conservatively during sea ice formation through an experimental simulation of incorporation of DOM into newly forming, young sea ice.

1.9 Chapters Outline

Chapter 1 provides a theoretical background to the thesis, introducing the concept of organic matter, its characterisation and reviewing the sources and removal mechanisms of DOC. The second part of the chapter focuses on the importance of

organic matter in the Southern Ocean environment, with a physical and ecological overview of the marine and seasonal sea ice ecosystem.

Chapter 2 summarises the analytical protocols employed, the methodologies adopted and equipment used for both chemical and biological determinations, including specifications and details on accuracy and precision. Methods are described specifically according to the study presented in each of the chapters.

Chapter 3 summarises the distribution of POC, PON, DOC and DON in surface water profile in a sub-Antarctic area of the Southern Ocean during early austral spring. It provides a survey of organic carbon dynamics at the shelf and in the oceanic waters off the island of South Georgia, which is a productive and interannually variable area, where no previous survey had been carried out in this period of the year. The turnover of DOC is estimated and the data is discussed in relation to biological data available.

Chapter 4 presents a monthly monitoring of seasonal and interannual variability in DOC and POC concentrations in coastal shelf waters at Ryder Bay, Rothera Station, western Antarctic Peninsula. The variation in concentrations is considered in relation to changes in the phytoplankton abundance over a four year period with a bi-weekly to monthly sampling resolution.

Chapter 5 addresses the distribution of DOC and POC concentrations in profiles of seasonal and multiannual ice cores sampled from floes of the semi-closed pack ice of the Weddell Sea during late winter and early spring. Variations in the sectioned cores are related to potential factors affecting the concentrations.

Chapter 6 presents the results of a novel experiment using indoor large scale facilities in order to simulate the incorporation of DOC into newly forming sea ice in virtually abiotic conditions and quiet growth conditions.

The thesis concludes with a general summary in Chapter 7 highlighting the overall results and recommendations for future investigations.

CHAPTER 2

METHODOLOGIES

2.1 Introduction

The present chapter summarises the analytical procedures used during the research project. Specific methods, materials and experimental designs are described in each of the following chapters in relation to the specific study. The core of this chapter lies in the determination of the particulate and dissolved organic matter (POM and DOM) in aquatic samples of oceanic origin. DOM was partly characterised in the form of monosaccharides and dissolved free amino acids (DFAA) for the experimental part of the thesis (Chapter 6). Bacterioplankton abundance was the only biological parameter determined. The present chapter is divided in the following sections: section 2.2 describes the analysis of dissolved organic carbon (DOC), section 2.3 the determination of particulate organic carbon and nitrogen (POC and PON), section 2.4 describes the determination of dissolved organic nitrogen (DON); sections 2.5 and 2.6 summarise analytical protocols for monosaccharides and DFAA, concluding with bacterial abundance estimation in section 2.7.

Chlorophyll *a* (chl *a*) data were provided courtesy of J. Priddle (British Antarctic Survey, BAS, Chapter 3). Primary production data were provided courtesy of L. Gilpin (Napier University, Chapter 3). Bacterial biomass and bacterial production data were provided courtesy of R. Leakey (Dunstaffnage Laboratory, Chapter 3). All dissolved inorganic nutrients data were analysed courtesy of M. Whitehouse (BAS, Chapter 3) on board the JR25 research cruise. Chl *a* and temperature data from the Rothera Time Series (RaTS) oceanographic programme were provided courtesy of A. Clarke (BAS, Chapter 4). Chl *a* and inorganic nutrients data from the Winter Weddell Gyre study sea ice cores were provided courtesy of H. Eicken (University of Alaska Fairbanks, Chapter 5). Dissolved inorganic nutrient data in the sea ice simulation experiment (Chapter 6) were provided courtesy of G. Kattner (Alfred

Wegener Institute, AWI). Brine volumes and ice temperatures were provided from the sea ice growth experiment (Chapter 6) courtesy of C. Haas (AWI).

2.2 Dissolved Organic Carbon

A range of methods and instruments have been introduced over the last 40 years to determine the amount of organic carbon in aquatic samples. The approaches are based on wet chemical oxidation (WCO; Menzel and Vaccaro, 1964), ultraviolet oxidation (UVO; Williams, 1969), dry combustion and the more recent and widely used direct aqueous injection/high temperature combustion (DI/HTC) method (Sharp, 1973). Following the paper of Sugimura and Suzuki (1988) reporting DOM values in the North Pacific Ocean up to four times higher than previously measured with a high temperature catalytic oxidation (HTCO-Platinum catalyst) method, an international debate on the adequacy and performance of methods was initiated. Despite a later retraction (Suzuki, 1993), a great number of studies has been dedicated to the analytical determination of organic matter and to the oxidation efficiency of instrumentation.

The basic principle of all organic carbon determinations lies on the complete oxidation of organic carbon to carbon dioxide (CO_2). This is followed by the detection of CO_2 by using a range of techniques, i.e. conductometry, titrimetrically with a pH indicator, potentiometrically and the more often used non-dispersive infra-red analysis (NDIR) due to its greater sensitivity (Mopper and Quian, 1999). WCO methods use a strong oxidant added to the sample, from which dissolved inorganic carbon is removed by sparging and acidification. However, WCO techniques tend to have a low oxidation efficiency and are labour-intensive in comparison to UVO or HTC (Mopper and Quian, 1999). UVO has better oxidation efficiencies (95%) than WCO but certain algal compounds may be refractory to UV oxidation and other problems may be the ageing of the lamp, deterioration of performance and ozone production (Chen and Wangersky, 1993).

HTC analytical instruments generally show 100% oxidation efficiency of dissolved organic matter to CO_2 for marine water samples up to 400 µM C when compared to

the method developed by Fry et al., (1993) using long term sealed tube combustion, which employs oxidation times 200-10,000 times greater than the other techniques (Peltzer et al., 1996). Differing makes and models of HTC have been introduced commercially and comparison of samples taken onboard in the North Atlantic Ocean with three differing HTC instruments resulted in a good agreement of results as the coefficient of variation (CV[1]) was 5.7% (Fitzwater and Martin, 1993). The most widely used methods are based on HTC, although the greatest obstacle in all organic carbon determinations at present appears to be the difficulty in achieving a reasonably DOC-free water blank.

All DOC samples were measured in the laboratory by HTC on a total organic carbon analyser (model specification: TOC-5000, MQ 1001) according to the protocol in Quian and Mopper (1996). Water samples for DOC determination were collected in pre-cleaned and rinsed 1 dm^3 Duran bottles. Water was filtered through pre-combusted (500 °C, 3 h) 25 mm Whatman GF/F glass fibre filters, (nominal pore size 0.7 μm) using an all glass, pre-cleaned filtration flask. Pre-cleaning of glassware consisted of acid-washing (10% HCl) and copious rinsing with deionised water, followed by pre-combustion at 500 °C for 3 h. Samples were dispensed in pre-combusted (500 °C, 3 h) 30 cm^3 glass ampoules (500 °C, 3 h) (Smith et al., 1995). Heat-sealed, leak-tight ampoules were preserved in the dark at -20 °C until analysis. Ampoules were kept at 4 °C in the dark for over 12 h, then shaken vigorously and sub-samples transferred to pre-combusted (500 °C, 3 h) 5 cm^3 borosilica amber glass vials and placed on the instrument autosampler.

The instrument used for DOC determination is based on direct motorised injection of seawater into a HTC furnace. The machine is equipped with a double-needle arrangement (loop-type autoinjector) which ensures that in-between sample injection the needle is air sparged with ultra-high purity oxygen (99.999%; BOC Special Gases, UK) at 150 ml min^{-1} as the carrier gas. The oxidising column is filled with pure quartz beads (Elemental Microanalysis Ltd.) enabling the direct conversion of DOC to CO_2. Any remaining reduced material is oxidised by the copper oxide

[1] $CV = \frac{SD}{\bar{x}}$, SD = standard deviation, $\bar{x}$ =arithmetic mean

converting carbon monoxide (CO) to CO_2. The CO_2 produced through combustion is channelled and measured on a non-dispersive infrared absorbance Li-Cor analyser Model 6252 and water vapour is retained by a column of anhydrous magnesium perchlorate, the contents of which are discarded and replaced daily.

Chemicals used in the routine analysis were of reagent grade quality and aqueous solutions were prepared using freshly UV-irradiated (1 h) deionised water (Peltzer and Brewer, 1993). All glassware was soaked overnight in 10% Decon 90, drained and rinsed 5 times with de-ionised and Milli-Q water and pre-combusted (500 °C, 3 h). Sample and blank acidification was achieved by the addition of 10 µl of 85% phosphoric acid (v/v) to 3.2 ml of sample in pre-combusted (500 °C, 3 h) borosilica glass vials, resulting in a pH of <2. Prior to injection acidified samples were automatically sparged for 5 minutes with a stream of ultra-high purity oxygen and standard zero grade nitrogen gas to further remove any trace of inorganic carbon.

Triplicate 100 µl samples were injected in the analyser at the processing rate of 15 samples h^{-1} (sample frequency of 4 minutes). The oxidation column was conditioned by several repeated injections of freshly UV-irradiated water to obtain low and stable water blanks prior to analysis. Eight-point standard addition curves, in the range 25-800 µM C, were made at the beginning and end of each run with potassium hydrogen phthalate (KHP, Aldrich) added to de-ionised UV-irradiated water, with standards placed in ascending concentration order. During the run, freshly UV-irradiated water was included with every other sample and sample signals were blank-corrected. The DOC concentrations were calculated from verified peak area integration using specific TOC-5000 Peak Windows 95 software.

Calibration curves obtained were linear from 25 to 800 µM added C. The detection limit of the TOC analyser in optimal conditions is 2-3 µM C with a 60 µl sample loop, a column temperature of 750 °C and a flow rate of 140 ml min^{-1} (Quian and Mopper, 1996), however the limit of detection during analyses was approximately 8 µM C. The DOC concentration measured in replicate analyses of seawater collected from the Menai Strait (n = 10, DOC = 118 µM C) had a coefficient of variation (CV) of <5%. The CV for replicate analysis of a 50 µM C standard was between ±

5-7 μM. The CV for replicate analyses of UV-irradiated water was ± 8-10% and blanks were equivalent to 10-15 μM C.

2.3 Particulate Organic Carbon and Nitrogen

The analytical procedure for measuring levels of POC and PON was originally introduced by Gordon (1969) and Kerambrun and Szekielda (1969), with later modifications by Sharp (1974). The present assay follows the original procedures with analytical modifications suggested by the instrument manual (Europa Scientific Ltd.). The analysis of POC and PON was performed by gas chromatography on a Europa Scientific RoboPrep Biological Sample Converter CN Analyser by combustion at 1020 °C, using high purity helium as the carrier gas (Hedges and Stern, 1984).

Water samples for the determination of POC and PON were collected in pre-cleaned polypropylene bottles and known volumes filtered onto 25 mm diameter pre-combusted GF/F filters (Whatman, 500 °C, 3 h) under mild vacuum (5-10 psi). Filters were placed in plastic Petri dishes and preserved in the dark at –20 °C until analysis. Prior to analysis filters were punched with a laboratory-built stainless steel corer to retain only the filtered material. In order to remove any inorganic carbon present in the samples, carbonates from shells, exoskeletons and tests, the filters were placed in a desiccator saturated with concentrated hydrochloric acid (HCl) vapour (reagent grade, Merck), used given its non-oxidising nature (Hedges and Stern, 1984; King et al., 1998). Filters were oven-dried at 60 °C for 24 hours and wrapped in pre-combusted (500 °C, 3 h) aluminium discs (30 mm diameter, Elemental Microanalysis Ltd.). Discs were shaped in the form of small pellets and kept in an under-vacuum desiccator filled with oven-dried silica gel pellets until analysis.

The analyser oxidation furnace was packed with chromium trioxide (Cr_2O_3), an oxidation catalyst, overlaying copper oxide wires, to convert CO to CO_2, and silver wool, to remove traces of sulphur, all separated by a layer of fine quartz wool. The organic carbon and nitrogen are respectively converted to carbon dioxide and

nitrogen oxides, and the oxides of nitrogen are subsequently reduced to molecular nitrogen gas (N_2). Both gases are separately detected on a gas chromatography column at 100 °C by a thermal conductivity detector. Peak areas were integrated using an ANCA integrator software programme.

Acetanilide was used as the primary calibration standard ($C_6H_5NHCOCH_3$ Molecular Weight = 135.16, BDH Chemicals, National Bureau of Standards recommended), used commonly for reference for its long-term stability. Standards and weighing tin boats were weighed out on a CAHN electronic microbalance (accuracy ± 1 μg) directly before each batch run and wrapped in pre-combusted (500 °C, 3 h) aluminium discs (Merck, UK) (Verardo et al., 1990). Calibration of the instrument was performed prior to and after each batch of samples analysis.

A linear response was obtained for 6-point calibration curves covering the range 2-50 μM C and 0.2-6 μM N. The CV of replicate (n = 6) Menai Strait seawater samples was <8% for POC and <6% for PON. Limit of detection estimated as three times the standard deviation (SD) of the blank (Taylor, 1987) resulted in 5.7 μg C and 1.28 μg N (n = 19).

2.4 Dissolved Organic Nitrogen

In order to determine DON the method requires conversion to a final analyte, usually NO_3^- + nitrite NO_2^-, ammonium NH_4^+ (see review by Sharp, 2002). The three methodologies developed available for the determination of DON are the persulphate oxidation (Menzel and Vaccaro, 1964; Koroleff, 1977), ultraviolet light oxidation (Armstrong et al., 1966) and high-temperature oxidation (Sharp, 1973; Suzuki and Sugimura, 1985). A comparison between these latter methods available to determine total dissolved nitrogen found that the persulphate oxidation has the highest recovery and lowest limit of detection (Bronk et al., 2000). New techniques are now being developed to simultaneously determine DON and DOC on the same manifold (Raimbault et al., 1999; Sharp et al., 2002).

The analysis of organic nitrogen in solution in the present study was performed by a wet chemical oxidation using the persulphate oxidation technique, adapted from the method of Koroleff (1983) (G. Kattner, pers. comm.). Analysis was performed within a few hours of seawater samples collection. Water samples were collected from Niskin bottles in pre-combusted (500 °C, 3 h) Duran bottles and then filtered through pre-combusted GF/F filters (500 °C, 3 h) under vacuum. The samples were oxidised by adding an alkaline oxidising reagent solution composed of 7.5 g sodium hydroxide (NaOH), 15 g potassium persulphate ($K_2S_2O_8$), and 25 g boric acid (H_3BO_3) dissolved in Milli-Q water. Samples were transferred to 80 cm^3 capacity, screw-cap Teflon bottles and digested by autoclaving under pressure at 120 °C for 1 h. The samples were removed from the autoclave, allowed to cool and analysed for the inorganic products nitrate, nitrite and ammonium using standard procedures on a Technicon Autoanalyser according to Whitehouse (1997). The concentration of DON was calculated from the difference between the dissolved inorganic nitrogen (composed of the sum of nitrate NO_3^- + nitrite NO_2^-, ammonium NH_4^+) measured initially before oxidation and the total dissolved nitrogen after the oxidation.

2.5 Determination of Monosaccharides

Carbohydrates are compounds of carbon, hydrogen and oxygen and have the general formula $(CH_2O)_n$. In order to analyse monosaccharides such as glucose, galactose and fructose, with 6 carbon atoms (i.e. exoses), the method of analysis used was based on the spectrophotometric protocol by Avigad (1968), later modified by Myklestad et al. (1997). The method has advantages in comparison to other methods determining carbohydrates in seawater (Duursma and Dawson, 1981): most other methods require desalination and concentration steps which are not necessary for this method.

The determination of the carbohydrate concentration is a sensitive colorimetric determination of ferrocyanide formed by reducing sugars. The reduced iron is allowed to react with a reagent for Fe^{2+} [tripydridyl-*s*-triazine (TPTZ)] to give a strongly violet/blue $Fe(TPTZ)^{2+}$ complex (Myklestad et al.,1997). The samples were collected into pre-cleaned and rinsed 1 dm^3 Duran bottles, filtered through pre-

combusted Whatman GF/F filters (500 °C, 3 h) and dispensed into 30 cm^3 pre-combusted glass ampoules (500 °C, 3 h) which were heat-sealed and stored in the dark at -20 °C. Ampoules were thawed for 15-18 h at 4 °C in the dark. Glassware was immersed for 24 h in 10% Decon 90, rinsed 5 times with distilled water and 5 times with Milli-Q water and combusted at 500 °C for 3 h. Molar concentrations of monosaccharides were determined from the control-corrected absorbance data using a glucose standard. All samples were run as triplicates and care was taken in the experimental set-up to shield the reaction from light sources due to photosensitivity of the method. Reagents were stored in amber glass bottles and wrapped in aluminium foil to prevent light degradation. Calibration was linear over the range 8-133 μM C. The CV for replicate analyses of seawater was <4%.

2.6 Determination of Dissolved Free Amino Acids

Amino acids are defined as the organic molecules containing an amino group ($-NH_2$) and a carboxylic group (-COOH) and are the monomeric building blocks of proteins. Analytical methods for the determination of free amino acids range from protein sequencing, colorimetric methods (Rosen, 1957) to high pressure liquid chromatrography (HPLC) methods. However, because of the unavailability of an HPLC instrument at the time of analysis the wet chemical method of pre-column derivatisation was chosen and glycine was determined by the ortho-phthalaldehyde fluorometric analysis which is specific for primary amines according to Parsons et al., (1984), based on adaptations of the original methods (Benson and Hare, 1975; Dawson and Pritchard, 1978; Lindroth and Mopper, 1979).

Glycine was determined by the reaction of primary amines with the fluorogenic reagent ortho-phthlaldehyde in the presence of 2-mercaptoethanol to form fluorescent derivatives. Glassware was immersed overnight in 10% Decon 90 and rinsed 5 times with distilled water and 5 times with Milli-Q water and combusted at 500 °C for 3 h. Samples were analysed in triplicate. The fluorescing products are measured at 450 nm emission wavelength and excitation at 340 nm on a Hitachi Fluorescence Spectrophotometer F-2000 using a 1-cm quartz cell. Molar concentrations of glycine were determined from the control corrected absorbance data using a glycine standard. A 6-point calibration curve was linear over the range

0.2-10 μM N. The detection limit is 0.04 μM N. The CV from replicate seawater samples (n = 9, average concentration = 0.9 μM) was 5-6%.

2.7 Estimation of Bacterioplankton Abundance

The methodologies available to determine total bacterial counts range from plate spreading to flow cytometry counts, however the two fluorochrome staining techniques, using either acridine orange (AO, Hobbie et al., 1977) or 4', 6-diamidino-2-phenylindole (DAPI; Coleman, 1980; Porter and Feig, 1980) are the most widely used for determining the total bacterioplankton counts. Both methods are based on the staining of bacterial nucleic acids (DNA and RNA). The DAPI method was used in the present study as it allowed for up to 24 weeks time interval between slide-preparation and counting in comparison to only two weeks recommended by the AO technique and it appears to be highly specific, whereas the AO technique has been found to bind to colloidal or detrital matter (Sieracki et al., 1985).

However bacteria non-growing nucleoids, labelled as bacteria "ghosts" have been observed in samples analysed (Zweifel and Hagström, 1995), thus a part of the stained cells may not be living. Other studies have pointed out that 10-25% of the enumerated bacteria cells are prochlorophytes and not heterotrophic bacteria (Sieracki et al., 1995). Water samples for bacterial abundance were collected in 20 cm^3 autoclaved glass vials and were preserved with 2 ml of 20% buffered formaldehyde (final concentration 1% v/v) and were kept refrigerated in the dark at 4 °C until staining. Before filtration samples were sonicated for 5 minutes in order to prevent clumping of bacterial cells. Sub-samples were filtered onto 0.2 μm Nucleopore polycarbonate filters, precoloured with Irgalan black, stained with the fluorochrome DAPI. Filters were mounted on glass microscope slides and the slides were stored in the dark at -20 °C. Free-living bacterial cells were enumerated by epifluorescence microscopy x 1250 magnification (Leitz) under a UV light (Porter and Feig, 1980). Thirty whole microscopic fields of view were examined and total bacterial numbers counted amounted to between 200 and 400. The precision in the

method is determined by the number of field of views analysed, more than the number of sub-samples (Kirchman et al., 1982).

Bacterial production (BP) was measured according to the tritiated radiolabelled {3H-methyl}-thymidine (^{3}H-TdR) DNA incorporation method of Fuhrman and Azam (1982), courtesy of R. Leakey. The quantification of bacterial production from incorporation measurements (either thymidine or leucine) depends on the use of a specific conversion factor. No universally accepted factor is available for converting either bacterial abundance to biomass or ^{3}H-TdR incorporation to biomass production (Steinberg et al., 2001). Conversion to bacterial carbon biomass was calculated using bacterial cell counts and a chosen conversion factor of carbon density of bacterial cells of 25 fg C cell^{-1}, according to Lee and Fuhrman (1987). The factor represents a high-end of the scale density for cellular carbon as Carlson et al., (1999) used a lower carbon content of 7-13 fg C cell^{-1} in Antarctic waters. The conversion factor used was 2 x 10^{18} cells mol^{-1} thymidine incorporated (see Kemp, 1994). Pomeroy and Wiebe (2001) have recently argued that bacterial production may be underestimated when using a conversion factor according to Fuhrman and Azam (1980).

CHAPTER 3

ORGANIC CARBON DYNAMICS IN SURFACE COASTAL AND OCEANIC WATERS OFF THE ISLAND OF SOUTH GEORGIA, SOUTH ATLANTIC

3.1 Introduction

The following chapter presents the results obtained from an oceanographic survey carried out between 28 October and 9 November 1997 at an on-shelf and offshore station in ice-free surface waters of the island of South Georgia in the South Atlantic sector of the Southern Ocean. The aim of this study was to investigate and compare the dynamics of organic carbon and nitrogen in the dissolved (DOC, DON) and particulate (POC, PON) fractions in response to an austral spring bloom in surface shelf and oceanic waters. The chapter is divided as follows: section 3.2 provides a brief environmental setting to the area, followed by a description (section 3.3) of the location of the sampling sites (see Chapter 2 for analytical methods), section 3.4 presents the findings by comparing the shelf and oceanic sites in terms of DOC and POC distribution and providing a scenario on the basis of relevant biological and physical parameters. The chapter concludes with a discussion (section 3.5) of factors affecting DOC and its turnover in relation to the phytoplanktonic and microbial community.

3.2 Environmental Setting

The study was set off the north-west coast of the island of South Georgia, in the South Atlantic Sector of the Southern Ocean (Fig. 3.1a). The island lies in a permanently ice-free zone, to the south of the Polar Front (PF). The PF is a circumpolar boundary between cold, surface Antarctic waters meeting warmer, sub-Antarctic water masses and varies in position, but is usually found at ~50° S in the South Atlantic sector (Whitworth, 1988). The PF or Antarctic Convergence is characterised by the sinking of southern, cold, dense water masses below milder water masses from lower latitudes, resulting in an area of complex hydrography, with eddies and meander formations. The cold polar waters are collectively known

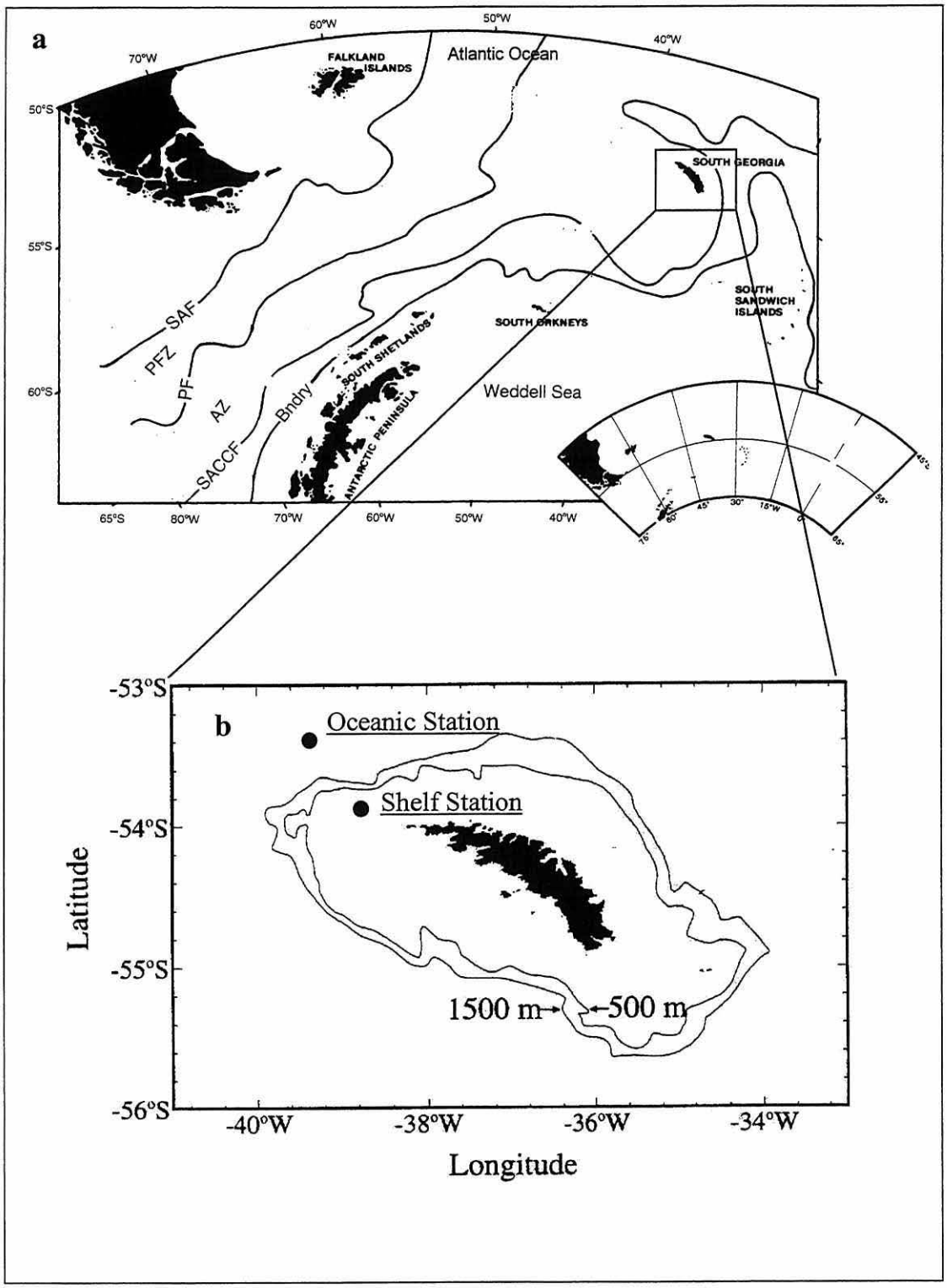

Fig. 3.1. a) Map showing the position of the sampling area located within the South Atlantic sector of the Southern Ocean. Shown are the main hydrographic provinces and fronts. Abbreviations are as follows: SAF = Sub-Antarctic Front, PFZ = Polar Front Zone, PF = Polar Front, AAZ = Antarctic Zone, SACCF, Sub-Antarctic Coastal Current Front. **b**) The map shows the location of the oceanic and shelf sampling stations (•) visited during the 1997 JR25 Spring Processes oceanographic cruise on board the RRS *James Clark Ross*. The arrows indicate the 500 m and 1500 m bathymetric contours. The figures were adapted from Atkinson and Sinclair (2000) and Atkinson et al., (2001).

as the Antarctic Circumpolar Current (ACC), approximately 200 m deep, primarily wind-driven, overlying warm and nutrient-rich circumpolar deep water. The ACC flows eastwards and reaches the island of South Georgia to the north and west, contributing with wind-stress to the glaciation of over 50% of its area (Whitworth, 1988). The ACC also meets the clockwise Weddell Gyre from the south-east, rich in silicate, giving rise to the Weddell-Scotia Sea Confluence boundary (Bianchi et al., 1992; Whitehouse et al., 1996).

The ACC collectively comprises three areas, each separated by frontal systems: the northernmost Sub-Antarctic Zone (SAZ), the relatively constant Polar Frontal Zone (PFZ) and the Antarctic Zone (AZ), the latter comprising both stations sampled during the present study (Whitehouse et al., 2000, Fig. 3.1a). A broad shelf of approximately 500 m depth extends around South Georgia to 50-150 km from the coastline. This area is subject to shallow water processes, including tidal mixing, ice-melt and island run-off. Off-shelf, water depth drops to 1500 m, reaching up to 3000-4000 m further offshore (Brandon et al., 1999, Fig. 3.1b). A degree of exchange between water masses has been observed to occur at shelf fronts (Deacon, 1982; Brandon et al., 1999).

The Southern Ocean is one of three areas in the global context referred to as a High Nutrient Low Chlorophyll (HNLC) area similarly to the equatorial and sub-Arctic Pacific (Banse, 1995). This concept refers to the abundance of inorganic nutrients (nitrate, ammonium, phosphates) but a general low response in terms of productivity. Studies have suggested a suite of limiting or co-limiting factors may control phytoplankton productivity, such as the availability of dissolved iron, temperature, light intensity and water column mixing (Martin et al., 1990; de Baar et al., 1995; Boyd et al., 2000).

South Georgia is uncharacteristic of HNLC areas in this sense since it shows bouts of high productivity. Background winter phytoplankton abundance averages 0.2 μg chlorophyll *a* (chl *a*) l^{-1}, rising over tenfold to >2 μg l^{-1} in the spring/summer, but significant episodic summer blooms have been reported to reach >25 μg chl *a* l^{-1} (Whitehouse et al., 1996; Atkinson et al., 2001). Long-term data indicate that due to the complex hydrography of the island of South Georgia there can be extreme

seasonality and inter-annual variability in its physico-chemical conditions, temperature profiles, nutrient dynamics and primary productivity (Priddle et al., 1986, 1995). As a consequence of its local productivity and efficiency of energy transfer between trophic levels, South Georgia has supported large biomass of Antarctic krill (*Euphausia superba* Dana) and krill-dependent fish stocks and predators (Murphy et al., 1998; Atkinson et al., 2001). The coastal area of South Georgia is also characterised by benthic production and the presence of kelp beds (*Macrocystis pyrifera* Linnaeus) and other seaweeds (Chown, 1996). During ice formation and ablation processes macrophytes can be mechanically macerated and together with processes of natural degradation this can induce release of particulate organic matter and leaching of dissolved organic matter (Sala and Güde, 1999).

The definition of spring phytoplankton blooms are net autotrophic events reaching >1 μg chl *a* l^{-1}, that initiate following the build-up of favourable conditions, such as sufficient nutrient availability, solar irradiation and water column stratification (Parsons et al., 1970). In the Southern Ocean the transition from winter into spring is a crucial period which can produce high pulses of productivity, in particular in the seasonal receding ice-edge zone, as a result of ice-melting (Cota et al., 1990). However, sometimes dissolved primary production does not encounter the pathway of efficient microbial loop users: a time lag has been observed between the phytoplankton and bacteria response during high primary productivity (Karl, 1993).

3.3 Methods

Fieldwork was carried out between 28 October and 8 November 1997 to the north-west of the island of South Georgia during the Spring Processes JR25 cruise of the British Antarctic Survey, onboard RRS *James Clark Ross* (see Ward and Shreeve, 1999; Whitehouse et al., 2000). Two visits were made at a shelf station, located at approximately 43 km from the island of South Georgia coastline in 180 m water depth and at an oceanic station at 3800 m depth, approximately 100 km from the shelf break, to the north-west of South Georgia (Fig. 3.1b). The study started at the oceanic station and each site was occupied for 2 to 4 days and samples taken from a fixed station (Table 3.1).

Table 3.1. Summary of geographical positioning of sampling stations, dates of occupation during the first and second visits and total water column depth (m) at the two stations located off the north-western coast of the island of South Georgia, visited during the JR25 Spring Processes research cruise.

Station	Station co-ordinates		Date of occupation		Total water depth (m)
	Latitude	Longitude	First	Second	
Oceanic	53° 02′S	39° 21′W	28-29 Oct	4-5 Nov	3800
Shelf	53° 53′S	38° 39′W	31 Oct –3 Nov	8-9 Nov	200

All samples were collected using a General Oceanics 12-position bottle rosette multisampler fitted with a Neil Brown Mark IIIb conductivity-temperature-depth (CTD) unit. Temperature and salinity were determined and logged from deployment of the CTD unit (courtesy of M. Brandon). Water samples for the determination of DOC, DON, POC, PON were collected from General Oceanics 10 dm^3 Niskin bottles immediately after the collection of the gas samples. Water was drained from the Niskin bottles through silicon rubber tubing into 10 dm^3 polypropylene aspirators and known volumes filtered onto pre-combusted (500 °C, 3 h) 25 mm Whatman GF/F filters under vacuum. All results are expressed as means ± 1 standard deviation (SD), except where stated otherwise.

Water samples for the determination of inorganic nutrient concentrations were filtered through a mixed ester membrane (Whatman WME, pore size 0.45 μm) and the filtrate analysed colorimetrically on-board for dissolved nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), silicate ($Si(OH)_4$) and phosphate (PO_4^{3-}) by an automated method, using a Technicon segmented flow analyser (courtesy of M. Whitehouse; Whitehouse and Woodley, 1987; Whitehouse, 1997).

Water samples for the determination of chl *a* concentration and phaeopigments were filtered on pre-combusted (500 °C, 3 h) Whatman GF/F filters and extracted in 10 ml of 90% acetone for 24 h in the dark at 2 °C (Parsons et al., 1984; courtesy of J. Priddle). Absorbance was determined on board by use of a Turner Designs Model 10 through-flow bench fluorometer calibrated against a chl *a* standard (Sigma). Samples from 30 m depth were taken for the taxonomic identification of the major diatom, dinoflagellate and ciliate groups and preserved in 1% acid Lugol's iodine solution. A

50 cm^3 aliquot of each sample was settled for 24 h using the Utermöhl technique (1958) and enumerated under an inverted microscope at x 200 magnification.

The rate of size-fractionated primary production was measured (courtesy of L. Gilpin) by on-deck ^{14}C uptake incubations from water collected before dawn from discrete depths in the range 97-1% surface irradiance (Steemann-Nielsen, 1952). Following incubation, samples were filtered sequentially through 20, 2 and 0.2 μm polycarbonate membranes, fumed over hydochloric acid (HCl) and placed in a desiccator. Carbon fixation in each of the size fractions was determined by use of an on-board Beckman liquid scintillation counter (courtesy of L. Gilpin).

Microbial enumeration and bacterial production determinations were provided courtesy of R. Leakey. Bacterial abundance was provided only for the surface 10 m and estimated by epifluorescence microscopy (Porter and Feig, 1980). Bacterial carbon (i.e. bacterial biomass, BB) was calculated using biovolumes according to Fuhrman and Azam (1982). Bacterial production was measured by tritiated thymidine uptake (courtesy of R. Leakey).

3.4 Results

3.4.1. Shelf Station

The water column was mostly weakly stratified, with the depth of the surface mixed layer reaching around 80-100 m on the first visit, decreasing to 50-80 m a week later. A degree of depth-variability of the mixed layer was observed on each visit, possibly due to internal waves along the sharp pycnocline. Mean surface temperatures were in the 0.40-0.55 °C range and 0.6 °C at around 120 m depth and remained almost unvaried on both visits (Fig. 3.2a,b). A storm taking place between shelf visits rendered water column temperatures more homogenous (M. Brandon pers. comm.). Near-surface silicate ($Si(OH)_4$), nitrate (NO_3^-) and phosphate (PO_4^{3-}) concentrations were close to ranges previously observed during winter conditions (25-30, 25-26.5 and 1.5-2 mmol m^{-3} respectively, Table 3.2, data courtesy of M. Whitehouse). A reduction in silicate was observed in surface shelf waters between visits. Initially average surface nitrite (NO_2^-) and ammonium (NH_4^+) concentrations

were 0.2 mmol m^{-3} and 0.3 mmol m^{-3} respectively, but on the second visit, despite no relative change in nitrite (NO_2^-), mean ammonium (NH_4^+) concentration doubled to 0.6 mmol m^{-3} in the mixed layer (Table 3.2). The surface dissolved oxygen was almost 100%, just below saturation on-shelf, with oxygen production rates of <1 mmol m^{-3} d^{-1} (C. Robinson, pers. comm.).

On the first visit chl *a* concentration was invariant throughout the water column, reaching a maximum of 0.63 μg l^{-1} in the upper 50 m, declining with depth to negligible values (<0.2 μg l^{-1}) down to 120 m (Fig. 3.2a). One week later at the shelf station chl *a* was also homogeneously distributed in the water column to 150 m, never exceeding 0.2 μg chl *a* l^{-1} down to 150 m depth (Fig. 3.2b). Phaeopigments were negligible on the first visit, but on the second visit phaeophytin *a* accounted for >70% of total pigments (J. Priddle pers. comm.). In order to determine the amount of POC associated with algal biomass, the integrated chl *a* data over 40 m was considered and converted to POC and compared with integrated POC data. Integrated algal biomass (0-40 m) over the two visits was 0.44 g C m^{-2} using a POC:chl *a* ratio of 50 (Hewes et al., 1990; Atkinson et al., 1996) (n = 2, see Table 3.3, Ward and Shreeve, 1999). Integrated total primary production (sum of all size fractions) was 0.25 g C m^{-2} day^{-1} (0-40 m) on the first occupation to the shelf station, with the highest contribution by the >20 μm fraction (L. Gilpin pers. comm.). Between visits primary production decreased by over 90% to negligible values of 0.02 g C m^{-2} day^{-1} and was homogeneously distributed in the water column (L. Gilpin pers. comm.).

POC and PON within the mixed layer were generally low on the first visit throughout the top 100 m of the water column (17 ± 14 μM POC, 1.5 ± 1 μM PON in correspondence to the low phytoplankton biomass (0.5–0.8 μg chl *a* l^{-1}, Fig. 3.3a,c). On the second visit POC remained almost unaltered throughout the water column down to 100 m depth and the POC:PON ratio increased to >10 (Fig. 3.3b,f). POC:chl *a* ratios were high (>100) in the mixed layer on the first visit and increased to 750 on the second visit (Fig. 3.3g,h).

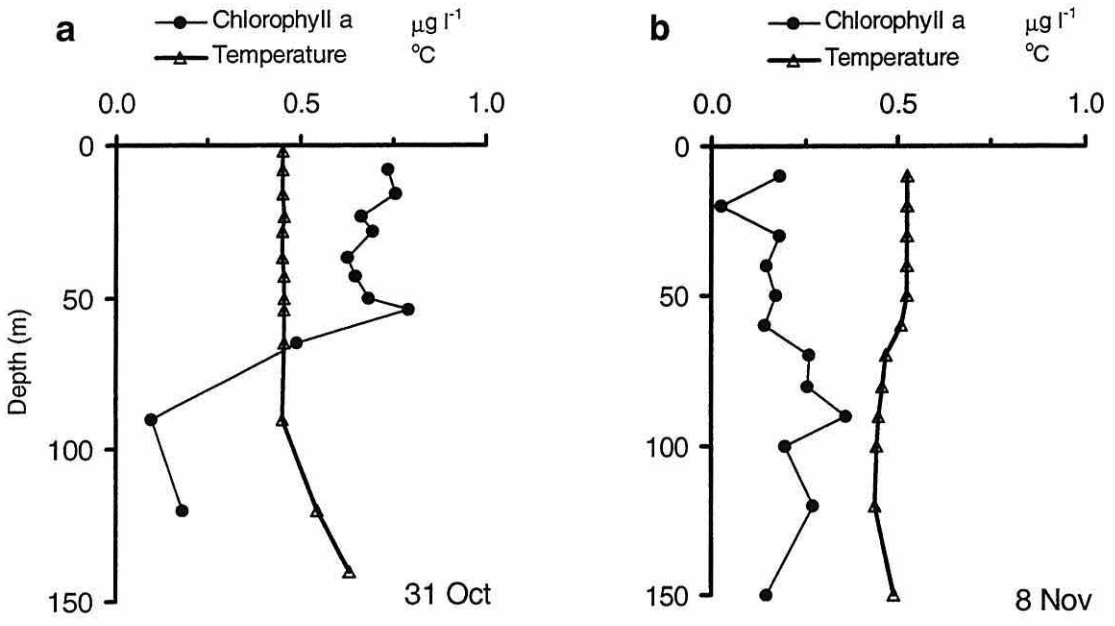

Fig. 3.2. Vertical depth profiles of chlorophyll *a* (µg l^{-1}) and temperature (°C) at the shelf site on the first visit (**a**, 31 October 1997) and second visit (**b**, 8 November 1997) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic. Chl *a* data were provided courtesy of J. Priddle, British Antarctic Survey.

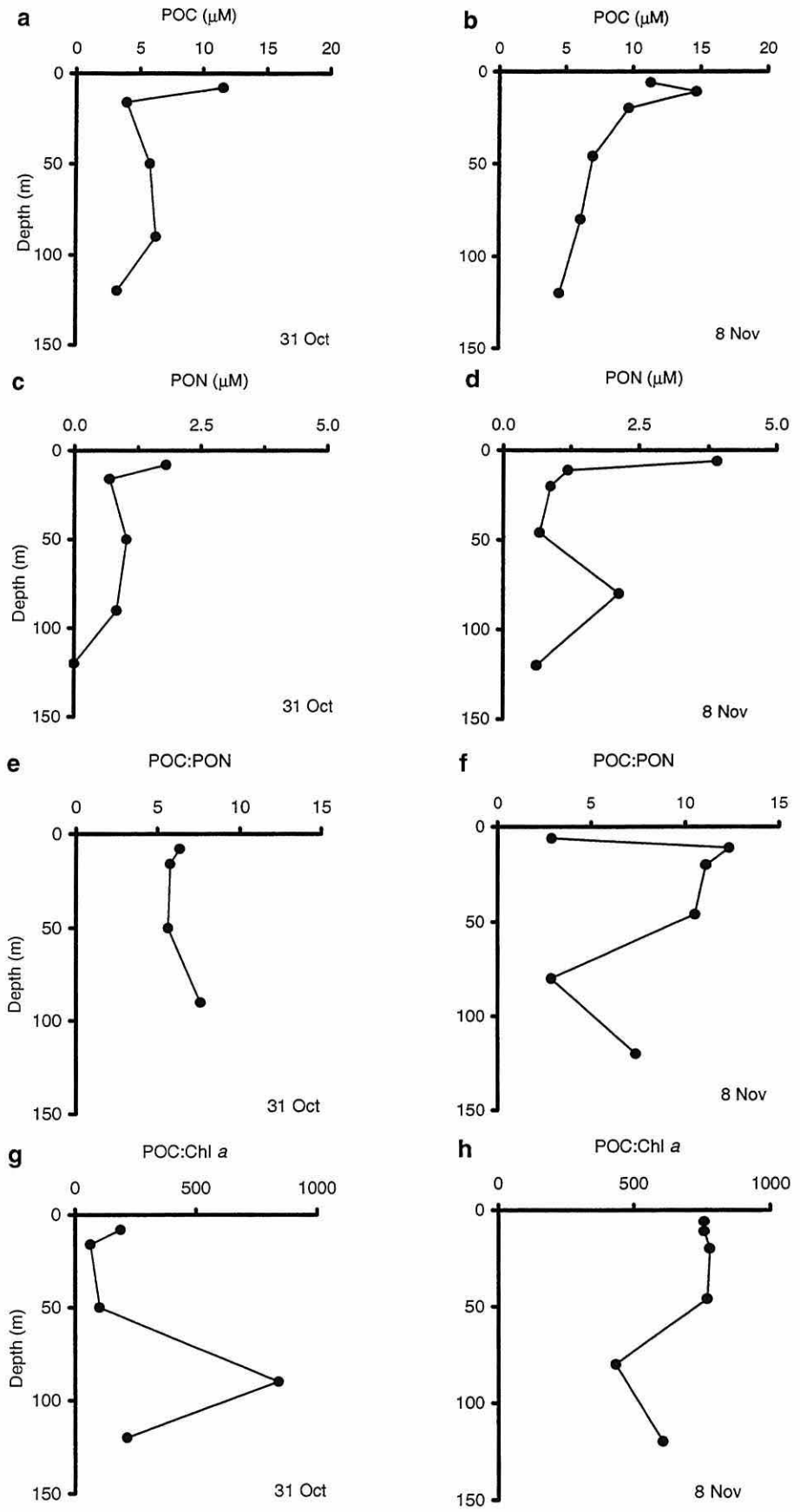

Fig. 3.3. Comparison of vertical depth profiles of particulate organic carbon (POC) concentration, particulate organic nitrogen (PON) concentration, POC:PON molar ratio, POC:Chlorophyll *a* ratio at the shelf site on the first (31 October, a,c,e,g) and second visit (8 November, b,d,f,h) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic.

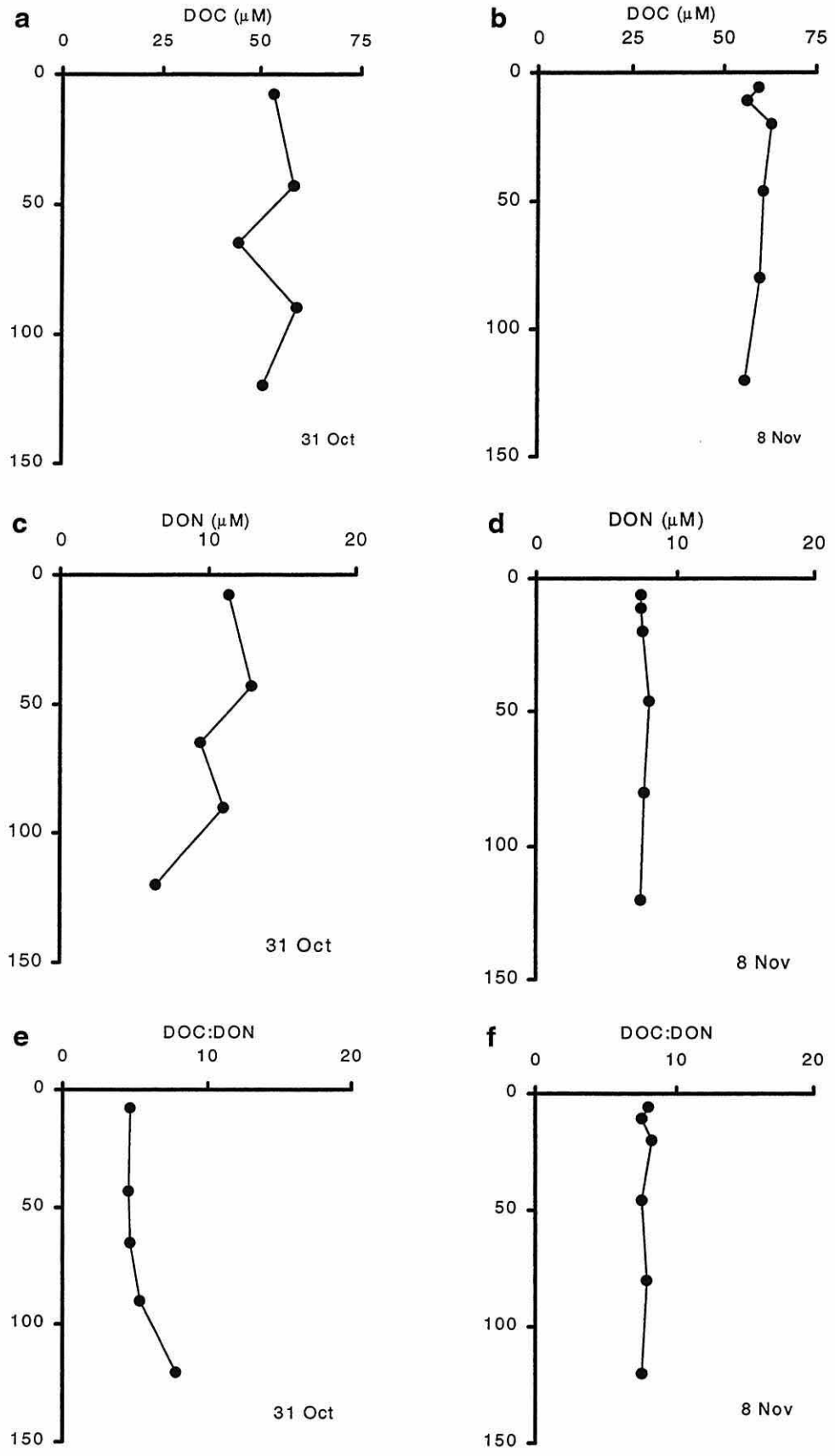

Fig. 3.4. Comparison of vertical depth profiles of dissolved organic carbon (DOC) concentration, dissolved organic nitrogen (DON) concentration, DOC:DON molar ratio at the shelf site on the first (31 October, a,c,e) and second visit (8 November, b,d,f) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic.

Table 3.2. Mean inorganic nutrient concentrations (silicate, nitrate phosphate, ammonium, nitrite, units in mmol m^{-3}) and ranges (minimum and maximum values are noted in brackets) during the first and second visit at the shelf site in near surface waters (0-50 m) during the 1997 South Georgia JR25 research cruise. Inorganic nutrient concentrations data were provided courtesy of M. Whitehouse.

	Shelf Station	
	First Visit (31 Oct –3 Nov)	Second Visit (8 Nov -9 Nov)
Inorganic nutrient	Mean Concentration (mmol m^{-3}) (minimum-maximum)	Mean Concentration (mmol m^{-3}) (minimum-maximum)
Silicate $Si(OH)_4$	33.11 (28.48-37.47)	24.27 (23.06-25.70)
Nitrate (NO_3^-)	27.44 (26.02-28.33)	27.53 (27.34-27.81)
Phosphate (PO_4^{3-})	1.92 (1.82-1.98)	1.98 (1.85-2.23)
Ammonium (NH_4^+)	0.30 (0.23-0.39)	0.65 (0.60-0.74)
Nitrite (NO_2^-),	0.24 (0.23-0.24)	0.23 (0.22-0.23)

Table 3.3. Algal carbon biomass and phytoplankton taxonomic composition at the shelf and oceanic site during the JR25 research cruise to South Georgia (October-November 1997). Integrated algal carbon biomass (g C m^{-2}) calculated from the mean chl *a* along the vertical profile over 0-40 m and 0-125 m using a POC:chl *a* ratio of 50 (Atkinson et al., 1996). Phytoplankton taxonomic composition (numbers ml^{-1}) over the two visits were counted from 30 m depth. Diatoms have been placed in size categories according to dimensions of individual cells. Table redrawn from Ward and Shreeve (1999).

	Shelf (n=2)			Oceanic (n=2)		
Algal carbon biomass (g C m^{-2}) (0-40 m)	0.44 ± 0.49			5.2 ± 1.51		
Algal carbon biomass (g C m^{-2}) (0-125 m)	1.23 ± 0.73			11.95 ± 2.42		
Phytoplankton taxa (numbers ml^{-1}) according to size categories	<5 µm	<20 µm	>20 µm	<5µm	<20 µm	>20 µm
Diatoms	0.6	0.8	0.0	239	26	264
Flagellates	6.0	9.6	0.4	4.2	22	4.6
Ciliates	0.0	0.0	0.0	0.2	0.5	1.2
Phaeocystis spp.	0.0	0.0	0.0	0.0	0.0	3.2

Table 3.4. Summary of means of variables ± standard deviation (SD), ranges (minimum and maximum) and sample size (n) measured during the first and second visits to the shelf site during the JR 25 Spring Processes research cruise at South Georgia, South Atlantic. Abbreviations used are Chl *a* = chlorophyll *a*, POC = particulate organic carbon, PON = particulate organic nitrogen, DOC = dissolved organic carbon, DON = dissolved organic nitrogen. Chl *a* data courtesy of J. Priddle.

Visit	Variable	Mean	± SD	Minimum	Maximum	n
First	Chl *a* ($\mu g\ l^{-1}$)	0.46	0.31	0.09	0.76	9
	POC (μM)	8.5	5.4	3.2	20.7	10
	PON (μM)	1.0	0.6	0	1.8	10
	POC:PON	7.7	2.1	5.7	12.1	9
	POC:Chl *a*	375	340	62	949	9
	DOC (μM)	62	13	44	82	5
	DON (μM)	11.9	3.4	6.5	17.9	9
	DOC:DON	5.4	1.1	4.5	7.9	9
Second						
	Chl *a* ($\mu g\ l^{-1}$)	0.15	0.08	0.02	0.27	11
	POC (μM)	8.9	6.0	3.2	22.1	11
	PON (μM)	1.5	1.1	0.6	3.8	11
	POC:PON	7.0	3.9	2.9	16.6	11
	POC:Chl *a*	1159	1135	144	3684	11
	DOC (μM)	59	3	56	63	6
	DON (μM)	7.6	0.3	7.4	8.1	6
	DOC:DON	7.8	0.3	7.5	8.3	6

There was little variation in DOC concentrations on both casts throughout the water column, and they remained unchanged up to a depth of 120 m (Fig. 3.4a,b). The average DOC on the first visit at the shelf was 62 ± 13 μM and on the second visit was 59 ± 3 (Table 3.4). Within the 120 m depth range DON was between 6-12 μM on the first visit at the shelf site, decreasing to <7 μM throughout the water column one week later (Fig. 3.4c,d). Average DON for the first visit was 11.9 ± 3.4 and on the second visit was 7.6 ± 0.3 (Table 3.4). Surface DOC:DON ratio was on average 5.4 ± 1.1 (4.5-7.9) and was 7.8 ± 0.3 (7.5-8.3) on the second visit (Fig. 3.4e,f; Table 3.4).

Bacterial abundance data (measured in triplicate, n = 3) was available for only one depth at the shelf station on the first and second visit (courtesy of R. Leakey). Bacterial abundance decreased from 3.25 ± 0.35 x 10^8 cells dm^{-3} (n = 3) on the first visit taken at 8 m depth to 2.74 ± 0.34 x 10^8 cells dm^{-3} (n = 3) one week later at a depth of 10 m (Table 3.5). The bacterial abundance datum (from one depth only) was converted to bacterial biomass by a carbon conversion factor of 25 fg C $cell^{-1}$ (R. Leakey pers. comm.), corresponding to 0.8 mg C m^{-3} on the first visit to the shelf station and 0.69 mg C m^{-3} on the second shelf visit (Table 3.5).

The contribution of bacterial biomass (BB) to total biomass (TB, phytoplankton + bacterial) increased from 2.6 to 20.6% between the first and second occupation, in parallel to a tenfold decrease in phytoplankton biomass (Table 3.5). Integrated bacterial production (0-40 m) ranged between 0.3 to 0.5 g C m^{-2} day^{-1} and represented approximately <30% of primary production both on the first and second shelf visit (Table 3.6).

Table 3.5. Chlorophyll *a* (Chl *a*) abundance, phytoplankton biomass (PB), bacterial abundance (BA) provided for one depth only courtesy of R. Leakey, Dunstaffnage Laboratory, bacterial biomass (BB) and bacterial to total biomass (TB) ratio on the first and second visit to the shelf station during the 1997 Spring Processes JR25 research cruise at the island of South Georgia. Bacterial data provided.

Visit	Date	Depth (m)	Chl *a* (μg l^{-1})	BA (x 10^8 cells l^{-1})	PB (mg C m^{-3})	BB (mg C m^{-3})	BB:TB (%)
1	03.11.1997	8	0.62	3.25	31.81	0.81	2.55
2	09.11.1997	10	0.05	2.74	3.32	0.69	20.60

Table 3.6. Bacterial production (BP), primary production (PP) and percentage ratios (BP:PP) determined on the first and second visit to the shelf station during the 1997 Spring Processes JR25 research cruise at South Georgia, South Atlantic. Data are integrated over 40 m depth. Bacterial and primary production data were provided courtesy of R. Leakey and L. Gilpin respectively.

Visit	Date	BP (0-40m) (mg C m^{-2} d^{-1})	PP (0-40m) (mg C m^{-2} d^{-1})	BP:PP (%)
1	03.11.1997	39.6	155.2	25.5
2	09.11.1997	21.9	81.8	26.8

3.4.2 Oceanic Station

At the oceanic station the average surface mixed-layer was 68 m on the first visit and shallowed to 40-45 m on the second visit, with little change observed in the type of water masses (M. Brandon pers. comm.). The mean surface temperature was initially 0.2-0.3 °C, but increased to 0.4-0.5 °C by the second visit within the mixed layer (Fig. 3.5a,b). A temperature minimum (−0.1 °C) was recorded around 100-120 m, with a large intrusion of warmer water (>1.2 °C) observed below 150 m depth (Fig. 3.5b; M. Brandon pers. comm.).

Table 3.7. Mean inorganic nutrient concentrations (silicate, nitrate phosphate, ammonium, nitrite, units in mmol m^{-3}) during the first and second visit at the oceanic station in near surface waters (0-50 m) during the 1997 South Georgia JR25 Spring Processes research cruise. Minimum and maximum values are noted in brackets. Inorganic nutrient concentrations were provided courtesy of M. Whitehouse, British Antarctic Survey.

	Oceanic Station	
	First Visit (28 Oct-29 Oct)	Second Visit (4 Nov-5 Nov)
Inorganic Nutrient	Mean concentration (mmol m^{-3}) (minimum-maximum)	Mean concentration (mmol m^{-3}) (minimum-maximum)
Silicate $Si(OH)_4$	35.65 (32.95-41.21)	33.57 (31.58-36.16)
Nitrate (NO_3^-)	26.93 (24.74-28.74)	25.99 (25.49-26.99)
Phosphate (PO_4^{3-})	1.75 (1.56-1.94)	1.75 (1.66-1.84)
Ammonia (NH_4^+)	0.24 (0.16-0.30)	0.34 (0.20-0.58)
Nitrite (NO_2^-)	0.27(0.26-0.28)	0.27 (0.27-0.29)

$Si(OH)_4$, NO_3^- and PO_4^{3-} concentrations within the mixed layer were 33-35, 26-27 and 1.6-1.7 mmol m^{-3} respectively and no discernible change was observed between visits (Table 3.7). Concentrations of NO_2^- and NH_4^+ remained low in the mixed layer

(0.2 mmol m^{-3} and 0.3 mmol m^{-3} respectively), and again there was little change in NO_2^- or NH_4^+ (Table 3.7). The surface dissolved oxygen saturation was 103-105% and oxygen production rates on the second occupation were >5 mmol m^{-3} d^{-1} (C. Robinson, pers. comm.)

On the first visit chl *a* concentration was distributed uniformly >2 μg l^{-1} down to 100 m depth. On the second visit phytoplankton abundance peaked at 4-6 μg l^{-1} at 25 m and sharply decreasing at 100 m to approximately <1 μg l^{-1}, indicating the development of a spring bloom (Fig. 3.5a,b). Phaeophytin was 15-20% of total pigments in the surface mixed layer on the first visit and was <8% one week later (J. Priddle pers. comm.). Pre-screening with a 200 μm filter showed that up to 20% of phytoplankton was represented by the >200 μm size fraction. During our two occupations of the oceanic site, integrated algal biomass was 5.2 g C m^{-2}, an order of magnitude greater than at the shelf station (Table 3.3).

Although no complete measurements were carried out to determine taxonomic composition of the phytoplankton assemblage, phytoplankton taxa counts showed that the large chain-forming centric diatoms (*Thalassiosira sp.,* in particular *T. antarctica* Comber) were the dominant phytoplankton species (J. Priddle pers. comm., Table 3.3). Initially primary production (integrated over 40 m) was 1.4 g C m^{-2} day^{-1} but increased to 1.6 g C m^{-2} day^{-1} on the second visit (Table 3.10). On both visits at the oceanic station primary production peaked at a depth of around 20-30 m (L. Gilpin pers. comm.).

POC concentration range was significantly higher on the second visit at the oceanic station (27-60.6 μM) (Fig. 3.6b). The average POC value on the first visit was (16.0 ± 1 μM) and increased to 21.5 ± 17.1 (Table 3.8). On the first and second visit PON remained relatively unvaried (1-5 μM); the POC:PON ratio increased to up to ~20 at a depth of 25 m on the second visit as a result of greater POC (Fig. 3.6e,f). In the surface mixed layer the POC:chl *a* ratio was 50 on the first visit and increased to 80 one week later, increasing at depth (Fig. 3.6g,h).

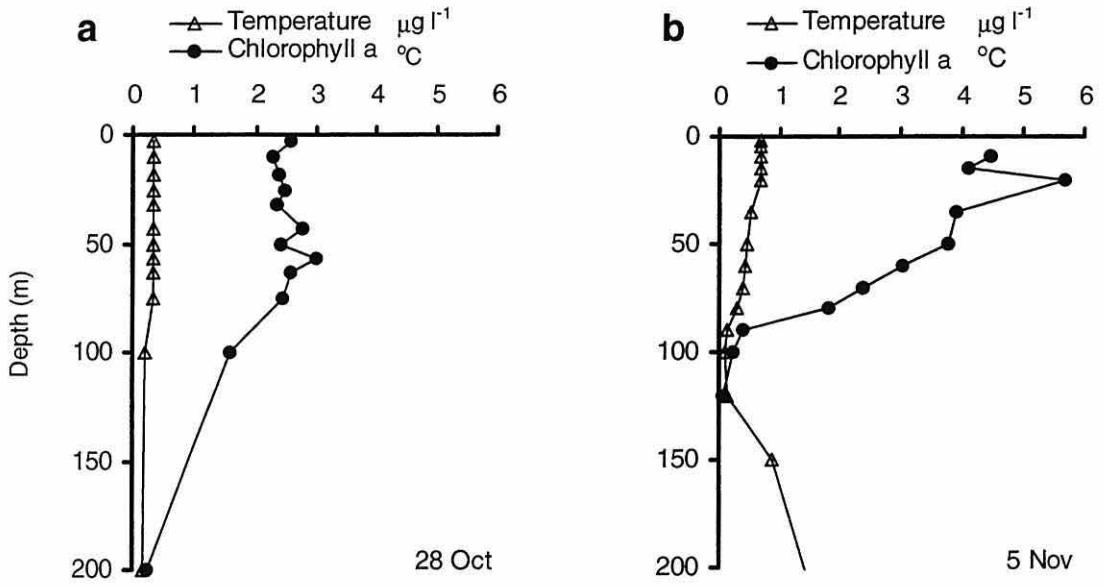

Fig. 3.5. Vertical depth profiles of chlorophyll *a* (µg l^{-1}) and temperature (°C) at the oceanic site on the first visit (**a**, 28 October 1997) and second visit (**b**, 5 November 1997) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic. Chl *a* data courtesy of J. Priddle (British Antarctic Survey).

Table 3.8. Summary of means of variables ± standard deviation (SD), ranges (minimum and maximum) and sample size (n) measured during the first and second visits to the oceanic site during the JR 25 Spring Processes research cruise at South Georgia, South Atlantic. Abbreviations used are Chl *a* = chlorophyll *a*, POC = particulate organic carbon, PON = particulate organic nitrogen, DOC = dissolved organic carbon, DON = dissolved organic nitrogen. Chl *a* data courtesy of J. Priddle.

Visit	Variable	Mean	± SD	Minimum	Maximum	n
First	Chl *a* ($\mu g\ l^{-1}$)	1.59	1.70	0.05	6.62	16
	POC (μM)	16.0	9.1	4.6	30.4	19
	PON (μM)	2.7	1.5	0.5	5.5	19
	POC:PON	6.1	13.7	1.16	18.9	19
	POC:Chl *a*	738	1711	14.2	7286	17
	DOC (μM)	49	7	41	64	12
	DON (μM)	7.6	1.8	5.4	10.0	5
	DOC:DON	7.2	2.1	5.5	9.9	5
Second						
	Chl *a* ($\mu g\ l^{-1}$)	2.29	1.83	0.07	5.67	12
	POC (μM)	21.5	17.1	4.5	60.6	12
	PON (μM)	1.96	0.89	0.60	3.13	12
	POC:PON	10.1	5.4	4.8	19.9	12
	POC:Chl *a*	343	374	35.7	1032	12
	DOC (μM)	53	5	47	62	16
	DON (μM)	5.8	2.2	3.0	9.4	15
	DOC:DON	10.1	3.5	10.1	17.2	15

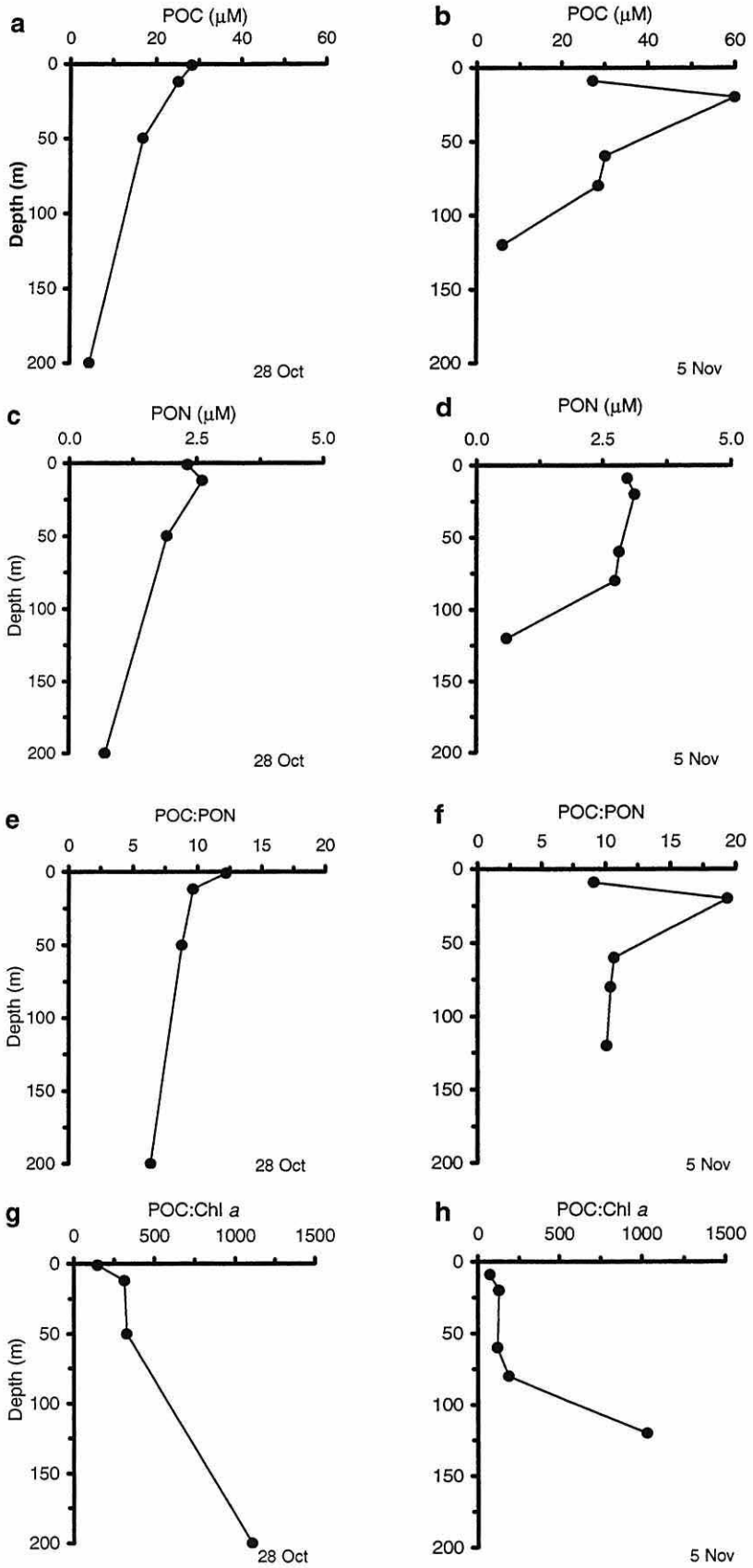

Fig. 3.6. Comparison of vertical depth profiles of particulate organic carbon (POC) concentration, particulate organic nitrogen concentration (PON), POC:PON molar ratio, POC:Chlorophyll *a* ratio at the oceanic site on the first (28 October, a,c,e,g) and second visit (5 November, b,d,f,h) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic.

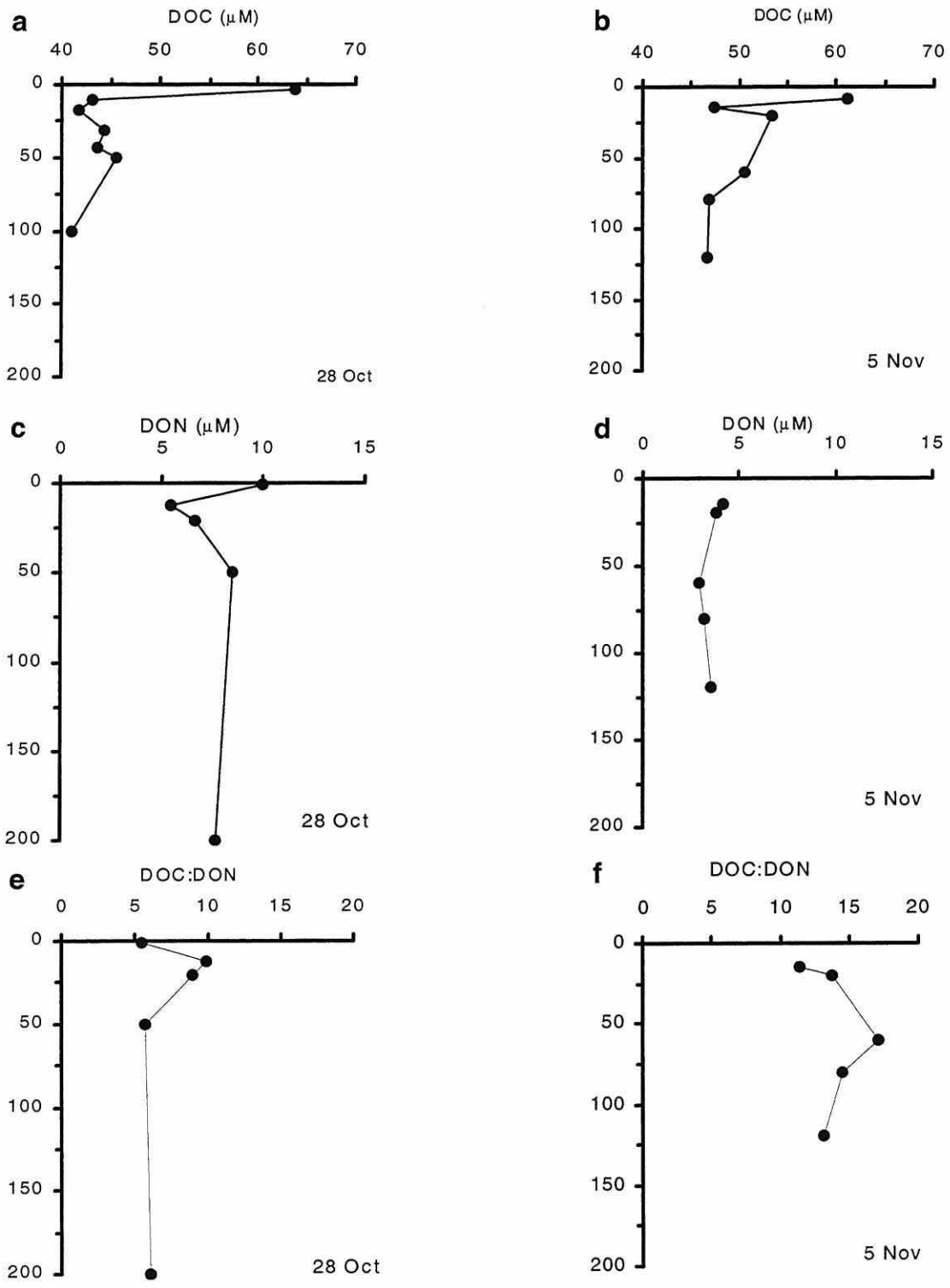

Fig. 3.7. Comparison of depth profiles of dissolved organic carbon (DOC) concentration, dissolved organic nitrogen (DON) concentration, DOC:DON molar ratio, at the oceanic site on the first (**a**, 28 October 1997) and second visit (**b**, 5 November 1997) during the JR 25 Spring Processes Cruise at South Georgia, South Atlantic.

On the first visit the average DOC concentration was 49 ± 7 μM (range 41-64 μM), and the concentrations were lower and variable with depth (Fig. 3.7a,b). DOC concentrations maxima were reached on both visits within the first 30 m (Fig. 3.7a,b). On the second sampling visit surface DOC was 53 ± 5 μM (range 47-62 μM). On the first visit DON was variable with a maximum of 10 μM in upper surface waters and decreasing in concentration with depth. The average surface DON was 7.6 ± 1.8 μM (Fig. 3.7c) whereas DON was invariant (5.8 ± 2.2) with depth from surface layers to 120 m depth (Fig. 3.7d). The average DOC:DON ratio changed from an initial average of 7.2 ± 2.1 on the first visit 10.1 ± 3.5 on the second visit (Fig. 3.7e,f).

Bacterioplankton abundance data was available for only one depth (courtesy of R. Leakey). Between the first and second visit at the oceanic site surface bacterioplankton abundance increased by over 60% from an average of 2.79 ± 0.34 x 10^8 cells dm^{-3} (n = 3) measured at 6 m depth to 4.53 ± 0.70 x 10^8 cells dm^{-3} measured at 9 m depth (n = 3) (Table 3.9). Bacterial biomass was 0.85% and 0.51% of total biomass (phytoplankton + bacteria) on the first and second oceanic visit at 6 and 9 m depth respectively (Table 3.9). Bacterial production was 1-2 mg C m^{-3} day^{-1} on both visits, with the highest production coinciding with the chl *a* peak on the second visit (R. Leakey pers. comm.). The integrated (0-40 m) bacterial production was estimated at 0.05 g C m^{-2} d^{-1} on the first visit to the oceanic station, rising to 0.072 g C m^{-2} d^{-1} one week later (Table 3.10). Bacterial production was twenty times lower than primary production on both the first and second visit, indicating that autotrophic processes dominated (Table 3.10).

Table 3.9. Bacterial and phytoplankton variables measured at one depth on the first and second visit to the oceanic station during the 1997 Spring Processes JR25 research cruise at the island of South Georgia. Abbreviations used are Chl *a* = chlorophyll a, BA = bacterial abundance, BB = bacterial biomass, PB= phytoplankton biomass, TB = total biomass, BP = bacterial production and PP = phytoplankton production. Bacterial abundance and biomass courtesy of R. Leakey.

Visit	Date	Depth (m)	Chl *a* ($\mu g\ l^{-1}$)	BA (10^8 cells l^{-1})	PB (mg C m^{-3})	BB (mg C m^{-3})	BB:TB (%)
1	29.10.97	6	1.62	2.79	81.92	0.70	0.85
2	05.11.97	9	4.46	4.53	224.21	1.13	0.51

Table 3.10. Bacterial production (BP), primary production (PP) and percentage ratios (BP:PP) determined on the first and second visit to the oceanic station during the 1997 Spring Processes JR25 research cruise at South Georgia, South Atlantic. Data are integrated over 40 m depth. Bacterial and primary production data were provided courtesy of R. Leakey and L. Gilpin respectively.

Visit	Date	BP (0-40m) (mg C m^{-2} d^{-1})	PP (0-40m) (mg C m^{-2} d^{-1})	BP:PP (%)
1	29.10.97	51.4	1404	3.7
2	05.11.97	72.0	1586	4.5

3.5 Discussion

The physico-chemical conditions at both stations were characterised by low temperatures and a slow shallowing and stabilization of the mixed layer (M. Brandon, pers. comm.). At both sites the temperatures in the surface mixed layer never exceeded 0.7 °C, typical of a winter to spring transitional period. In contrast, summer temperatures in the area are typically around 2 °C (see Whitehouse et al., 2000, Table 3.11). The inorganic nutrient concentrations were characteristic of the pre-growth winter season both at the oceanic and shelf site: generally with low levels of ammonium and nitrite and higher silicate, phosphate and nitrate and no apparent depletion was observed during the cruise, despite above-winter chl *a* concentrations (see Whitehouse et al., 2000).

Table 3.11. Typical mean temperature and chlorophyll *a* concentrations determined during the austral winter and summer seasons around South Georgia surface waters (≤30 m). Minimum and maximum values are noted in brackets. Data extracted from Whitehouse et al., (1996).

	Winter	Summer
	Mean (minimum, maximum)	Mean (minimum, maximum)
Temperature (°C)	0.43 (-0.95, 1.75)	2.42 (0.21, 4.44)
Chlorophyll *a* (μg l^{-1})	0.23 (0.12, 0.35)	2.05 (0.14, 26.83)

Significant changes in nutrient concentrations between visits were only seen for silicate and ammonium at the shelf site. Silicate concentrations decreased (33 to 24.3 mmol m^{-3}) despite no commensurate increase in parameters of phytoplankton growth. The increase in NH_4^+ (0.30 to 0.65 mmol m^{-3}) could be indicative of bacterial remineralization processes or excretion due to the grazing pressure.

At the offshore site phytoplankton biomass increased threefold within a week between the first and second visit. On the second visit chl *a* concentrations reached 4-5 μg l^{-1} in the mixed layer, within the range of values reported by previous studies in the area and by a study in the marginal ice zone during austral spring (4 μg chl *a* l^{-1}, Nelson et al., 1987). In contrast, the shelf site phytoplankton biomass was initially low (<1 μg chl *a* l^{-1}) and declined within a week in parallel with a decrease in primary production to almost negligible values. Primary production rate in oceanic waters increased to a maximum value sevenfold the maximum rate on-shelf. All evidence suggests that the offshore site was characterised by a developing spring bloom. Phaeopigments, in particular phaeophytin *a*, representing breakdown products of chlorophyll, remained low throughout the oceanic site occupation, within an order of magnitude less than values at the shelf site. On-shelf there was a high contribution of phaeopigments, which may indicate the presence of senescing phytoplankton cells, possibly due to a bloom preceding sampling. In addition, although the study concentrates on the planktonic system a possible input may have originated from the rich benthic production in the coastal area at time of ice melting.

Overall the bloom activity observed at the offshore site was typical of the area and of other island regions (Perissinotto et al., 1990): dominated by contribution of microphytoplankton (size >20 μm), rather than the smaller-sized picoplankton (2-20 μm) or nanoplankton (0.2-2 μm). Previous work also observed large celled centric diatoms (e.g. *Thalassiosira scotia* and *T. antarctica*) to be the highest contributors of the phytoplankton bloom to the north-west of South Georgia in early austral spring (Fryxell et al., 1979; Fiala and Delille, 1992) and in the Scotia Sea in austral summer (Hewes et al., 1990). However, a study in the early spring of 1992 along the 6° W transect between 47° and 59° S found that during non-bloom conditions (0.3 g C m^{-2} day^{-1}) picoplankton was the dominant size-fraction, contributing to 50% of the production (Jochem et al., 1995). Similarly, Weber and El-Sayed (1987) observed that the <20 μM fraction accounts for 90% of total chl *a* in Antarctic waters. Present findings appear consistent with observations of diatom community dominance during spatially and temporally restricted blooms in the Southern Ocean (Smetacek et al., 1990). It has also been postulated that the size and composition of phytoplankton community may influence the quality of dissolved organic matter (DOM) produced. For instance where picoplankton and nanoplankton dominate

plankton biomass and production (e.g. in the Sargasso Sea) they may be involved in supporting a large microbial food web resulting in tighter coupling between the autotrophic and heterotrophic systems (Carlson et al., 1998). It has been observed that in oceanic oligotrophic systems, such as the North Pacific gyre, bacterial heterotrophic biomass represents a large percentage of total biomass (Cho and Azam, 1990).

The maximum values of POC were observed in surface layers at the oceanic site as a result of the spring diatom bloom development, thus there was a direct effect of planktonic bloom on the particulate organic matter (POM) pool. Similar POC concentrations, in the range of 2-15 μM C were found by Dehairs et al., (1992) in the austral spring/summer of 1988, between 57° and 62° S, 49° W. Cadée (1992) also observed POC in the 16-33 μM C range in early summer in Scotia Sea waters, but little other data is available for the spring season.

There was considerable variability in POC:PON ratios on both stations samplings and throughout the water column on each sampling event. C enrichment on-shelf may suggest that sinking particles were of non-living origin, also given the low contribution of algal POC (<5%). At the oceanic station the low initial POC:PON ratio suggests a relatively high content of proteinaceous material.

An overall mean surface POC:PON ratio found during a 1988 spring cruise to the Scotia and Weddell Seas found was 5.5 (Leynaert et al., 1991). Similar POC:PON ratios were observed in the marginal ice zone of the Ross Sea (5.9) and in the Indian sector of the Southern Ocean (5.5) (Copin-Montégut and Copin-Montégut, 1978; Nelson and Smith, 1986).

At both sites POC:chl *a* ratios were generally lower in surface waters, increasing with depth and were relatively unchanged within visits. Oceanic POC:chl *a* ratios values were in the range of values for living phytoplankton: although species-specific, in diatoms POC:chl *a* ratio is typically in the 30 to 60 range (Geider, 1987). In flagellates and heterotrophic organisms POC:chl *a* is >200 (Strickland, 1960; Pollehne et al., 1993). The high POC:chl *a* ratios recorded on-shelf, together with the high contribution of phaeopigments, suggest that the water column was characterised

by the breakdown products of phototrophic organisms and/or a large contribution by heterotrophic organisms or the presence of suspended detrital matter. Furthermore there might be an influence from the remnants of shallow water macrophytes around South Georgia (e.g. kelp beds, Chown, 1996) which may be contributing to the suspended particulate matter in the coastal area. Not only do macroalgal beds degrade naturally and are a source of DOM leachates (Anesio et al., 2000), but the coastal ice acts on fronds and thalli mass milling and scouring them may be giving rise to suspended material then released upon ice melt.

Mean POC:chl *a* ratios for the oceanic site are in the same low range found during spring in the Weddell-Scotia Sea at 59° S (mean POC:chl *a* = 32, Nelson et al., 1987). Dehairs et al., (1992) and Cadée (1992) also found average POC:chl *a* ratios of 134 ± 41 in surface summer waters of the Scotia Sea and 450 in deeper waters (120-150 m). However, POC:chl *a* for Antarctic Ocean region are known to be in higher ranges from 200 (Holm-Hansen and Huntley, 1984; Sakshaug and Holm-Hansen, 1986) to 530 during winter in the Weddell-Scotia confluence (Cota et al., 1992) to <600 (El-Sayed and Taguchi, 1981; Ronner et al., 1983).

The DOC concentrations recorded were relatively unchanged at either stations. At the oceanic site, despite bloom conditions, no discernible change in DOC or production was observed. Concentrations detected are at the low end of the spectrum of published values reported for some Antarctic waters, for instance during *Phaeocystis* sp. blooms (>500 µM DOC, Bölter and Dawson, 1982). The latter is a colonial primnesiophyte, known for the forming of gelatinous chain colonies (El-Sayed and Fryxell, 1993), which may be extruding copious amounts of high molecular weight polysaccharide material. However, around South Georgia, blooms by the colonial primnesiophyte *Phaeocystis* sp. are undetected (Atkinson et al., 2001) and were not present in significant amounts in the present study (Table 3.3). In shelf areas macrophytes are also important contributors to the release of structural polysaccharides such as cellulose and hemicellulose and the degraded particles are often colonised by heterotrophic nanoflagellates (Sala and Güde, 1999). Overall, DOC concentrations recorded in this study are consistent with those reported from Antarctic waters (see Chapter 1, Table 1.1). This study found surface DOC values in

the same order of those recorded by Kähler et al., (1997) between 47° and 60° S and along 6° W (38-55 μM) in surface layers and generally lower concentrations at depth 34-38 μM (Table 1.2). Similarly, Carlson et al., (1998), measured DOC values in the 40-60 μM range over 150 m depth despite a spring-summer phytoplankton bloom in the Ross Sea. Ogawa et al., (1999) took vertical profiles along the Australian sector of the Southern Ocean (56-65° S) and surface DOC concentrations ranged between 45 and 55 μM. Wedborg et al., (1998) similarly recorded total organic carbon (TOC) concentrations not exceeding 45-60 μM in the Weddell Sea. Similar values have been reported by Cadée (1992), whereby DOC values varied between 41 and 80 μM C in surface waters of the Scotia-Weddell Sea Confluence. Generally values found lie within the background level of approximately 35-40 μM, characteristic of other oligotrophic or deep water masses DOC minima, e.g. North Atlantic (400 m, 42-43 μM C in the North Atlantic, Bodungen and Kähler, 1994), 35-39 μM C in the deep Pacific Ocean (Carlson and Ducklow, 1995).

In the present study, DOC in near-surface layers contributed on average to >70% of the total organic carbon (POC+DOC) pool during the evolution of the bloom at the oceanic occupations. At the shelf site up to 90% of the organic pool consisted of DOC at the first visit, reflecting that the DOC pool is the major organic fraction during non-bloom conditions and thus more refractory in comparison to POC. In comparison Dawson et al., (1985) found that 78% of the total organic pool consisted of DOC in the coastal area of King George Island (Scotia-Weddell Confluence) a higher percentage than that found at the oceanic site.

The surface DON concentrations remained relatively unvaried during the bloom development. The observed range of DON values during this study was in the same order of values recorded by Kähler et al., (1997) and higher than the average DON value measured by Hubberten et al., (1994) for both Arctic and Antarctic of approximately 3-4 μM N-DON (see Table 1.2). Sanders and Jickells (2000) found maximum concentrations of TON (PON + DON) on a cruise track in the Drake Passage of 6-7 μM and minima of 3-4 μM. Ogawa et al., (1999) measured surface DON concentrations from 1.8-9 μM. Maita and Yanada (1990) measured DON ranging from 1 to 10 μM in the North Pacific and Jackson and Williams (1985) in

California found average DON concentrations of approximately 6 μM. DON in the study contributes to over 20% of the nitrogen pool, an estimate exceeding the 16% DON contribution observed by Koike et al., (1986) in the nitrogen budget for Antarctic surface waters of the southern Scotia Sea. It is known that the use of nitrogen sources by phytoplankton can be preferential according to energetic efficiency, affecting release of DON in quantity and quality (Bronk and Glibert, 1991). It may be that preferential use of ammonium over nitrate by phytoplankton may explain the BP:PP ratios in the oceanic station.

Kähler et al., (1997) has shown that DOC:DON differ in the surface waters in comparison to depth. Mostly DOC:DON ratios averaged around 8 in the upper layers in comparison to 4-5 at depth, showing a relative carbon enrichment in solution in the euphotic zone. Ogawa et al., (1999) measured exceptionally low surface DOC:DON ratios (2.5-5) down to 75 m depth. The Antarctic DOC:DON ratios are low in comparison to typical ratios for Pacific and Atlantic Oceans (high molecular weight DOM average C:N = 16, Benner et al., 1997). Ogawa et al., (1999) hypothesised that there may be degradation of C compounds or supply of N-rich organic compounds. Free and combined amino acids, purines and methylamines have C:N ratios of about 3, thus the presence of labile compounds may contribute to lower DOC:DON ratios (Kerner and Spitzy, 2001). However, such highly reactive compounds may only be a small fraction of the DON pool, for instance in the Greenland Sea around 25% of DON is known to be in the form of free or combined amino acids (Lara et al., 1993). Also the bacterial exoenzymatic activity may be responsible for differential degradation of the large molecular weight compounds. Skoog et al., (1999) observed that β-glucosidase is ubiquitous in marine waters and it rapidly degraded polysaccharides to glucose and the latter rapidly assimilated by bacteria, in particular when inorganic N was available.

Pooled POC and PON data from both oceanic and onshore sites were positively correlated ($POC = 8.42\ PON + 1.46$, $r = 0.333$, $n = 30$, $p < 0.05$, Fig. 3.8a) within the classical Redfield ratio stoichiometry. Data for DOC versus DON showed the following relationship: $DOC = 1.83\ DON + 41.08$, $r = 0.52$, $n = 29$, $p < 0.05$ (see Fig. 3.8b). The intercept also shows a DOC background concentration equivalent to DOC deep water concentration of ~41 μM, similar to the background concentration

reported for deep waters of the Southern Ocean (Hansell and Carlson; 1998; Druffel and Bauer, 2000, Table 1.1). This apparent uncoupling of DOC and DON may be due to remineralization processes of differing speed and nature according to the composition of DOM. Smith et al., (1992) argued that due to differential protease activity by one to three orders of magnitude, carbon was solubilized more slowly than nitrogen in marine aggregates, with an increase in C:N with depth. DON has been inversely related to concentration of ammonium (Banoub and Williams, 1972; Butler et al., 1979). The different relationship within the dissolved pool is indicating that the processes driving the formation and assimilation of dissolved nitrogen and carbon species are different relative to Redfield stoichiometry, resulting in uncoupling between the two pools and differential losses of carbon and nitrogen. However, no correlation was found between individual elemental organic fractions (see Fig. 3.9a,b).

The major bacterioplankton abundance and production in surface waters indicate that the oceanic station supported a greater bacterial abundance than the shelf station. At the oceanic site bacterial abundance more than doubled in response to the substantial bloom, whereas no significant change was observed at the shelf site. However, the oceanic bacterioplankton biomass only contributed <1% of the total biomass, despite a threefold increase in chl *a* concentration. The ratios of bacterial to primary production and bacterial to algal biomass were low (Table 3.10), suggesting a weak bacterioplankton response during the phytoplankton spring bloom at the oceanic station. Similarly, Bird and Karl (1999) reported a general uncoupling between bacteria and phytoplankton with negligible bacterial biomass during the highest bloom sites in the Gerlache Strait, off the Antarctic Peninsula. At the location chl *a* was > 5 $\mu g\ l^{-1}$, but bacterial biomass was not greater than 2% of the total biomass (phytoplankton + bacteria) and as low as 0.3%. In the Arctic region of the Chukchi Sea in the summer the bacterial production was only 4% of primary production, whereas open oceans are known to generally sustain a 20% ratio and up to 76% has been observed in the Weddell Sea (Cota et al., 1990; Ducklow and Carlson, 1992; Kirchman et al., 1993). Bacterial production to primary production (BP:PP) percentage ratios of 10% have been observed in differing Southern Ocean waters with levels of bacterial production generally below 20 mg C $m^{-3}\ d^{-1}$ (see Fuhrman and Azam, 1980; Sullivan et al., 1990, Ducklow and Carlson, 1992; Kirchman et al.,

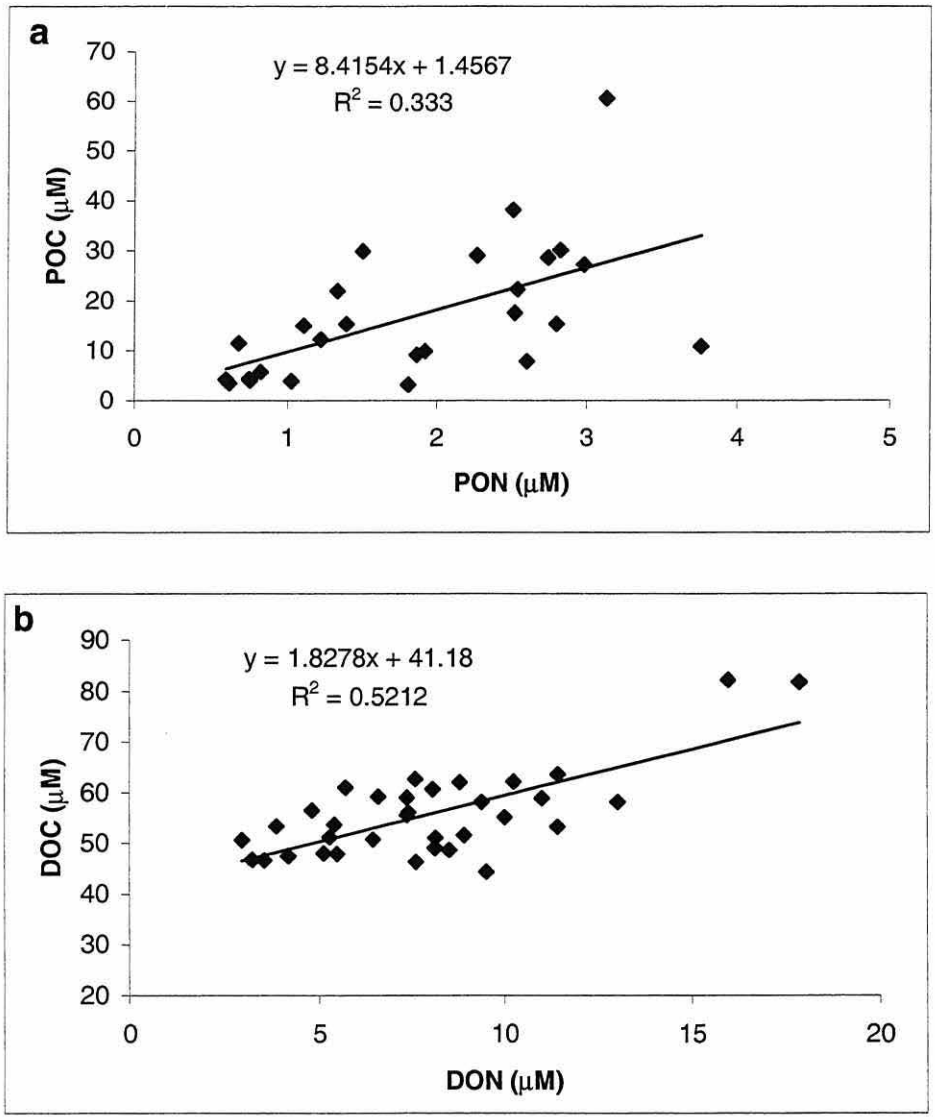

Fig. 3.8. **a**) POC as a function of PON in pooled data from shelf and oceanic visits. The solid line represents the regression between the data points. The dashed line represents the empirical Redfield ratio (POC:PON= 6.6). **b**) DOC as a function of DON in pooled data from the shelf and oceanic site. Solid line represents regression between data points.

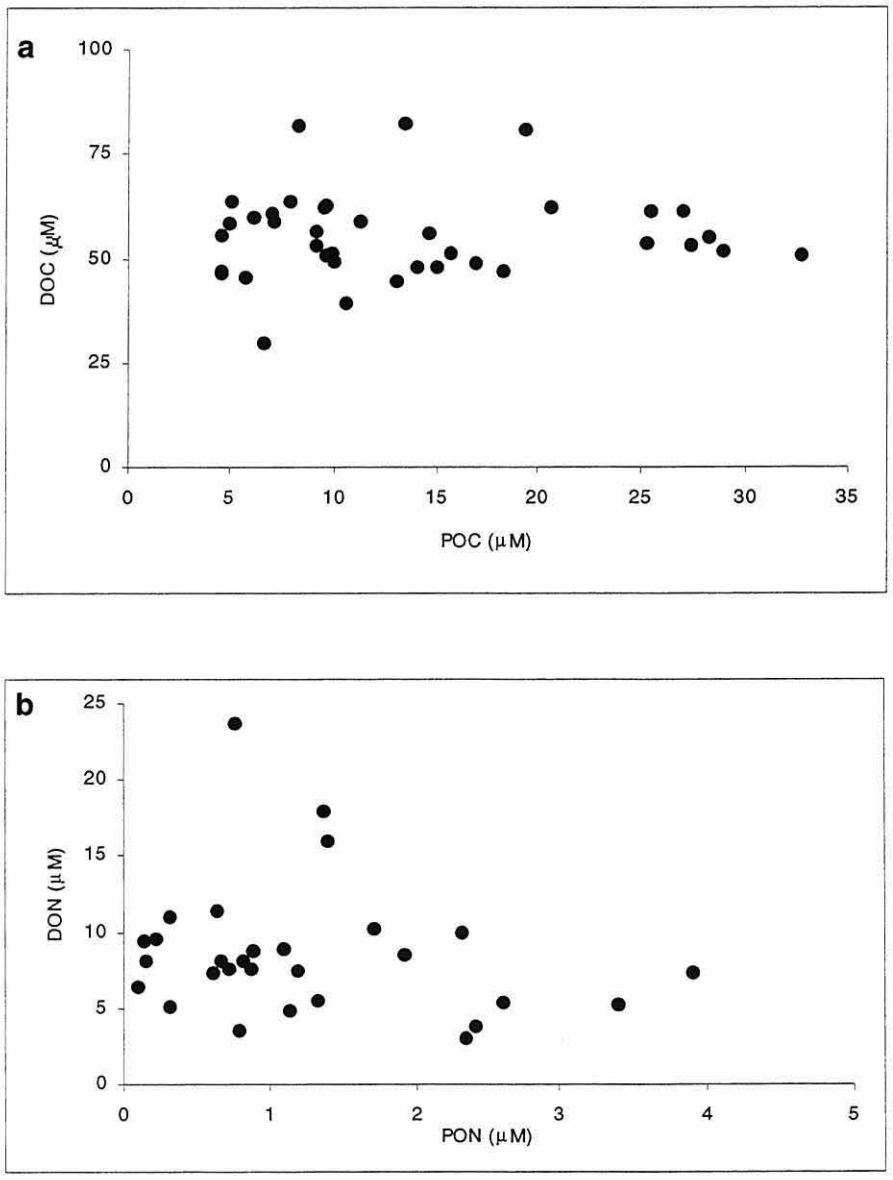

Fig. 3.9. a) Dissolved organic carbon (DOC) as a function of particulate organic carbon (POC) for pooled data from shelf and oceanic stations visits. **b)** Dissolved organic nitrogen (DON) as a function of particulate organic nitrogen (PON) in pooled data from the shelf and oceanic site.

1992) but other reports are in the higher range up to 2500% (Rivkin, 1990).

In the Southern Ocean bacterial communities appear to respond weakly to bloom events or have a delayed response (Kirchman et al., 1994; Blight et al., 1995; Bird and Karl, 1999). Uncoupling has been attributed to an interval between the presence of nutrients and their uptake by differing classes of consumers, leading to lack of synchronisation between bacterial and phytoplankton production (Fiala and Delille, 1992; Carlson et al., 1996). Preferential uptake of nutrients and competition between the bacterioplankton and phytoplankton have been suggested.

Resource-limitation is the classical cause put forward to control bacterial development (Ducklow and Carlson, 1992). However, nutrients in the area were sufficient and organic carbon was present at the oceanic station at high concentrations. Protozoan grazing by heterotrophic flagellates, dinoflagellates and ciliates (R. Leakey unpublished data) during the present study is a major controlling factor on bacterial metabolism, effecting a "top-down" control on bacterial population in terms of predatory pressure, preventing a full microbial response to bloom development (Klaas, 1997). In the area there was absence of krill and Ward and Shreeve (1999) indicated a dominance of zooplankton at the shelf site in the upper 150 m, with more than double the biomass of the oceanic site. In this study the data grazing data indicated that bacterivorous flagellate biomass was much higher in oceanic waters than shelf waters (R. Leakey, pers. comm.). The grazing impact of flagellates on the bacterioplankton reflected their biomass with oceanic populations removing 34-50% of bacterial biomass per day while shelf populations removed only 6-7% per day (R. Leakey, pers. comm). Bacterial production was relatively low at both sites and therefore the biomass removed was equivalent to over 200% of production in oceanic waters and between 30-40% in shelf waters (R. Leakey, pers. comm). Predation by bacterivorous protozoans therefore had a major controlling influence on bacterial biomass and production in turn preventing close coupling between the bacteria and phytoplankton communities. Early work by Johannes (1965) demonstrated experimentally that bacteria by themselves effected very little mineralization, this only occurred when protozoa were present. Nagata (2000) has equally pointed out the importance of protozoa in releasing labile organic carbon. In the Gerlache Strait, Antarctica, Bird and Karl (1999) also found that the uncoupling

of the microbial loop was by direct protist grazing activity during a bloom, causing a weak coupling between primary and secondary production.

The DOC turnover time indicates the residence time of DOC in the water column. It was derived from the equation in Smith et al., (1995) on the basis of its known concentration and the rate of its removal determined:

$$DOC_{\text{turnover time}} = \frac{[DOC]}{BCD} \qquad \text{(eq. 3.1)}$$

The amount of carbon needed to support bacterial production, defined as bacterial carbon demand (BCD) can be calculated (Carlson et al., 1999). The following equation was used to determine BCD (Goldman et al., 1987; Ducklow et al., 2000):

$$BCD = BP_g = \frac{BP_{net}}{BGE} = BP_{net} + BR \qquad \text{(eq. 3.2)}$$

where BP_g and BP_{net} are respectively gross and net bacterial production; BGE is bacterial growth efficiency, i.e. the efficiency of bacterioplankton in converting DOC into their bacterial biomass (Carlson et al., 1999) and BR is bacterial respiration. Typically BP is measured directly from leucine or thymidine uptake standard techniques (see Chapter 2) and BR from oxygen consumption. If R is not directly measured BGE can be derived by using bacterial variables. The present study used the following BGE formula, taken from the review of del Giorgio and Cole (1998) whereby:

$$BGE = \frac{BP}{BP + BR} = \frac{BP_{net}}{BP_g} \qquad \text{(eq. 3.3)}$$

If bacterial respiration is not directly measured BR can be derived by calculating the following equation from del Giorgio and Cole (1998):

$$BR = 3.7 \times BP^{0.41} \qquad \text{(eq. 3.4)}$$

In order to calculate BCD (3.2), a known BP was used and eq. 3.3 was solved using the BR obtained from equation 3.4. The resulting turnover times of DOC at the on-shelf and oceanic site, calculated on the basis of the available data set, were compared to turnover times estimated by using a representative BGE value (Table 3.12). The literature value chosen was BGE = 0.38, (according to Bjørnsen and Kuparinen, 1991), which was determined empirically in the Scotia Sea (see also Kähler et al., 1997).

At the shelf station the calculated residence time of DOC is up to 600 days (85 weeks), where productivity was low and all evidence indicates a tail-end of a bloom (see Table 3.12). Shorter residence times of 130 to ~200 days (18-28 weeks) were estimated at the more productive oceanic site during the spring bloom, indicating that the organic material available may be comparatively more available, labile, and rapidly utilised by the microbial community (Table 3.12).

Table 3.12. Dissolved organic carbon (DOC) turnover time (days) during the first and second visit at the shelf and oceanic site. DOC turnover was calculated in two ways: a) solving equations 3.1 to 3.4 using available data from this study and b) using a literature value (BGE = 0.38, Bjørnsen and Kuparinen, 1991) to calculate BCD (see text for further details).

	DOC Turnover Time (days)			
	Shelf		Oceanic	
Calculation Method	First Visit	Second Visit	First Visit	Second Visit
Equations 3.1-3.4	389	636	384	272
BGE = 0.38	205	362	199	134

High DOC turnover times were found in controlled experimental investigations: between 1 and 6 days in a mesocosm experiment by Smith et al., (1995) and during a spring phytoplankton bloom (Kirchman et al., 1991). Despite high bacterial efficiency in oxidising DOM at both sites, some DOM components may be highly resistant to degradation and accumulate in the water column due to their refractory nature. Bacterial respiration appears to be making use of newly produced, highly labile compounds (Fuhrman, 1987).

DOC was measured in bulk during the present study, therefore it may include a spectrum of compounds of differing lability, some more refractory and slow in their turnover time, such as chitin or humic compounds. The latter are refractory degradation products of organic material, estimated to account for 10-20% of DOC (Wedborg et al., 1998). Karl (1993) summarised results of kinetic uptake for the Antarctic Ocean and among the results turnover times of glucose varied widely, from 24 days in December (Kerguelen Island, Gillespie et al., 1976) to 833 days in McMurdo Sound (Bölter and Dawson, 1982). Doval et al., (2001) report DOC turnover in the order of 16 weeks in the polar frontal zone.

Another factor in the control of DOC may be the affinity of the bacteria for the substrates. The hydrolysis of organic matter is the rate-limiting stage in the release of inorganic nutrients back to the food web via the microbial loop (Davey et al., 2001). Turnover time may thus be related to extracellular enzyme activity by the microbial community. Dissolved and cell-associated bacterial enzymes are required for the hydrolytic breakdown of complex molecules to allow uptake (Hoppe, 1983). Protozooplankton produce digestive enzymes which they release in the surrounding water (Karner et al., 1994). The abundance of heterotrophic nanoflagellates observed in response to the bloom development may also contribute to increased enzymatic activity and a speeding up of the degradation process by the presence of protozoa recycling the organic matter present and thus quickly breaking down the organic carbon present in the water. Enzymes such as glucosidase and peptidase differ in their activity. It has been shown that the efficiency of bacterial mineralization depends upon the C:N ratio of the available organic matter (Goldman et al., 1987). In particular if the C:N ratio <10, bacterial cultures increase remineralization of nitrogen (Goldman et al., 1987).

Despite the present study showing some consistency with related literature, some limitations are identified that are going to be assessed. One of the limitations of the study is the short amount of time spent at each station which limits the description of temporal changes. Also there was a limited number of vertical depth profiles. It is difficult to identify the temporal evolution of processes when there is little continuity between samples and therefore long term time-series are essential in distinguishing patterns of processes and depth resolution at each profile may be improved to detect

processes at different depths within the euphotic zone and at greater depth and have greater confidence within dataset. The sample size is also important and a larger sample would improve confidence in the measurements. Due to limitations on the amount of CTD profiles and adverse weather conditions encountered during sampling, the proportion of determinations at the two sites was relatively restricted. Measurement of *in situ* respiration within different size fractions may be the way to construct a global picture of the processes occurring at the site and to have a better understanding of the bacterial carbon demand.

3.6 Conclusions

The study has reported on the DOC dynamics and interaction with algal and bacterial communities in the oceanic and coastal area of the island of South Georgia. Clear differences are shown. At the oceanic site there are pre-bloom and developing bloom conditions with increasing chl *a* concentrations. At the shelf site a bloom appears to have preceded sampling, due to high concentrations of phaeophytin pigments, high POC:chl *a* ratio and a decline in chl *a* concentrations. In addition the presence of higher ammonium at the base of the mixed layer in shelf waters supports evidence of remineralization processes. A constraint on conclusions is the potential influence of benthic macrophyte run-off. The benthic algae may become embedded into the ice and macerated by its mechanical action and released as particulate and dissolved organic material in the water column upon melting. The production of macrophytes such as kelps is considerable in the coastal area at South Georgia (Chown, 1996), and may therefore be an important factor affecting production and distribution of organic material.

At the oceanic site, while there is evidence of a phytoplankton bloom and increased bacterial abundance, a general uncoupling between auto- and hetero-trophs was observed. Microphytoplankton was dominant and the bacterial production was only 5-6% of primary production. This leads to a scenario of "bacterial droop" rather than loop at the time of the spring bloom. Data on grazing rates suggested that during the bloom, evolution a top-down control on bacterial abundance was important in controlling bacterial numbers. This may help explain the poor coupling of bacterial production to primary production despite sufficient nutrient resources and low

temperature variation. Despite increased phytoplankton abundance no significant change in DOC values were observed either onshore or offshore as a response to bacterial demand within the surface layers suggesting rather a difference in the quality/lability of substrate. Autotrophic and heterotrophic communities are major sources and sinks of organic carbon were investigated in terms of biomass and production to characterise coupling between the two communities. An uncoupled response of the bacterioplankton was observed as a result of increased primary production. The controlling factor appears the exertion of top-down control by protozooplankton grazing rather than substrate or temperature limitation. DOC was the dominant fraction of total organic carbon at both oceanic and shelf sites. The DOC pool was calculated to turn over on a time scale of over 4 months up to 1 year at the oceanic site, according to the BGE estimate used, and on a longer time scale at the shelf station showing the prevalent semi-labile/refractory nature of the dissolved substrates at both sites.

CHAPTER 4

SEASONAL AND INTERANNUAL VARIATION OF ORGANIC MATTER IN COASTAL WATERS AT ROTHERA, WESTERN ANTARCTIC PENINSULA

4.1 Introduction

The chapter focuses on the long-term monitoring of both particulate organic carbon (POC) and dissolved organic carbon (DOC) fractions over four consecutive years (austral summer 1997-austral summer 2001) in shelf-waters in a seasonal ice zone on the western coast of the Antarctic Peninsula (Ryder Bay, Rothera Point, Adelaide Island, 67° S, 68° W). The study aims at investigating seasonal and interannual dynamics of organic matter in relation to changes in phytoplankton abundance. The novelty of the study lies in obtaining a data-set over all four seasons year-round in coastal austral waters in an area of particular sensitivity to climatic change (Quayle et al., 2002).

The maritime Antarctic is an area characterised by the advance and retreat of the pack ice, with consequences on the ecology of apex predators such as seabirds, seals and whales along the trophic food chain which depend on the ice for the availability of food resources (Lizotte, 2001). To date few studies have concurrently determined a whole suite of biological and physical parameters year-round and at high frequency intervals over long-term in coastal or island mass areas of the Antarctic Continent (Clarke and Leakey, 1996; Smith et al., 2001; Kang et al., 2002). Selected research programs monitoring parameters over the whole seasonal cycle have only taken place in the last ten to twenty years at selected coastal or island-based scientific stations mostly within the Antarctic Peninsula or Ross Sea according to the research interests of individual nations. The Long Term Ecological Research (LTER) program at the USA Palmer research station is an example of multidisciplinary long-term study at the Antarctic Peninsula in the vicinity of Rothera in the western Antarctic Peninsula (Smith et al., 2001).

The present data set is a rare example of long-term temporal record of both dissolved

and particulate components of organic material (DOC and POC) for single complete years and with high-resolution sampling frequency. The significance of this data-set partitioning organic carbon will be greater when used in conjunction with other long-term observations. Physical data and information on community taxonomic composition, primary and secondary production, bacterial abundance may become useful in estimating the dynamics of organic carbon in relation to sources and sinks. The difference in the seasonal chl *a* and organic matter production, their export, type of food web, recycling efficiency, grazing pressure among other variables have also an impact on the benthic biomass (Clarke, 1988; Schloss et al., 1999; Fabiano et al., 1996) inducing an ecosystem to be a "retention" or "loss-type" system (Fischer et al., 1997).

The study site is found on the broad continental shelf which extends 200 km from the coastline. Circulation patterns are complex due to the numerous islands and the local hydrographic conditions inducing mesoscale eddy effects and local gyres. At the shelf break the area is influenced by the eastward flowing Antarctic Circumpolar Current (ACC) (see Chapter 3, Prézelin et al., 2000). Waters are characterised by a surface mixed layer of approximately 100 m depth and strongly affected by seasonal ice melt (A. Clarke pers. comm.). The site is in a seasonal ice zone where there is interannual variability in timing and cover area of pack ice. Typically there is a short pack ice formation period of 5 months starting in November and a longer retreat lasting up to 7 months, with minimum sea ice extent in February, when productivity is typically highest (Smith et al., 1998; Lizotte, 2001). It is known that sea ice coverage may vary interannually (Zwally et al., 1983) and longer sea ice seasons are believed to occur on a 7-10 year cycle and lasting for 2-3 years. In the coastal Antarctic Peninsula there are abundant inorganic nutrients and sources of elemental micronutrients such as iron (Harrison and Cota, 1991).

The plankton community structure appears to be variable. Diatoms appear to dominate the phytoplankton community at the site (Buma et al., 2001) in particular of the genera *Thalassiosira*, *Nitzschia*, and *Chaetoceros* (Mura and Agustí, 1998), although nanoplankton has been observed year-round in the area (Weber and El-Sayed, 1987). In the Antarctic Peninsula coastal area primary production is higher than in open ocean regions and downward flux of particulate matter provides a

regular seasonal signal to the benthos (Karl et al., 1991). The site is an ideal coastal area where DOC could be readily monitored year-round through all seasons and temporally with a high-frequency of sampling aiming at a long-term time series data-set. Organic carbon dynamics are of importance in a delicate environment such as the Antarctic Peninsula where in the last 40-50 years temperature rises have been measured (King, 1994).

4.2 Methods

Seawater samples were collected in duplicate or triplicate at the Rothera Time Series (RaTS) oceanographic station in Ryder Bay, on the continental shelf immediately south of Rothera Point (67°34′ S, 68°08′ W), Adelaide Island, western Antarctic Peninsula, Bellinghausen Sea, in the Eastern sector of the South Pacific Ocean between 5 April 1997 and 28 February 2001 (Fig. 4.1). Samples were taken from a fixed sampling station at 15 m depth from a small boat with a 5 l Niskin bottle. Total water column depth at the site is 350 m. During autumn and winter water samples were collected through a drilled borehole from the ice cover (Fig. 4.2).

The total chl *a* (<200 μm) and temperature data were measured weekly as part of the long-term RaTS oceanographic programme from austral summer 1997 to austral summer 2001 (data courtesy of A. Clarke; data absent from August to December 2000 and February 2001 to April 2001 due to fluorometer becoming unreliable, A. Clarke pers. comm.). Water samples for DOC, POC and particulate organic nitrogen (PON) determination were collected on a monthly basis from April 1997 until 28 February 2001 from the RaTS site. Sub-samples were vacuum-filtered and dispensed in pre-combusted (500 °C, 3 h) 30 cm^3 glass ampoules for DOC determination and filters preserved for POC:PON determination. The water samples and filters were stored at the local Bonner Laboratory, Rothera Station at –30 °C and subsequently sent to the UK by ship for analysis. Upon arrival in the UK samples were sent by courier to Menai Bridge in dry ice for laboratory analysis. All results are means ± one standard deviation (SD) except where stated otherwise.

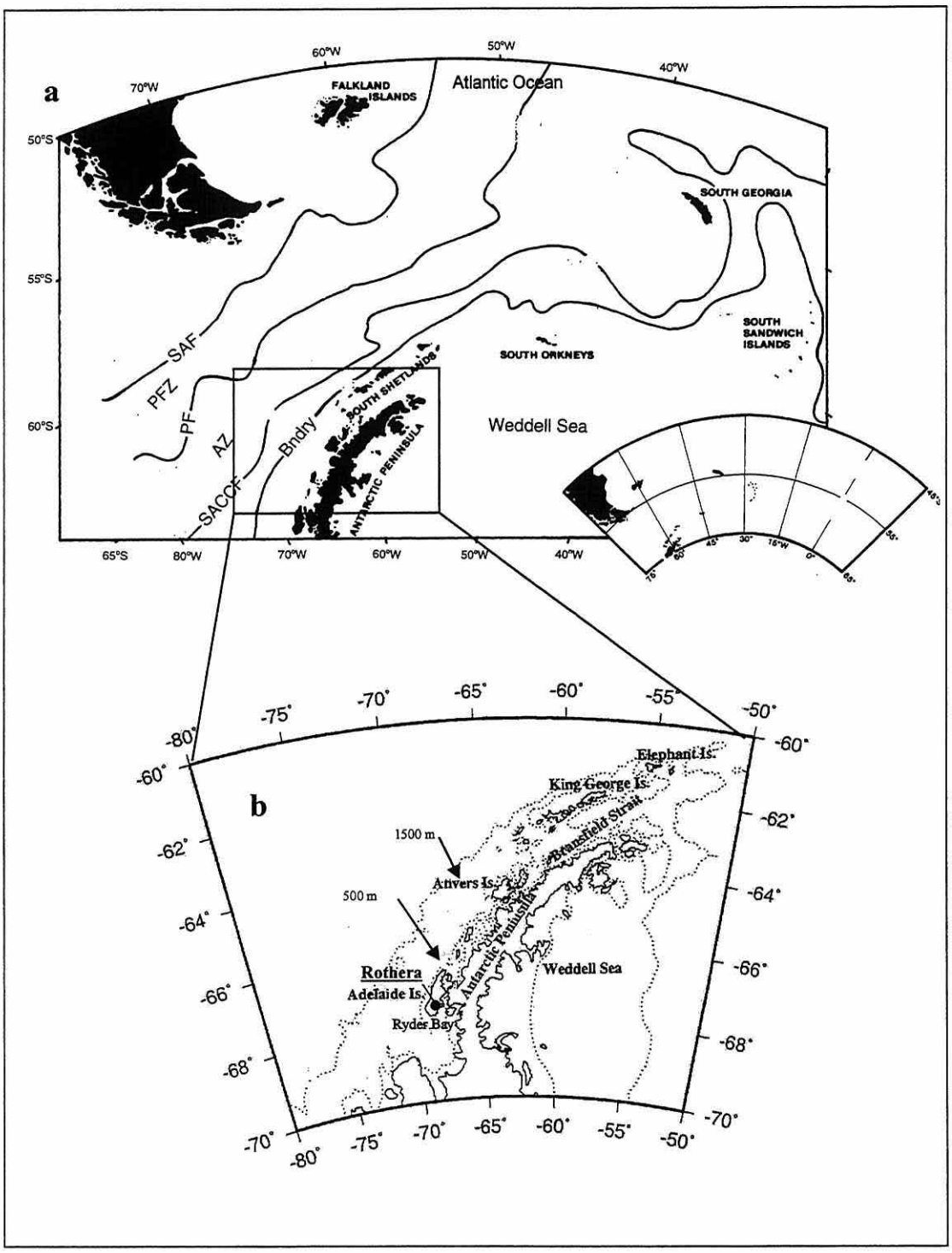

Fig. 4.1. a) Map showing the position of the sampling area located within the South Atlantic sector of the Southern Ocean. Shown are the main hydrographic provinces and fronts. Abbreviations are as follows: SAF = Sub-Antarctic Front, PFZ = Polar Front Zone, PF = Polar Front, AZ= Antarctic Zone, SACCF, Sub-Antarctic Coastal Current Front. **b**) The map shows the location of the Rothera Time Series site in Ryder Bay, Adelaide Island (•) where the time series study took place from 1997 to 2001. The arrows point to the inner and outer dotted lines indicating the 500 m and 1500 m bathymetric contours. The figures were adapted from Atkinson and Sinclair (2000) and Smith et al., (2001).

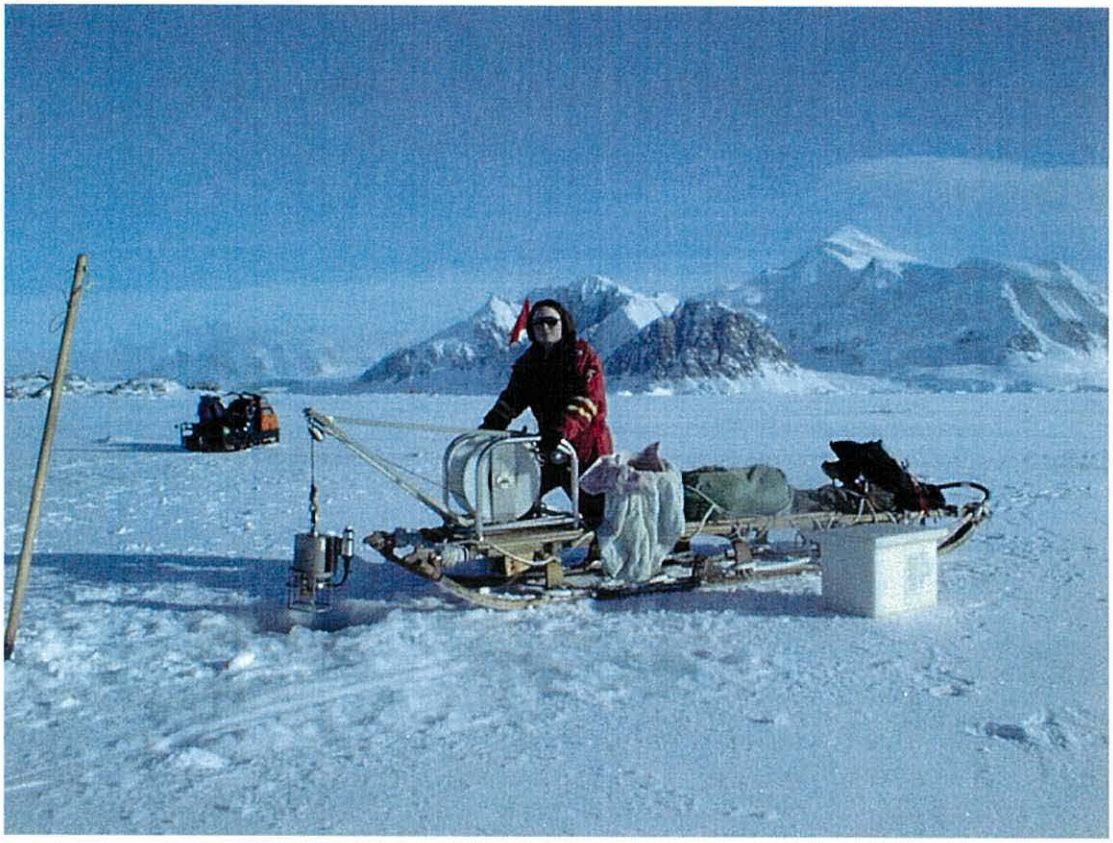

Fig. 4.2. Photograph showing water sampling through a conductivity-temperature-depth (CTD) unit cast at the Rothera Time Series (RaTS) site at 15 m depth in Ryder Bay, Adelaide Island, western Antarctic Peninsula in austral winter. The collection of water samples was carried out through a hole drilled in the consolidated pack ice. The photograph was provided courtesy of A. Clarke, British Antarctic Survey.

4.3 Results

Phytoplankton abundance showed a clear strong seasonal and interannual variation throughout the time series. The seasonal cycle of unfractionated chl *a* concentration (<200 µm) and water temperature over four consecutive years (austral summer 1997-austral summer 2001) is presented in Fig. 4.3 (data courtesy of A. Clarke).

During all autumn and winter seasons chl *a* was <1 µg l^{-1} (from April until September), with the absolute minimum recorded of 0.04 µg chl *a* l^{-1} in September of 1997. Phytoplankton abundance consistently increased at the end of each austral spring (November), sharply peaking in the summer (December, January, February). The maximum concentration recorded was 23.8 µg chl *a* l^{-1} in December 1999. Typically annual seawater temperature did not fluctuate more than approximately 3-4 °C (-1.7 °C in October to +1.8 °C in January or February). The results of the mean concentrations and ranges of all variables measured in the present investigation are presented in Table 4.1.

Table 4.1. Summary of mean values ± standard deviation (SD), range (minimum and maximum) and number of samples (n) of variables measured from seawater samples at the Rothera Time Series Site in Ryder Bay, at 15 m water-depth between April 1997 to February 2001. Abbreviations used are Chl *a*, DOC, POC, PON, POC:PON, POC:Chl *a*, TOC = chlorophyll *a*, dissolved organic carbon, particulate organic carbon, particulate organic nitrogen, molar particulate organic carbon to particulate organic nitrogen ratio, particulate organic carbon to chlorophyll *a* ratio, total organic carbon.

	Temperature (°C)	Chl *a* (µg l^{-1})	DOC (µmol l^{-1})	POC (µmol l^{-1})	PON (µmol l^{-1})	POC:PON (molar)	POC:Chl *a* (µg C µg Chl a^{-1}).	DOC:TOC %
Mean	-0.86	3.6	92	20	4.8	6.8	543	83
± SD	0.91	5.8	36.8	13.8	2.5	2.3	717	10
Minimum	-1.89	0.04	38	5	1.3	4.2	21.7	57
Maximum	1.82	23.77	198	51	10.4	11	3066	95
n	150	154	51	51	22	22	46	49

The amount of POC averaged 19.8 ± 14 µM C per annum (4.6-50.5 µM, n = 51, Table 4.1), but was found to increase in the late spring and throughout the summer season, reaching maxima of >45 µM C in February 1998 and in February 1999 and an absolute maximum of 50.5 µM C in January 2001 (Table 4.1, Fig. 4.4a). Both the seasonal and interannual pattern in POC corresponded to the trend in chl *a*

abundance. In particular POC peaks strongly coincided during phytoplankton bloom phases. During the 1999/2000 spring/summer season three distinct sharp bloom events took place, rather than a progressive bloom and decline, and the sequence was reflected by the POC concentration, matching each of the chl *a* peaks (Fig. 4.4a).

PON was below the detection limit during 1997 and 1998. However, PON averaged 4.8 ± 2.5 μM (range 1.3-10.4 μM) during bloom events in correspondence to the high summer POC peaks. The average POC:PON molar ratio (6.8 ± 2.3, range 4.2-11.9, Table 4.1) measured during the productive season was marginally over the Redfield ratio (6.6). A large seasonal fluctuation in the POC:Chl *a* ratio was observed. fluctuating from very low values of 20-40 in the summer months, at the peak of the blooms, then sharply increasing over 1 to 2 orders of magnitude during the dark and unproductive winter season to concentration maxima of 2506 in August 1997 and over 3000 in August 1998 in austral winter when chl *a* is in negligible concentrations (Table 4.1, Fig. 4.4a). The mean of the POC:Chl *a* ratio values 542.6 ± 717 (n = 46) suggests that there is a relatively high contribution of detritus in the water samples (Table 4.1).

The overall annual DOC mean concentration was 91 ± 37 μM (range 38-187 μM, n = 51), over four times the mean concentration of POC, but showing a smaller variation in mean concentration (Table 4.1). The minimum DOC concentration (38 μM) was recorded in mid December of 1997 (Fig. 4.4b). The increases in DOC were generally in coincidence with the phytoplankton peaks showing concurrent changes as a result of the bloom activity. DOC concentrations featured consistent trends of high peaks of >140 μM each summer up to a maximum 187 μM at the height of the bloom in February 2001 (Fig. 4.4b, Table 4.1).

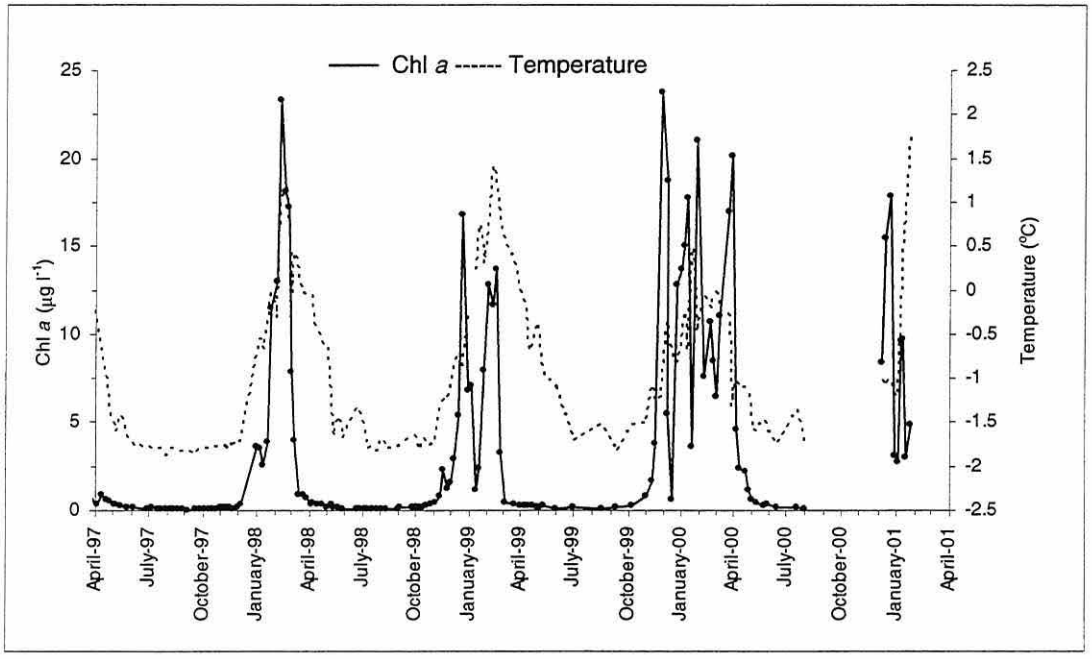

Fig. 4.3. Monthly cycle of chlorophyll *a* concentration (solid line) and temperature (dashed line) measured at 15 m depth (total water depth 350 m) at the coastal Rothera Time Series (RaTS) site in Ryder Bay, Adelaide Island, western Antarctic Peninsula from April 1997 to the end of February 2001. Data courtesy of A. Clarke, British Antarctic Survey.

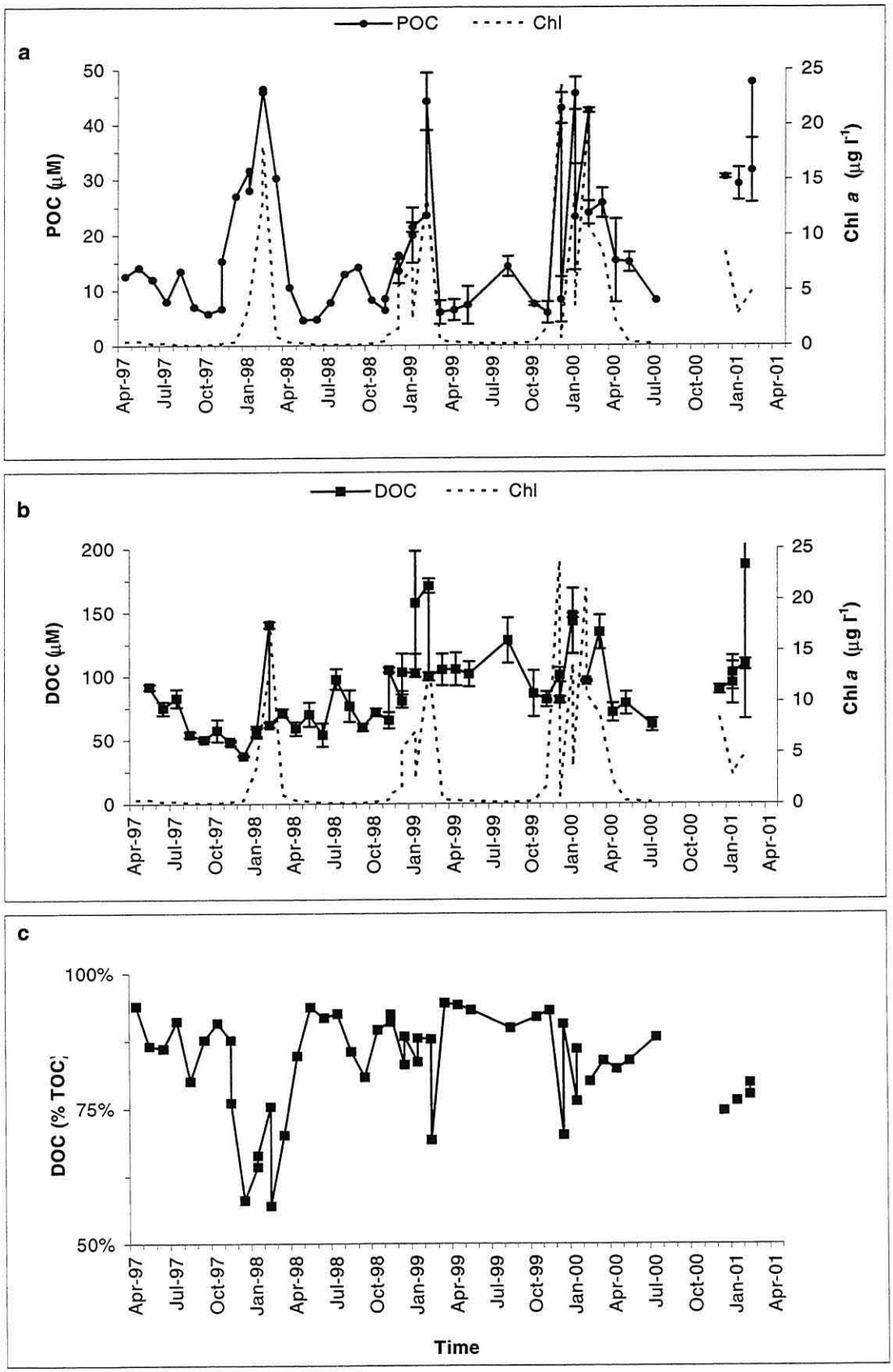

Fig. 4.4. Monthly cycle of **a**) particulate organic carbon (POC), **b**) dissolved organic carbon (DOC) concentration and **c**) the percentage of DOC in relation to total organic carbon (TOC). The dashed line indicates chlorophyll *a*. Error bars are ± 1 SD based on the duplicate or triplicate measurements. All data derived from seawater sampled at 15 m depth (total water depth 350 m) at the coastal Rothera Time Series site in Ryder Bay, Adelaide Island, Antarctic Peninsula, from April 1997 to the end of February 2001. Chlorophyll *a* data courtesy of A. Clarke, British Antarctic Survey.

The POC and DOC data were pooled to calculate total organic carbon (TOC), given by the sum of the dissolved and particulate organic fractions. The TOC was clearly partitioned in the dissolved form. DOC consistently represented over 50% of the total organic carbon pool (mean 83 ± 10% of TOC, range 57-95%, Table 4.1, Fig. 4.4c). The percentage contribution of the POC fraction relative to TOC increased particularly during every spring bloom period, but never exceeded 42%, observed during the austral summer of 1998 (Fig. 4.4c).

To explore differences in annual chl *a*, DOC and POC concentrations, a statistical comparison was made between different years (April to February). Preliminary analyses of normality and homogeneity of variance on the DOC concentrations at the Rothera site for four consecutive years (austral summer 1997-austral summer 2001) showed a lack of overall normality but homogeneity of variance (Levene's test = 0.473, p = 0.703). A Kruskal Wallis test was performed on the data to test for significant differences in the four annual median chl *a*, POC and DOC concentrations and results are shown in Table 4.2.

Table 4.2. Kruskal Wallis test results for the difference in median concentration of chlorophyll *a* (Chl *a*), particulate organic carbon (POC) and dissolved organic carbon (DOC) between four consecutive years (1997-2001). Seawater samples were collected at 15 m depth at the coastal Rothera Time Series (RaTS) site, Ryder Bay Adelaide Island, Antarctic Peninsula. Chl *a* data courtesy of A. Clarke, British Antarctic Survey.

Year (April-April)	Median Chl *a* ($\mu g\ l^{-1}$)	N	H	p
1997-1998	0.21	45	20.24	0.001
1998-1999	0.37	48		
1999-2000	0.70	30		
2000-2001	3.11	27		
Year (April-April)	Median DOC (μM)	n	H	p
1997-1998	57	14	15.79	0.001
1998-1999	89	16		
1999-2000	102	11		
2000-2001	91	8		
Year (April-April)	Median POC (μM)	n	H	p
1997-1998	13.5	13	4.64	0.201
1998-1999	13.2	16		
1999-2000	11.4	12		
2000-2001	25.9	9		

The test results show significant differences between interannual median chl *a* and DOC concentrations ($p < 0.01$, Table 4.2), but no statistically significant differences were observed between POC median concentrations over the four year period ($p > 0.05$, Table 4.2). There is an apparent increase in the quantity of annual chl *a* and DOC with time. In the spring and summer season of 1997/1998 DOC concentrations remained the lowest recorded with a median DOC (57 μM) almost half the median concentration in 1999-2000 (102 μM). The patterns are also characteristic of the phytoplankton abundance (Fig. 4.4b).

4.4 Discussion

From the time series results obtained from Rothera Point it is evident that chl *a* concentration in waters underlying sea ice was negligible in winter, below values typical of blue waters (containing <1 μg chl *a* l^{-1}, Hewes et al., 1990). Phytoplankton abundance increased either in single or multiple intense blooms (up to 23 μg l^{-1}), which are sustained either for a few weeks (<3 months) or are longer-lasting for the full spring-summer season. The trends are similar to those observed in other coastal Antarctic hydrographic provinces. For instance, Clarke and Leakey (1996) report up to 40 μg chl *a* l^{-1} at Signy Island in the Scotia Sea. Similarly, Smith et al., (2001) observed coastal water support high standing crop (20-30 μg chl *a* l^{-1}) and productivity in the austral spring and summer near Palmer station, Antarctic Peninsula (see Moline and Prézelin, 1996).

The factors causing substantial blooms are complex and include the advent of increasing incident solar irradiation, density stabilisation of the water column from the sea ice melting and retreating process and supply of adequate micro- and macro-nutrients in optimal concentrations, in particular of dissolved iron or reduced nitrogen (Nelson et al., 1989). Physiological limitation of phytoplankton by iron may not be the case for the nearshore, coastal phytoplankton which may be receiving glacial meltwater inputs and terrestrial material. Phytoplankton abundance exhibited strong seasonal and interannual variability, showing a high single bloom peak in 1997/1998, two sharp peaks in 1998/1999 and during the spring/summer of 1999/2000 it was characterised by three distinct elevated chl *a* peaks and sudden declines within the overall spring/summer period (Fig. 4.3).

It is interesting to note that the temporal duration is clearly different and increasing in time. During the last season of 1999/2000 the bloom occurred earlier in the year than the two previous seasons and persisted for a longer period of time (Table 4.3). Blooms are shown to progress in time and space from the ice edge with different timings according to latitude. In 1999/2000 the chl *a* concentration remained above a threshold of >0.5 μg chl *a* l^{-1} it for 182 days, approximately 6 months from spring (October 1999) to late summer (April 2000), as opposed to a duration of 107 days and 92 days during 1998/99 and 1997/98 respectively (Table 4.3). Although a degree of variation exists on the specification of bloom threshold in Antarctic waters, in this study a bloom was considered when chl *a* was >1 μg l^{-1} (Lizotte, 2000) rather than >0.5 μg l^{-1} (Tréguer and Jacques, 1992). Clarke and Leakey (1996) also showed high seasonality and significant interannual variability of fractionated chl *a* and POM over 15 years at Signy Island.

Table 4.3. Summary of starting dates (and julian days), peak concentrations and duration of seasonal austral blooms at Rothera Time Series Site, western Antarctica Peninsula during four consecutive years (austral summer 1997-austral summer 2001). Bloom based on threshold of 1.0 μg chl *a* l^{-1}. Chl *a* data courtesy of A. Clarke, British Antarctic Survey.

Year	Start of bloom		Maximum Concentration			Bloom Duration
	Julian Day	Date	Chl *a* (μg l^{-1})	Julian Day	Date	Days
1997/1998	2	02/01/98	23.3	40	09/02/98	92
1998/1999	322	18/11/98	16.7	362	28/12/98	107
1999/2000	314	10/11/99	23.8	340	06/12/99	182

It is clear from studies in the Antarctic Peninsula area that there can be a succession of species composition due to advection of water masses and tidal influences and wind stress (Lizotte, 2001; Kang et al., 2002). In the area the timing of sea ice formation and melting and the cover have been identified as controlling factors of primary production. Results from the Palmer research station (64°45′ S, 64°03′ W) in the western Antarctic Peninsula indicate that 1998 was a year when sea ice was below average for most of the winter (Smith et al., 2001). The high sea ice in the previous winter and spring is usually associated with high chl *a* biomass. This is a significant observation in view of climatic factors affecting biogeochemical cycles. This study confirms that blooms recorded were comparable to previously observed high phytoplankton standing stocks in coastal or continental shelf zones where it has

been seen that there are less constraints by euphausiid grazing or high mixing and micro- or macro-nutrient limitation (Clarke and Leakey, 1996).

Pearson product-moment correlation coefficients were calculated and results displayed in a matrix (Table 4.4) to assess relationships between all variables measured. Almost all variables were significantly correlated, in particular POC exhibited strong coupling with total chl *a* ($r = 0.845$, $p < 0.01$, $n = 46$) showing temporal peaks and valleys strictly coincident with those of algal growth and decline (Fig. 4.4a). Total POC and PON were positively correlated during the productive season, for which PON data were available ($r = 0.757$, $p < 0.01$, $n = 22$, Table 4.4). Although the data were limited, POC:PON variation with time shows some departure from the Redfield ratio both during spring/summer 1998 and particularly at the end of the blooms towards the austral autumn period (POC = 4.76 PON – 1.29, Fig. 4.5a,b). The relationship was obtained according to the major reduced axis method (P. J. LeB. Williams pers. comm.).

Table 4.4. Pearson correlation coefficient matrix between chlorophyll *a* (chl *a*), dissolved organic carbon (DOC), particulate organic carbon (POC) and particulate organic nitrogen (PON) measured from 1997 to 2001 at 15 m depth in Ryder Bay, Rothera Time Series Site, Adelaide Island, Western Antarctic Peninsula. All values are significant at $p < 0.01$ level, except where noted: * = $p < 0.05$; ns = not significant.

	Chl *a* (μg l^{-1})	DOC (μM)	POC (μM)
DOC (μM)	0.343*		
POC (μM)	0.845	0.348*	
PON (μM)	0.799	0.288 ns	0.757

POC data show a characteristic signal (10-16 μM POC) at the end of the austral winters of 1998 and 1999 (August) on average threefold lower in magnitude than that recorded during the bloom season in correspondence to negligible chl *a*, (see Fig. 4.4a). The observed flux of POC could be due to expulsion of dense brine waters from the ice, which may contain lithogenic material or ice-rafted detritus (IRD) in 350 m water column depth (Hebbeln, 2000). In the spring/summer season the melting ice may also release the sympagic communities, which may act as seed for phytoplanktonic blooms in the area. Moreover in the area the benthic production may also contribute as a source of particulate and dissolved organic matter and in the shallow waters the littoral and benthic

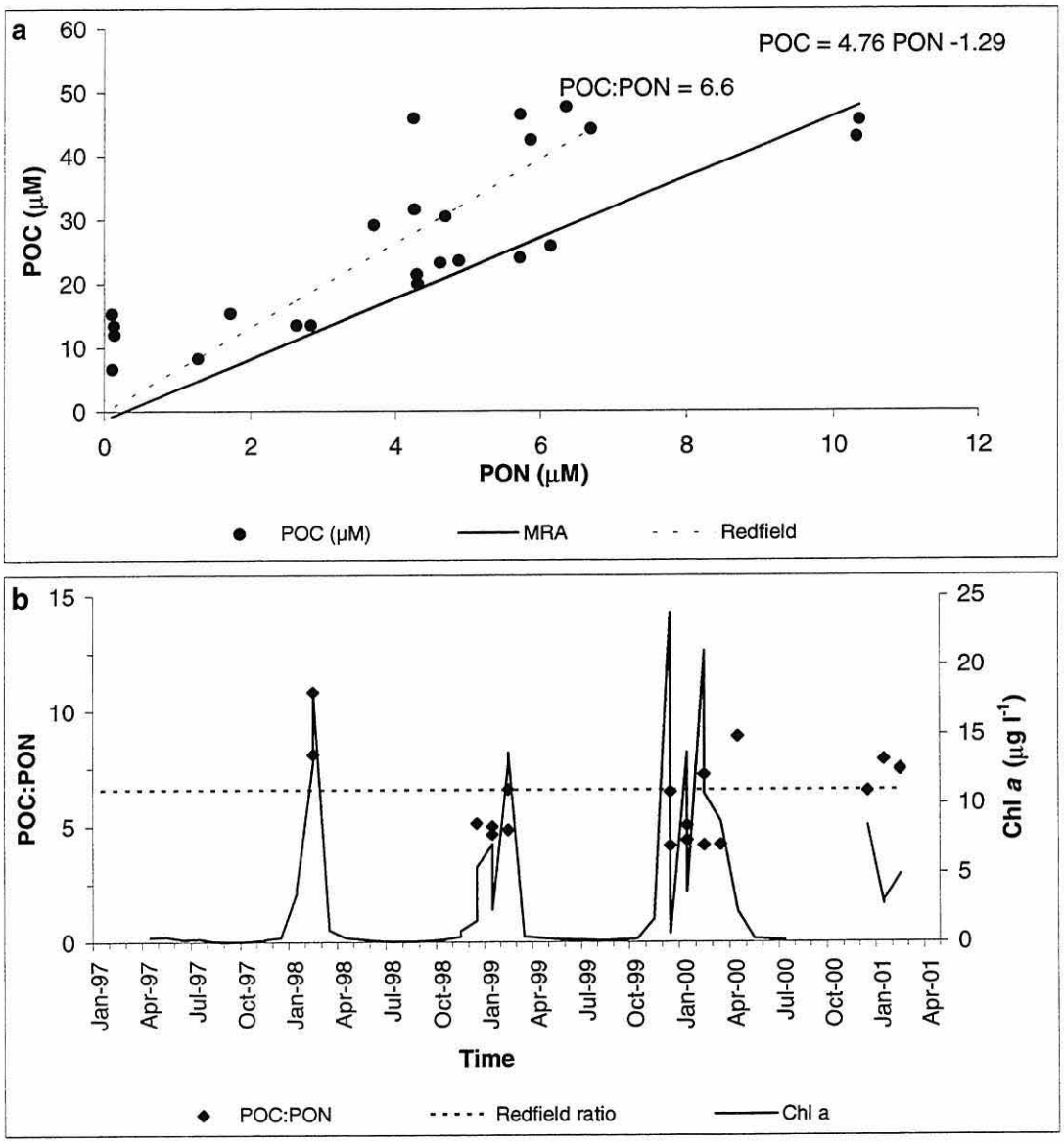

Fig. 4.5. a) Particulate organic carbon (POC) as a function of particulate organic nitrogen (PON) in surface water (15 m depth) of coastal Rothera Oceanographic Time Series site (RaTS, total water depth 350 m), Ryder Bay, Adelaide Island, Antarctic Peninsula from 1997 to 2001. Solid line indicates MRA regression (major reduced axis, MRA) between spring/summer POC and PON, dashed line indicates the Redfield ratio (6.6) between POC and PON. **b)** Seasonal cycle of chl *a* (dashed line) and POC:PON (closed diamonds) with time. The Redfield ratio (6.6) is depicted as a semi-continuous line. Chl *a* data courtesy of A. Clarke, British Antarctic Survey.

macrophyte enclosed in the ice may release leachates and exudates to the water column. No coincident POC:PON measurements are available to confirm the status of the organic matter but or POC:chl *a* ratio showed the large peaks of 2-3000 in correspondence to the input of POC, which may be of detrital origin from the ice above. POC:chl *a* has been observed to be species specific and the trends in ratios are related to both light and nutrients regime (Geider, 1987; Raven and Geider, 1988). Cañellas et al., (unpublished data) found variable POC:chl *a* ratio in the Western Antarctic Peninsula in summer 1993 averaging 167 ± 27 and ranging from 44 to 1337 g C g chl *a* l^{-1} but chl *a* never exceeded 4 μg l^{-1}.

DOC showed an increase during pre and post-bloom phases, and the newly produced DOC may be of a microbiologically labile nature, accumulating in the autumn and winter seasons, given the high concentrations as previously observed (Williams, 1995; Hansell and Carlson, 1998b; Carlson et al., 2000). Peaks in DOC only appeared to occur when phytoplankton concentration increased over 5-10 μg chl *a* l^{-1}. During the whole four year period DOC was positively correlated with total chl *a* ($r = 0.343$, $p < 0.05$, $n = 51$, Table 4.4), indicating that changes in dissolved organic matter are linked to phytoplankton developmental pattern and metabolic pathways. The correlation between DOC and phytoplankton abundance (Fig. 4.6a) indicates that DOC increases logarithmically with increasing chl *a* and that the products of synthesis and degradation are directly related to phytoplankton production. However only 29% of the variability in the DOC concentration is explained by the relationship with chl *a*. The occurrence of a variation in taxonomic composition and succession of microplankton taxa may be crucial in order to establish the contribution to the organic pool. Only Scott et al., (2000) have carried out similar studies in near-shore coastal waters (18 m depth) of eastern Antarctica (Davis research station). They measured size-fractionated DOC on a seasonal basis from May to February. They observed an annual mean of 1.51 mg l^{-1} total DOC and a variation from 30 μM in July to 260 μM in October. The results presented are at the lower end of that range due to the sampling location site being in deeper water depth (350 m) rather than in shallow inshore waters. Open waters have been described to support lower DOC than inshore waters (Guo et al., 1995). Similarly to our study, Scott et al., (2000) infer that during winter DOC is refractory and unavailable to the biological community. The

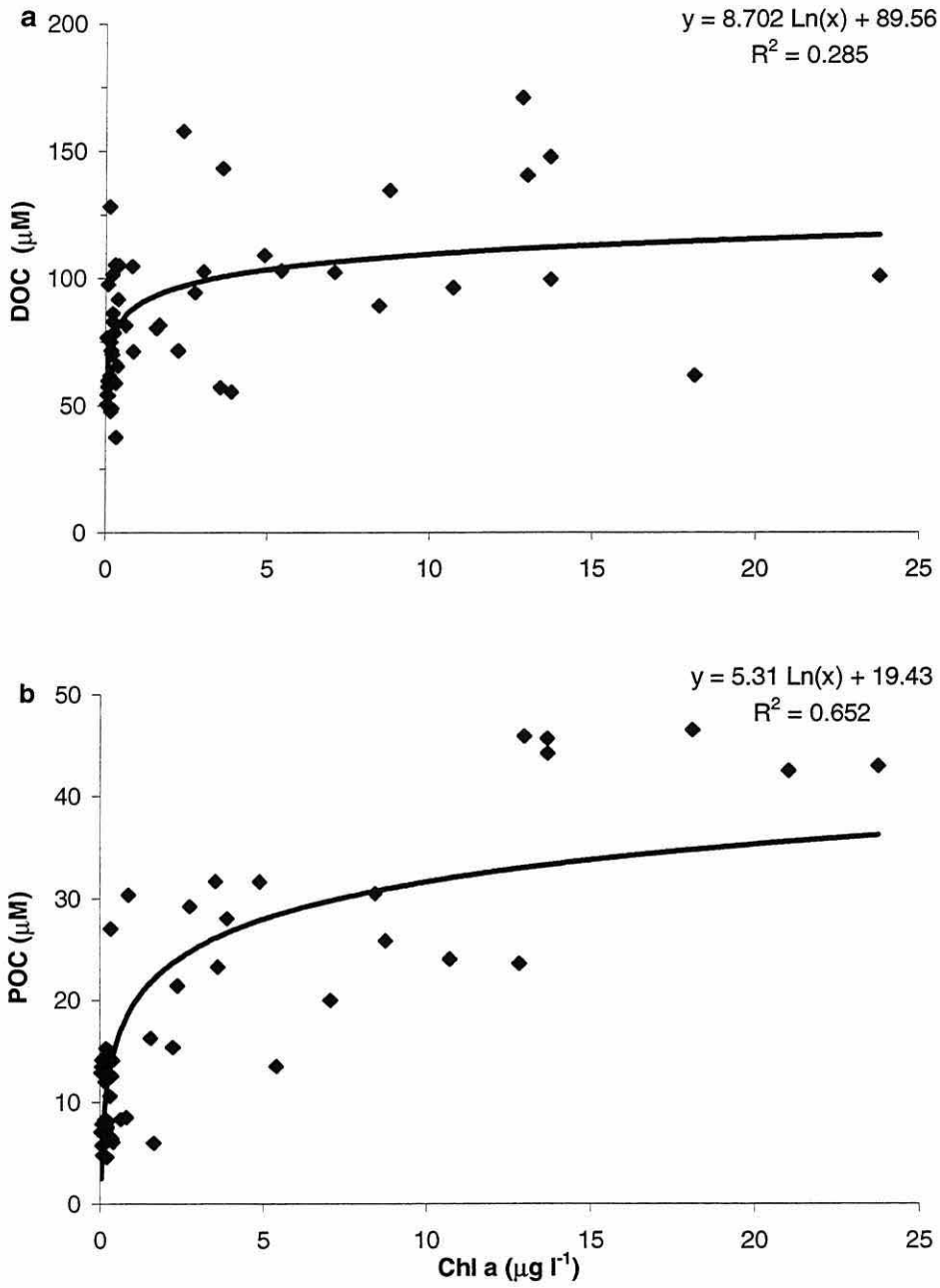

Fig. 4.6. **a**) Dissolved organic carbon (DOC) and **b**) particulate organic carbon (POC) concentrations as a function of chlorophyll *a* (chl *a*) in surface seawater collected from the coastal Rothera Oceanographic Time Series site (RaTS) at 15 m depth (total water depth 350 m), Ryder Bay, Adelaide Island, western Antarctic Peninsula from 1997 to 2001. Solid line indicates regression between data. Chl *a* data were provided courtesy of A. Clarke, British Antarctic Survey.

authors found a seasonal change in the concentration of different molecular weight size-fractions of DOC, obtained using ultrafiltration techniques. In particular, high molecular weight organic matter was greater at the beginning of spring and dominant (82%) in January during the maximum bloom period.

In comparison a tighter coupling exists between POC and chl *a*, where over 65% of the variation in POC concentration is explained by the concentration of chl *a* (Table 4.4, Fig. 4.6b). A variety of factors may control the distribution of DOC in comparison to POC. Local water masses, wind stress, tidal forcing and circulation and the influence of seasonal melt appear to be important in the coastal area bringing about new microalgal assemblages and macroalgal degradation products input from the sea ice which may change the composition of DOC in the water. The importance of wind and tidal influences in resuspending sediment material in shallower coastal areas of the Antarctic Peninsula has been shown by Kang et al., (2002) and Brandini and Rebello (1994). In particular the benthic algae are of importance and can begin to grow in parallel or even before the phytoplankton system begins to bloom (G. Dieckmann, pers. comm.). DOC may remain in the upper water column according to its lability and remineralizers activity can persist and show longer turnover time than POC, whose removal processes may vary in nature and action time (Wheeler et al., 1996), particularly driven by passive sinking and remineralization. Indeed, Becquevort and Smith (2001) found that particle-attached bacteria in the Ross Sea in spring were more metabolically active in the use of exoenzymes than free-living bacteria.

In the coastal area small temperature fluctuations are vital to the physiological ecology and growth of a variety of phytoplankton (cryptophytes) and marine invertebrates (Kang and Lee, 1995; Mura and Agustí, 1998; Moline and Prézelin, 2000; Brockington and Clarke, 2001). The degree of degradability must influence the persistence of DOC or its remineralization. The two organic pools, DOC and POC, were positively correlated ($r = 0.348$, $p < 0.05$, $n = 46$, Table 4.4), in particular during the spring-summer season, showing coupling between the two fractions and an indication of potential interaction and transfer of organic matter between pools. Moreover, DOC mirrored the characteristic rise shown by POC concentration in the autumn/winter seasons of 1998 and 1999, indicating a possible release of organic

material from the ice sheet either through dense brine drainage and expulsion during ice growth at the ice-water interface or after ice melting from the undersurface of the ice sheet due to warm water circulation (>0°C; Hebbeln, 2000). The latter hypothesis does not seem to apply in this instance as the winter water temperature measured *in situ* under the ice layer at 15 m depth in the area never exceeded -1.3°C.

The time series data from Rothera were available for almost four years, which is a relatively long, but yet limited number of years. A decadal cycle would be preferable to cover differing ice-cover and productivity scenarios, in view of the potential effects of climatic changes, such as the El Niño Southern Oscillation (ENSO). A higher sampling resolution, on a weekly or even daily scale, at different depths and in conjunction with sea ice and water primary production estimates and community characterisation may also indicate the processes and the time scale of variations in DOC down to diel cycles, narrowing the factors affecting the cycling of DOC and POC.

This study would equally benefit from complementary data regarding bacterioplankton ecological parameters such as abundance, production or respiration, from which a parallel estimate to that of South Georgia could be described in terms of bacterial carbon demand and residence time of the DOC pool. A parallel understanding of the plankton community structure may elucidate processes of release and uptake throughout the year.

An increasing number of studies are discriminating the purely dissolved DOC fraction (<1 kDa) from the colloidal fraction (>1 kDa). A limitation of the present study is the determination of bulk DOC without exploring size-fraction contributions or chemical characterisation at the molecular level. However, this is in view of only recent progress into analyses of DOC composition, which have become more accessible and increasingly sophisticated with analytical improvements in ultrafiltration, staining (Alcian blue) and nuclear magnetic resonance techniques (Krembs et al., 2001; Repeta et al., 2002). Equally, the importance of each size fraction has been under debate. At present colloidal matter appears at the forefront of interest. Recent observations by Repeta et al., (2002) through nuclear magnetic resonance spectra have highlighted that the high molecular weight (HMW, >1 kDa)

fraction of marine DOC is similar to the freshwater HMW fraction in its composition at the molecular level and the contribution of each fraction to total DOC is approximately 30% and 50% respectively.

4.5 Conclusions

A strong seasonal variation in phytoplankton abundance, DOC and POC concentrations in surface waters were observed at the coastal shelf station of Rothera in the western Antarctic Peninsula. Interannual variation was particularly significant for DOC and phytoplankton abundance. At the end of each summer maximum concentrations of DOC (>150 μM) and POC (40-50 μM) were consistently recorded in the month of February. In contrast, concentrations of organic matter became negligible in winter with the advent of ice cover and decline in phytoplankton abundance. There is evidence for a dominance of the contribution of DOC (80%) in the surface waters to TOC in all four seasons. DOC appears to be mostly refractory in the winter season. POC closely mirrored the rapid growth and decline of phytoplankton, whereas DOC is less coupled with chl *a* pattern of growth, suggesting different timing and processes of production and remineralization. The potential runoff deriving from benthic macroalgae degradation products, which can be released to the water column, may be a constraint to the conclusions to be drawn from the data, in particular as the variability in DOC concentration is explained only in part by the abundance of phytoplankton pigments.

CHAPTER 5

DISTRIBUTION OF ORGANIC MATTER IN WINTER PACK ICE OF THE WEDDELL SEA, ANTARCTICA

5.1 Introduction

This chapter presents the distribution of organic carbon in sea ice cores collected in late September to early October (austral winter to early spring) of 1989 along a transect from the Weddell Sea pack ice, Antarctica (64° S 44° W to 68° S 7° W) (see Augstein et al., 1991; Eicken et al., 1991). Due to the local hydrographical properties and circulation patterns, characterised by the presence of the Weddell Gyre, the Weddell Sea is characterised by seasonal sea ice growth and melting (Hibler and Ackley, 1983; Lange et al., 1989). Specifically, the western area is covered by a deeper layer of older and in part perennial sea ice while in the eastern area a thinner layer of seasonal younger sea ice exists (Eicken, 1992b). The floes sampled in this study reflect the gradient of properties and conditions of first- and second-year ice (Eicken, 1998).

Studies have shown evidence of the importance of the availability of nutrient supply within the pack ice of the Weddell Sea, often contributing to higher particulate organic carbon (POC) than expected purely from physical dilution (Dieckmann et al., 1991). It has been observed that dissolved organic carbon (DOC) and POC is abundant in Weddell Sea pack ice (Thomas et al., 1995, 2001; Kennedy et al., 2002). In this study the distribution of organic carbon from a number of floes was investigated to determine the partitioning of total organic carbon (TOC) between the dissolved and particulate phases. Organic carbon concentrations in sectioned profiles of second- and first-year ice were compared with variables such as ice stratigraphy and texture, inorganic macronutrient distribution and phytoplankton abundance. Dilution lines were plotted to distinguish whether DOC concentrations were consistent with conservative behaviour or whether biological mediation affected its distribution.

The aims of the study were to determine the factors controlling the distribution of DOC and POC within pack ice after its formation, in order to test whether DOC distribution is a result of physical incorporation or is affected primarily by biological processes. The chapter is organised as follows: section 5.2 is an introduction to the Weddell Sea pack ice ecosystem, followed by section 5.3 on the methodology employed to process the ice cores sampled. The results section 5.4 presents the sea ice cores physico-chemical characteristics and section 5.5 provides a general discussion on the main findings of the present study, concluding in section 5.6.

5.2 Environmental Setting

The Weddell Sea is in the South Atlantic sector of the Southern Ocean, bound to the west by the Antarctic Peninsula (60° W), to the south by the Filchner-Ronne coastal ice shelves and to the east by the 30° E meridian. In the north the Weddell Sea merges with the Scotia Sea at approximately 58° S (Deacon, 1977; Gammelsrød et al., 1994). Considerable seasonal thermodynamic ice growth occurs in open Weddell Sea water. Although subject to interannual variability, the seasonal pack ice typically reaches 60° S and a maximum surface area of 5.5 x 10^6 km^2 at the end of the austral winter (September). With the onset of spring in October-November the ice cover starts to recede and the minimum ice extent is usually recorded in February-March (1.5 x 10^6 km^2, Hibler and Ackley, 1983; Zwally et al., 1983).

Sea ice is "genetically" classified in two main classes, frazil and congelation ice, according to the mechanism of formation (Eicken and Lange, 1989). However, due to the variability of growth conditions, sea ice also shows distinct textural features which have been distinguished in classes and subclasses by examining microscopically thin and thick sections of ice crystals under polarised light (Eicken and Lange, 1989; Tison et al., 1998; see Table 5.1).

In contrast to the Arctic, Antarctic winter ice formation occurs during open water heavy turbulence, mixing and wind action. In the Antarctic hydrodynamic conditions induce the pack ice to form via an endogenous "pancake" ice cycle: from initial surface frazil ice crystals to pancake discs through increasingly large floes to

consolidated pack ice (Lange et al., 1989). The extent of the ice cover may vary on a scale from one (loose ice) to ten (closed ice) according to the degree of fragmentation. Often in sea ice large open-water areas (polynyas) up to >100,000 km^2 in surface area, classified either as latent or sensible heat, whether ice formation processes are removed by winds and/or currents or oceanic heat entering the region, occur in polar coastal areas (e.g. Weddell and Ross Seas) (Worby et al., 1998).

Table 5.1. Main classification of sea ice into texture classes and subclasses, and genetic classification of the ice explained according to the process of formation. Adapted from Eicken and Lange (1989) and Tison et al., (1998).

Ice Texture Class	Texture Subclassification	Genetic Ice Class	Formation Process
Columnar		Congelation	Tranquil freezing of seawater at the ice water interface
Granular	Polygonal	Snow ice	Infiltration and subsequent freezing of seawater in the snow cover
	Orbicular	Frazil	Individual crystals forming in the upper water column: Wind and wave induced
Intermediate columnar/granular		Congelation (Disordered)	Congelation of supercooled water at the ice water interface. Large degree of interlocking
Mixed columnar/granular			Domains of adjacent granular and columnar texture
Platelet		Frazil	Supercooling in rising water masses and passive transport to the front of ice shelves

Due to more dynamic conditions, Antarctic sea ice is predominantly composed of first-year ice (seasonal) or second-year ice (lasting over one summer melt) as opposed to the Arctic, where more than 90% of ice is multi-year or perennial, i.e. lasting for more than two summers melting processes (Eicken, 1992a). The Weddell Sea, due to local physical conditions, is characterised by a combination of both ice types (Fig. 5.1).

The local circulation pattern and the presence of the Weddell Gyre, a major cyclonic current, located within the central Weddell Sea causes westward transport and drift of sea ice with speeds up to 16 km d^{-1} (Deacon, 1977; Zwally et al., 1983; Nicol and Allison, 1997; Parkinson, 1998, see Fig. 5.1). The Weddell multi-year ice represents 40% of the Southern Ocean ice cover and over 80% of the perennial ice in the

Antarctic found in other sectors such as the Bellinghausen, Amundsen and eastern Ross Seas (Lizotte, 2001).

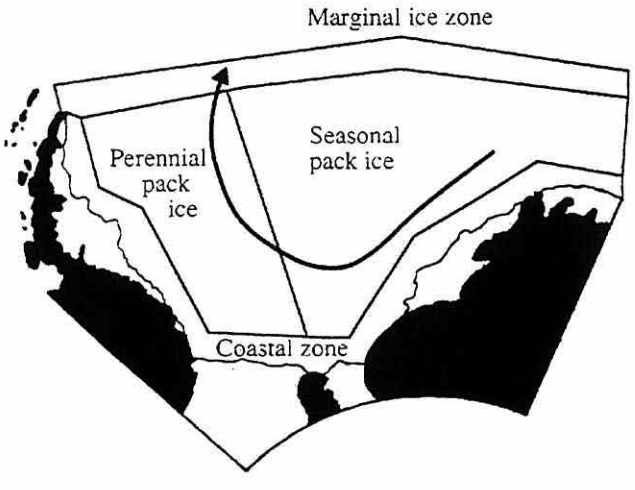

Fig. 5.1 The different areas of the Weddell Sea, Antarctica: the coastal zone, the seasonal pack ice and the consolidated, perennial pack ice. The direction of the major cyclonic water circulation, induced by the Weddell Gyre is indicated by the arrow. Adapted from Eicken (1992a).

Studies have shown that physical enrichment is responsible for concentrating phytoplankton and bacteria in young sea ice by "ice crystal scavenging" (Garrison et al., 1983; Grossmann and Gleitz, 1993; Grossmann, 1994; Grossmann and Dieckmann, 1994). Sea ice can support an active array of microbial organisms, microalgae and meiofauna (Garrison et al., 1987; Kottmeier et al., 1987; Garrison, 1991; Smith et al., 1997). High values of algal biomass and growth up to 2000 µg chlorophyll *a* (chl *a*) l^{-1} have been observed in Weddell Sea pack ice, compared to the concentrations of 0.01 to 0.3 µg chl *a* l^{-1} observed in the underlying or open waters of the Weddell Sea (Garrison and Close, 1993; Nicol and Allison, 1997). In the Weddell Sea ice-algae primary production is estimated at 15.8 x 10^{12} g C, higher than in any other sector in the Southern Ocean, contributing to almost 50% of the annual Antarctic sea ice primary production (Garrison and Close, 1993; Fritsen et al., 1994; Arrigo et al., 1998).

The sympagic communities inhabiting the sea ice matrix are physically constrained when ice forms, but light, salinity, temperature and inorganic and organic nutrients are important in determining their survival and growth (see Horner, 1985). From the freezing process until melting, different stages of ice growth and physical conditions can alter the biology and chemistry. Because of temporal succession and thermodynamic processes an ice floe and its sympagic community may be layered (Jeffries, 1997). Surface, interior and bottom algal assemblages are known to occur in sea ice (Palmisano and Garrison, 1993). In particular, surface infiltration and freeboard communities have been described as the most productive environments in Antarctic sea ice due to nutrient replenishment (Cota et al., 1987, 1990; Arrigo et al., 1997; Haas et al., 2001; Kennedy et al., 2002). Fritsen et al., (1994, 1998) have shown that flood-freeze cycles within autumn sea ice benefit algal growth in multi-year pack ice of the western Weddell Sea from nutrient exchange and input.

Garrison and Close (1993) found high winter biomass in thicker and multi-year ice cores where POC was >3000 μM. It has been shown (Kennedy et al., 2002) that POC can accumulate in excess of 6000 μM in summer sea ice floes replenished by nutrients. The outstanding factor appears the retexturing and nutrient replenishment rendering the ice an open system to nutrient exchange and enhanced biological activity. Recent studies also indicate that carbohydrates may be a major fraction of DOC and that the majority of DOC may be produced in the form of C-rich transparent exopolymer particles (TEP) which could act as a cryoprotectant helping algae to overwinter through pitting and smoothing of the ice crystal matrices (Raymond et al., 1994; Amon et al., 2001; Krembs et al., 2001).

However, to date there have been a limited number of studies investigating the biochemical composition of sea ice in relation to its physical structure. Field investigations have sampled pack ice mostly in the spring and summer due to the relative inaccessibility and difficulties of sampling in adverse conditions. Work by Thomas et al., (1998, 2001) has investigated DOC in sea ice of the Amundsen and the Weddell Sea. However no previous study appears to have determined the concentration of DOC and POC contemporaneously in pack ice from the Weddell Sea in winter immediately after ice formation. It is aimed that the present study will fill the gap in knowledge in winter ice cores chemistry, providing a range of DOC

and POC concentrations across a variety of ice types. It is also hypothesised that young ice is a site of lower biological activity in comparison to older ice in view of different ice growth conditions and biological activity.

5.3 Methods

A north-west to south-east transect was performed on cruise ANT VIII/2 on the ice-breaker RV *Polarstern* in the Weddell Sea (64° S 44° W to 69° S 15° W) in the compact pack ice from 17 September to 13 October 1989. Full details of methodologies employed are presented in Augstein et al., (1991). Figure 5.2 shows the location of sampling stations (floes) occupied along the cruise track. The pack ice in the transect area was characterised by floes mostly in contact or leads (aperture from 7/10 to 8/10, Augstein et al., 1991).

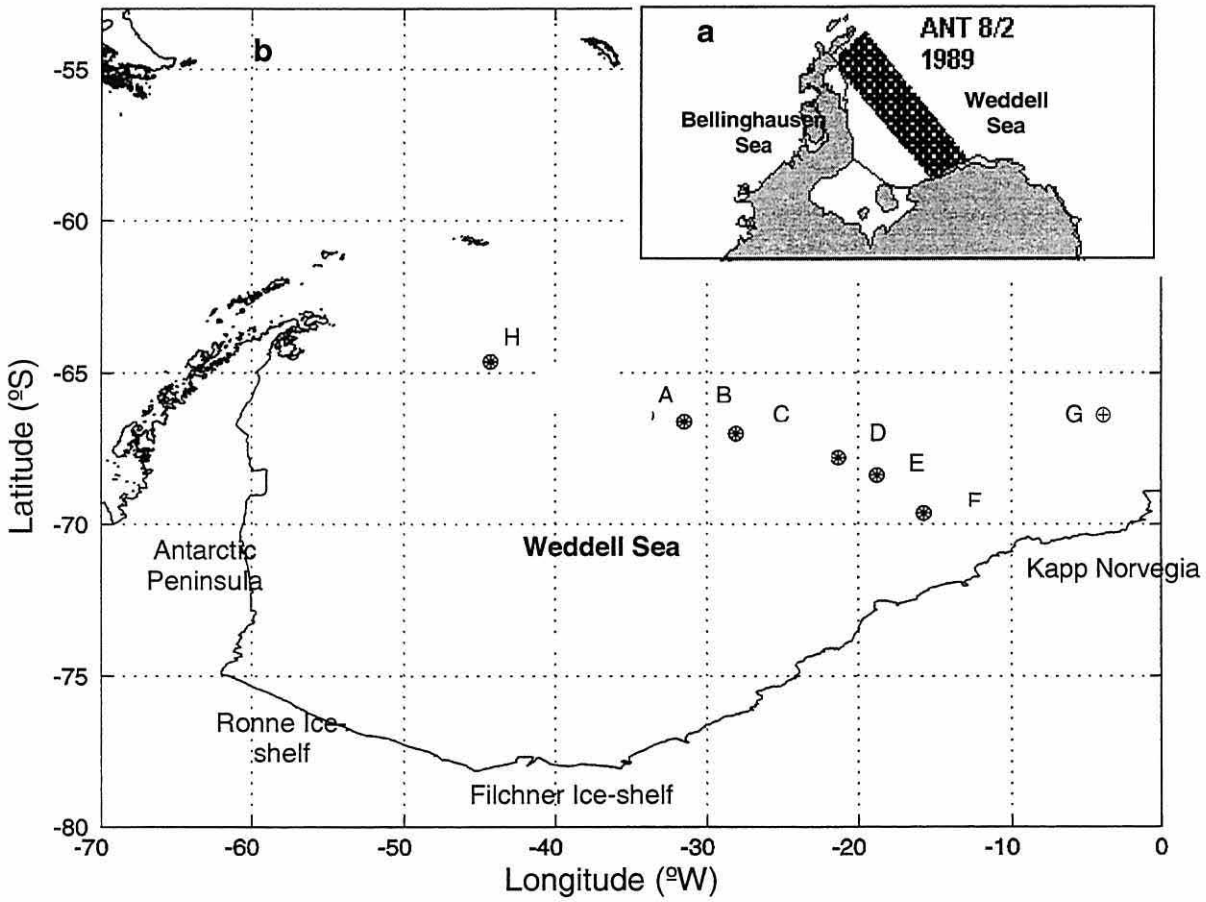

Fig.5.2 (**a**) Study area visited during leg 2 of the Winter Weddell Sea Gyre cruise AN VIII in September-October 1989 and (**b**) location of sampling stations occupied by the Research Vessel *Polarstern*. Station codes denote floes sampled (H = second-year ice, A-F = first-year ice, G = young ice) The oceanic pack ice was sampled in late austral winter to early spring (September-October 1989) on a north-west to south-east cross section along the Weddell Sea, Antarctica. The ice edge was located at approximately 60°S.

Ice cores were distinguished in two age classes, corresponding to first-year and second-year ice on the basis of ice core stratigraphy, thickness, textural composition and snow cover (see Augstein et al., 1991). A summary of numbers of cores sampled per station (floe), ice depth, snow cover and textural composition parameters is presented for 15 sea ice cores (Table 5.2, see Eicken et al., 1991; Eicken, 1998). The second-year ice floe was located in the western part of the transect and sampled at station 16/158 (Table 5.2).

Table 5.2. A summary of sea ice cores sampling date, station number, individual core code, station position (floe), ice texture composition collected during the RV *Polarstern* ANT VIII/2 cruise (Augstein et al., 1991). Abbreviations used are F = frazil ice, C = congelation ice, n.d. = not determined.

Ice Age	Date	Latitude (°S)	Longitude (°W)	Floe Code	Station Code	Sea ice Core Code	(%) Texture Composition
First-Year							
	25.09.89	66° 25'	33° 59'	A	16/166	26801	(60-80% F)
	26.09.89	66° 37'	31° 29'	B	16/168	26901	(60-80% F)
	27.09.89	67° 00'	28° 04'	C	16/171	27101	(60-80% F)
	27.09.89	67° 00'	28° 04'	C	16/171	27111	(60-80% F)
	27.09.89	67° 00'	28° 04'	C	16/171	27121	(60-80% F)
	03.10.89	67° 48'	21° 18'	D	16/176	27601	(>80% C)
	04.10.89	68° 23'	18° 45'	E	16/178	27701	(>80% C)
	05.10.89	69° 38'	15° 42'	F	16/181	27801	(60-80% C)
	13.10.89	68° 59'	07° 56'	G	16/199	28651	n.d.
Second-Year							
	17.09.89	64° 38'	44° 16'	H	16/158	26001	(60-80% C)
	17.09.89	64° 38'	44° 16'	H	16/158	26003	(60-80% C)
	17.09.89	64° 38'	44° 16'	H	16/158	26005	(60-80% C)
	18.09.89	64° 38'	44° 16'	H	16/159	26101	(60-80% C)
	18.09.89	64° 38'	44° 16'	H	16/159	26103	(60-80% C)
	18.09.89	64° 38'	44° 16'	H	16/159	26105	(60-80% C)

The air temperature along the transect between 17 September to 13 October averaged –6.9 ± 5.5 °C, showing high daily variability (Fig. 5.3). A maximum of 0 °C was recorded at the beginning of the transect, whereas a minimum of –18 °C was observed on 29 September at station 16/171 (Fig. 5.3). All sea ice cores showed a linear temperature gradient from the sea ice level to the ice-water interface, where they are just below the seawater freezing point (-1.9 °C, Fig. 5.4 a-i). Only one second-year ice core (26101) temperature profile was available and it showed a mean integrated temperature averaging –2.9 ± 0.5 °C; a distinctive warm layer was observed in the top 0.4 m of the second-year ice core (Fig. 5.4a). Increasingly stronger temperature gradients were observed in shorter first-year ice cores and in the cores sampled in the central and eastern part of the transect. First-year ice core 27601 (Fig. 5.4g) showed the strongest gradient, varying from –7 °C at the ice surface to –2.5 °C at the ice-water surface with a mean profile temperature of –4.8 ± 1.5 °C.

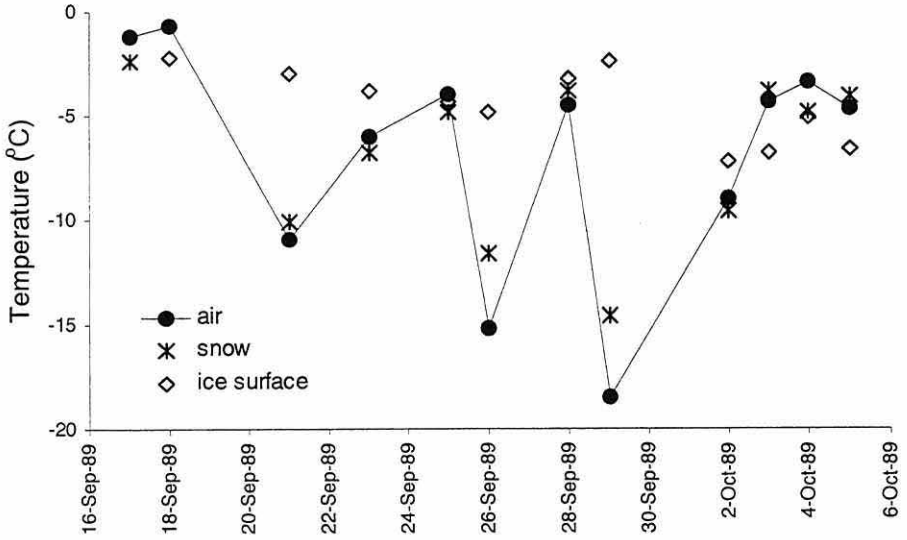

Figure 5.3 Variation of air temperature, surface snow temperature and ice surface temperature recorded at all sampling stations occupied between 17 September and 5 October 1989 along the west-east transect in Weddell Sea pack ice. Data provided courtesy of H. Eicken.

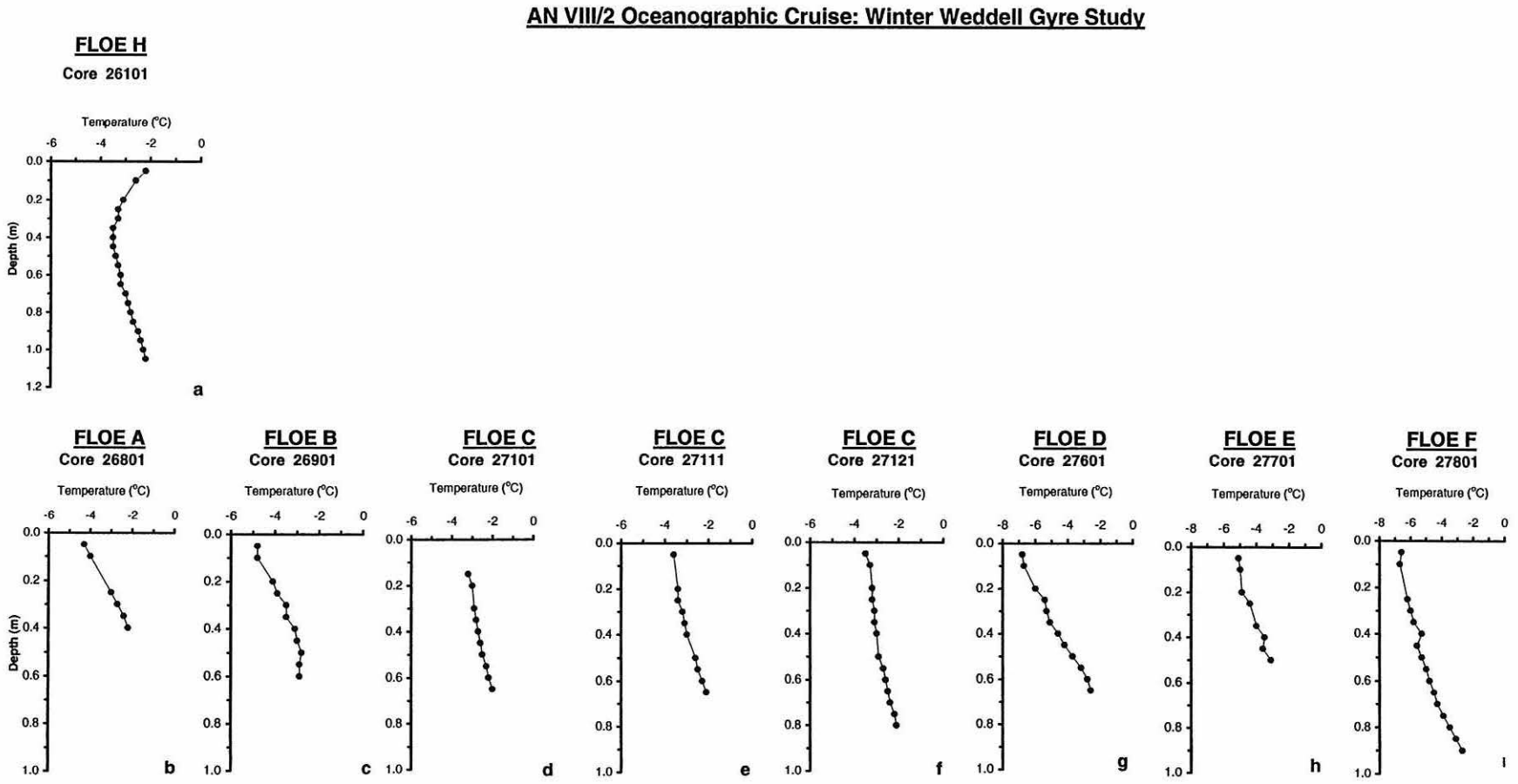

Fig. 5.4. Temperature profile in second-year (Fig. 5.4a) and first-year (Fig. 5.4b-i) sea ice cores sampled from a west-east transect in the Weddell Sea pack ice during RV *Polarstern* cruise ANT VIII/2 during September-October 1989. Note only one temperature profile was available from a second- year ice core (Fig. 5.4a) and eight were available for first-year ice cores. Data courtesy of H. Eicken.

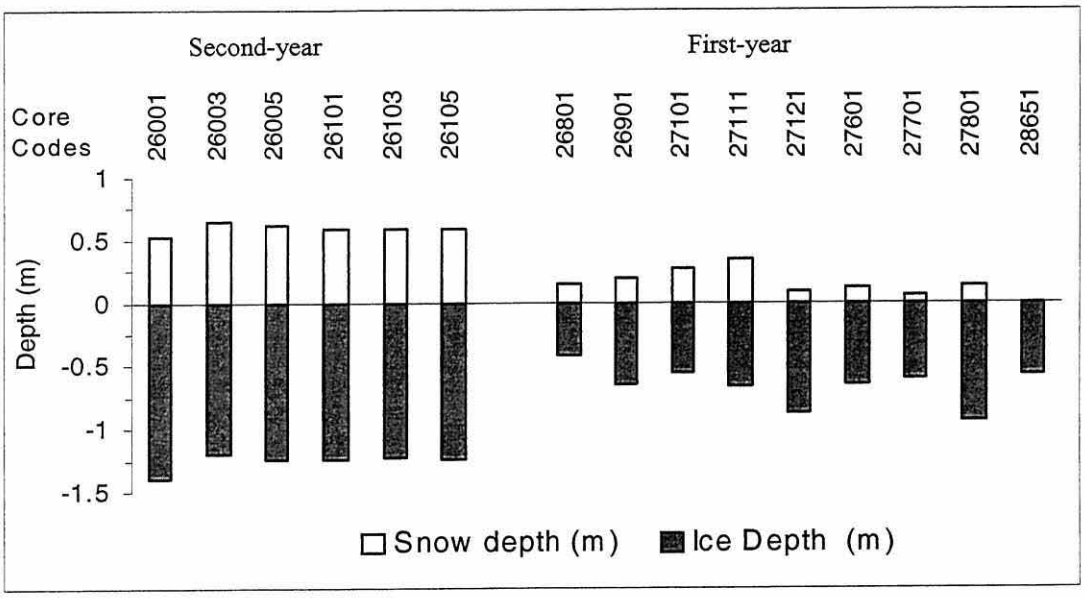

Figure 5.5 Schematic diagram showing six individual second-year cores (codes 26001 to 26105) and nine first-year sea ice cores (codes 26801 to 28651) sampled chronologically in the order presented. The shaded area indicates ice depth (m) of second- and first-year ice cores. The white area represents the depth of the overlying snow cover (m). First- and second-year ice cores sampled in late winter to early spring from floes along a transect across the Weddell Sea pack ice during the Winter Weddell Gyre Study, cruise ANT VIII/2 (September-October 1989). Snow cover depth and sea ice cores depth data courtesy of H. Eicken, University of Fairbanks, Alaska.

On each of the floes (station), typically between one and up to three ice cores were sampled at ice level with a Cold Regions Research and Engineering Laboratory (CRREL) fibreglass-barrel ice coring auger (0.1 m internal diameter) (full details in Eicken et al., 1991; Eicken, 1998). Mean ice thickness was recorded from each floe. Second-year ice was distinctly thicker than first-year ice, on average 1.25 ± 0.07 (SD) m deep (ranging between 1.19-1.39 m) with very low variability between cores (Fig. 5.5). *In situ* temperature (°C) of air, snow, ice surface and vertical ice core profiles was measured at the time of sampling with a Testotherm probe. Snow cover depth (m) was measured above each core.

Cores were immediately transported from the sampling stations to a cold laboratory (<-25 °C) onboard the RV *Polarstern* and individual sea ice cores were cut into sections of 0.02-0.2 m according to ice textural structure, determined under polarised-light filters (see Eicken and Lange, 1989; Eicken et al., 1991). The ice sections were subsequently sub-divided into further sub-samples for a range of determinations. All second-year ice was composed of 60-80% congelation ice,

indicative of quiescent conditions at the ice-water interface. A deep snow layer covered the second-year ice (0.6 m) (Fig. 5.5), resulting in a high average ratio of snow depth to ice thickness, varying from 0.38 to 0.5. In contrast, first-year ice floes were all under 1.0 m depth (Fig. 5.5), but highly variable according to the area sampled. Ice texture analysis (Eicken et al., 1991) showed a high proportion of frazil ice growth (60-80%) up to station 16/171. In the eastern area of Weddell Sea congelation ice was again dominant. First-year ice averaged 30% less snow depth cover than second-year ice, but snow/ice depth ratios were variable, over >0.3 west of station 16/171 and variable in the eastern stations (Fig. 5.5).

For the analysis of inorganic nutrients, which was made onboard the research ship RV *Polarstern*, ice cores sections were melted in PVC containers at 5 °C in the dark for 24 h. The resulting sea ice melt was filtered through pre-combusted (500 °C, 3 h) Whatman GF/F filters. Chl *a* was determined fluorometrically (Augstein et al., 1991; Dieckmann et al., 1998) and further details of phytoplankton pigment concentrations are summarised in Nöthig et al., (1991) and Gradinger (1999). Inorganic macronutrients concentrations (ammonium, NH_4^+, nitrate, NO_3^-, nitrite, NO_2^-, phosphate, PO_4^{3-}, silicate, $Si(OH)_4$ were determined using standard autoanalyser techniques (Kattner and Becker, 1991). Sub-samples of melted ice cores were used for the determination of salinity by use of a conductivity salinometer (WTW LF2000, Weilheim, Germany). For the analysis of DOC, POC and PON the remaining core sub-sections were individually stored in 0.2 mm polyethylene bags at −30 °C in the dark and shipped in dry ice to the UK. In 2001 they were analysed for DOC, POC and PON in the Menai Bridge laboratory, University of Wales, Bangor. The ice samples were handled with clean latex gloves to avoid any contamination and before thawing their surface was melted with copious amounts of UV-irradiated (1 h) Milli-Q water. In order to obtain a sufficiently stained filter-area for the analysis of POC and PON and a sufficient volume of sample for the DOC determination, some of the samples were pooled according to depth. Each ice sample was thawed in the dark at ambient temperature in pre-combusted glass containers (500 °C, 3 h). After complete melting, the resulting water volume was determined gravimetrically and immediately vacuum-filtered onto pre-combusted (500 °C, 3 h) 25 mm Whatman GF/F filters. Filters and filtrates were frozen at −20 °C before being analysed for POC and PON using a Europa Scientific C/N Analyser and DOC

with a TOC analyser (see Chapter 2, sections 2 and 3). In some instances not all chemical parameters were determined on each core due to the limited volume of melt water available, however the majority were described in terms of DOC and POC. All values measured in the study are presented as means ± one standard deviation (SD) except where stated otherwise.

Brine volume of the sea ice is determined as a function of the ice salinity, temperature and density, in the temperature range -2 to -30 °C (Assur, 1958; Cox and Weeks, 1983). The equation used in this study to determine the brine volume (courtesy of D. Thomas, pers. comm.) followed the formula of Cox and Weeks (1983):

$$V_b/V = pS_i/F_1(T)$$

Where V_b= volume of the brine

V= bulk volume

p = bulk density (g cm^{-3})

S_i = salinity of the ice (parts per thousand)

and $$F_1(T) = p_bS_b(1 + k)$$

where T = ice temperature (°C),

p_b = brine density (g cm^{-3})

and S_b and k are determined from Assur (1960).

5.4 Results

The results of the mean concentrations of dissolved and particulate organic and inorganic nutrients, physico-chemical properties in the sectioned first- and second-year ice cores are summarised for comparative purposes in Table 5.3. Depth distribution profiles of salinity, organic carbon, major inorganic nutrients and ice texture have been plotted for individual sea ice cores (see Figs. 5.6-5.14). In second-year cores the bulk salinity of the second-year cores was low, with a mean of 5.3 ± 3.4 (ranging from 1 to 21, Table 5.3) and the process of desalination typical of older

cores is clear in the uniform salinity profiles (see Fig. 5.6 and 5.7). The highest salinity was found at the ice-snow surface of both first- and second-year categories, reaching values >25. First-year ice cores were more saline, showing a mean bulk salinity of 5.78 ± 3.75 and stronger salinity gradients from the surface to the ice-water interface (salinity range from a minimum of 1.79 to a maximum of 22.2) (Table 5.3). Some of the first-year cores showed a C-shape salinity profile typical of newly formed ice (e.g. see floe C, cores 27101 to 27121, Fig. 5.11).

Phytoplankton abundance, despite high variability in values, was clearly enriched in all second-year ice cores. Chl *a* showed an average value of 10.1 ± 12.2 μg l^{-1}, varying from 0.6 to a maximum of 56 μg l^{-1} (Table 5.3). The chl *a* concentration increased from below the ice-snow interface and consistently attained highest concentrations in the upper half of the second-year ice, at a depth of 0.6 m in all second-year ice cores (Fig. 5.6 and Fig. 5.7). Chl *a* maxima were often coincident with complex ice texture (mixed columnar/granular ice or intermediate columnar/granular ice). The average and maximum chl *a* in first-year ice cores was around 30% lower than second-year ice cores, averaging 2.5 ± 3.5 μg l^{-1} (range from 0.01 to 18.7 μg l^{-1}).

In second-year ice DOC concentrations averaged 144 ± 121 μM and ranged widely from 30 to a maximum of 872 μM (Table 5.3, Fig. 5.6 core 26001). A clear trend was discernible in the second-year cores, each showing high DOC peaks characteristically in the upper portion (0-0.6 m) of the cores at, or above, the chl *a* maximum (Fig. 5.6, 5.7). For instance, the maximum DOC concentrations found in the upper half of second-year core 26001 (>500 μM, see Fig. 5.6) reflected the high pigment content of >50 μg chl *a* l^{-1}. In all second-year ice cores a particularly strong DOC concentration gradient was evident, ranging over a factor of 30 from the ice-snow surface to the ice-water interface (see Fig. 5.6, 5.7).

Table 5.3. A summary of the mean, range, standard deviation and sample size of variables studied from first- and second-year sea ice cores collected in winter pack ice from the Weddell Sea, Antarctica (cruise ANT VIII/2, September-October 1989). Abbreviations used are SD = standard deviation, n = number of samples, Chl *a* = chlorophyll *a*, DOC = dissolved organic carbon, POC = particulate organic carbon and PON = particulate organic nitrogen. The ice thickness, salinity, chl *a* and inorganic nutrient concentrations were provided courtesy of H. Eicken.

Ice Age	Variable	Mean	± SD	Minimum	Maximum	n
First-Year						
	Ice thickness (m)	0.66	0.16	0.42	0.94	9
	Salinity	5.78	3.75	1.79	22.20	63
	Chl *a* (μg l^{-1})	2.5	3.5	0.01	18.7	71
	DOC (μM)	83	52	16	290	66
	POC (μM)	87	55	24	374	49
	PON (μM)	11.9	5.0	3.4	23.6	39
	POC:PON (molar)	9.5	28.7	3.6	203	39
	Silicate (μM)	5.94	3.6	0.50	16.3	34
	Nitrate (μM)	4.2	3.6	0.60	13.5	34
	Ammonia (μM)	3.51	1.5	1.22	7.7	34
	Phosphate (μM)	0.11	0.14	0	0.63	34
	Calculated Brine Volume (ml)	73	39	33	202	65
	DOC in brine (μM)	1367	960	269	4835	60
Second-Year						
	Ice thickness (m)	1.25	0.07	1.19	1.39	6
	Salinity	5.33	3.4	1.03	21.0	86
	Chl *a* (μg l^{-1})	10.13	12.2	0.60	56	85
	DOC (μM)	144	121	31	872	84
	POC (μM)	131	72	30	330	68
	PON (μM)	10.0	5.6	2.8	26.7	55
	POC:PON (molar)	18.5	16.8	2.8	76	55
	Silicate (μM)	5.93	3.5	1.40	16.20	39
	Nitrate (μM)	2.6	2.3	0.50	8.8	39
	Ammonia (μM)	4.03	2.4	1.36	10.1	39
	Phosphate (μM)	0.61	0.42	0.06	1.92	39
	Calculated Brine Volume (ml)	93	82	19	483	86
	DOC in brine (μM)	1971	1359	234	7526	83

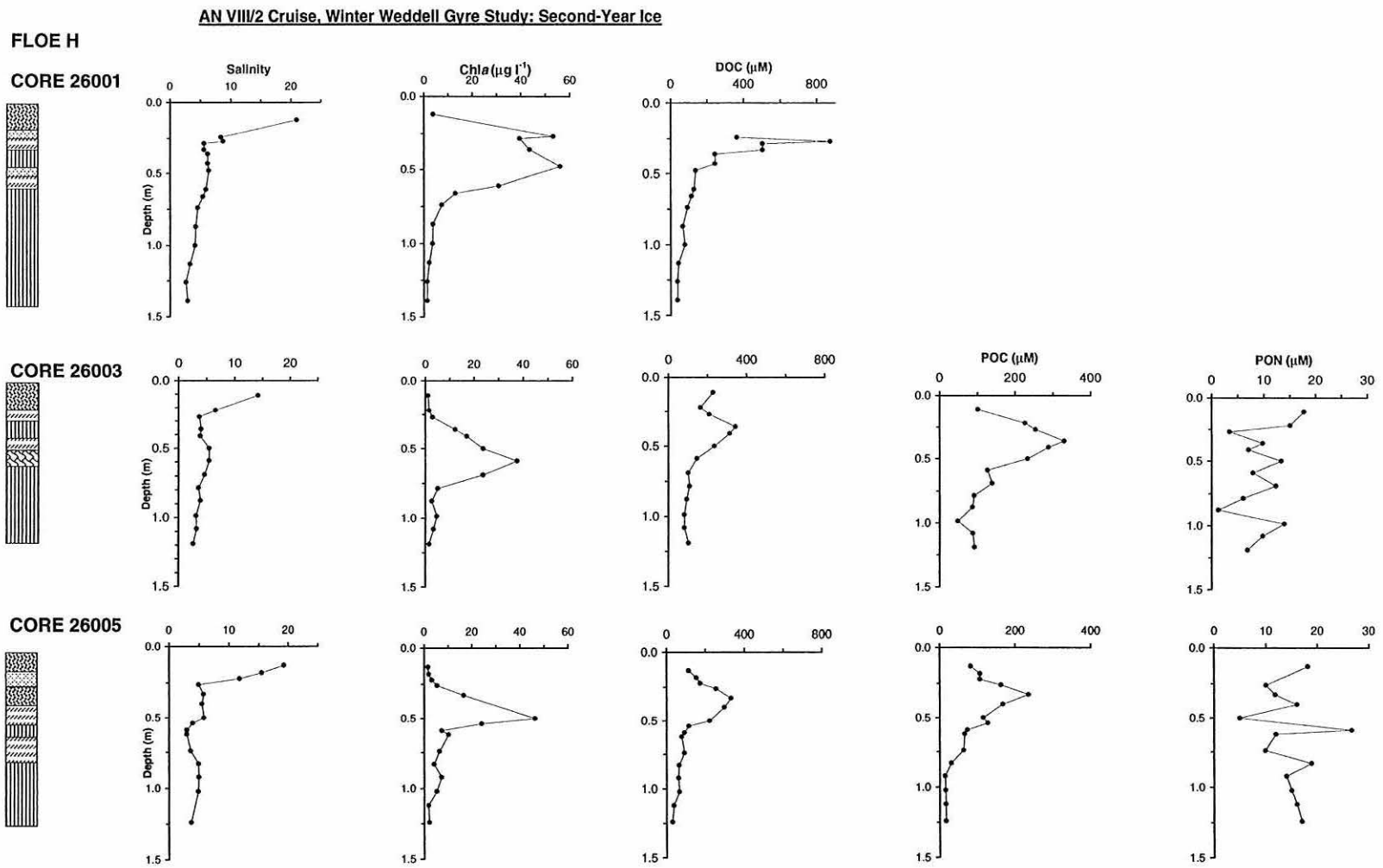

Fig. 5.6. Composite ice texture stratigraphy and vertical profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC) , particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations in second year ice cores (26001, 26003, 26005) collected from Floe H. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll a, salinity data courtesy of H. Eicken.

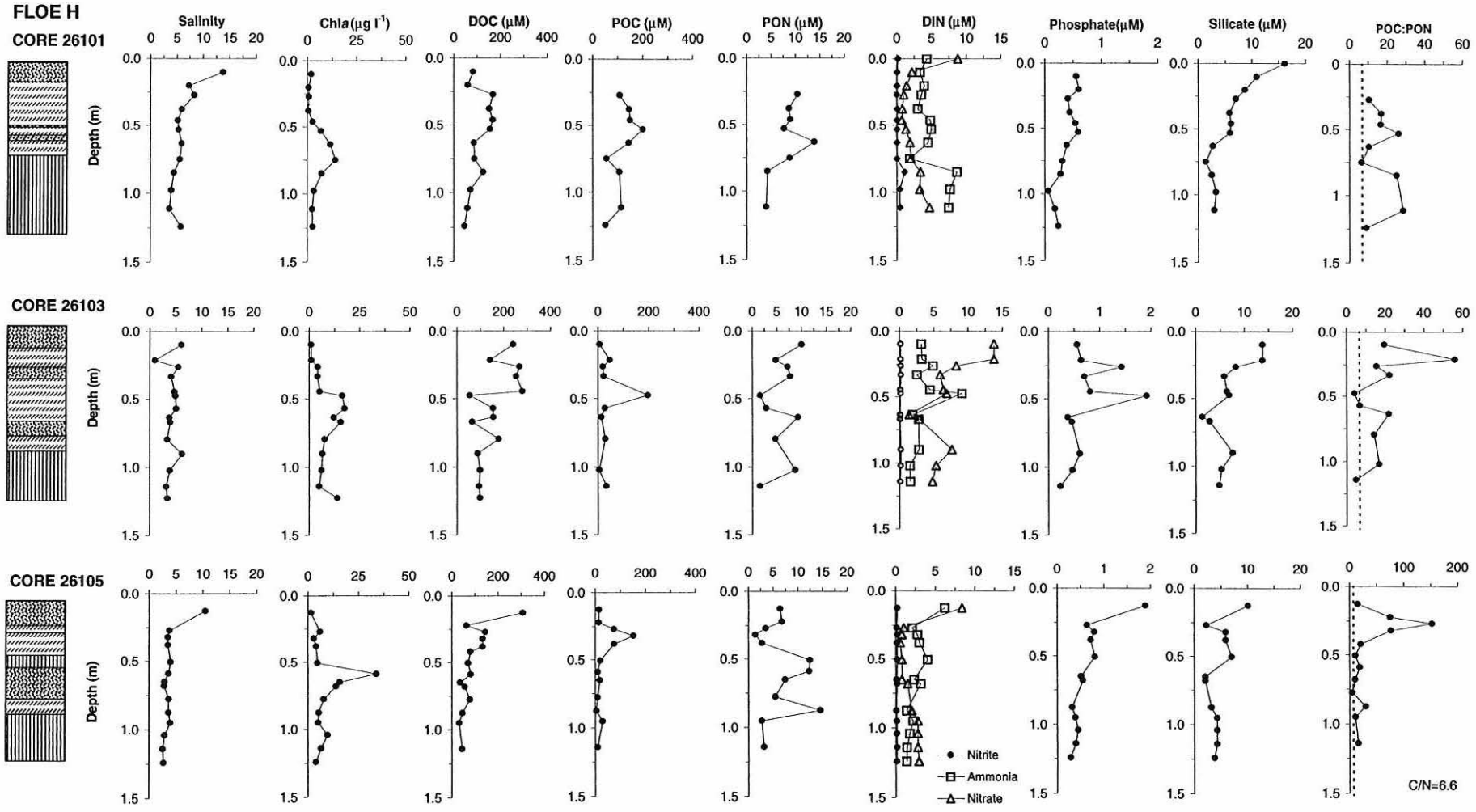

Fig. 5.7. Composite ice texture stratigraphy and vertical profiles of salinity, chlorophyll *a* concentration, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), inorganic nutrient concentrations and POC:PON ratio in second-year ice cores (26101, 26103, 26105) collected from Floe H. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity data courtesy of H. Eicken. Ice texture legend as in Fig. 5. 6.

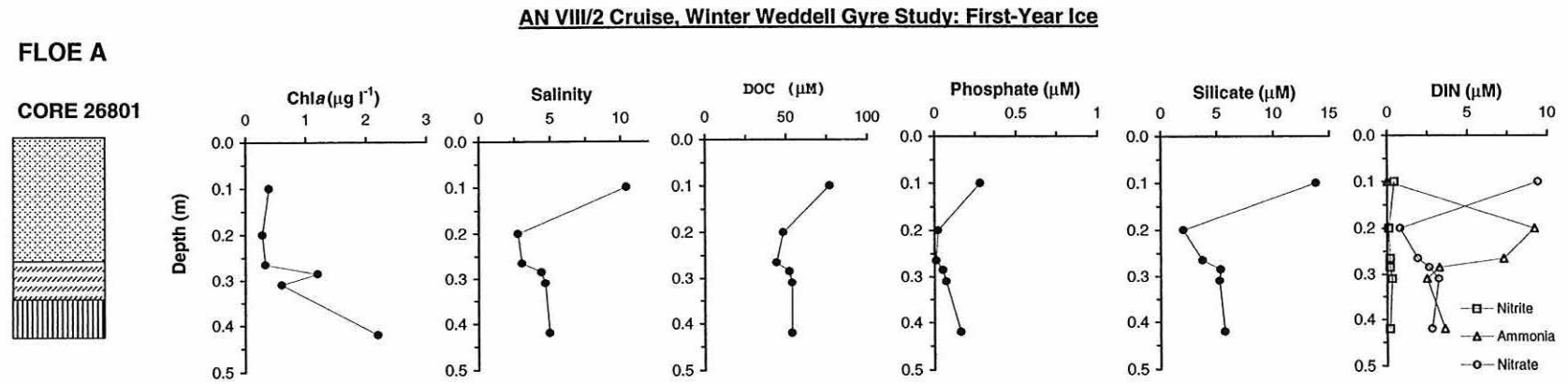

Fig. 5.8. Composite ice texture stratigraphy and vertical profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), phosphate, silicate and dissolved inorganic nitrogen (DIN) concentrations in a first-year ice core (26801) from Floe A. Samples were taken from a transect in pack ice of the Weddell Sea in September-October 1989. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity and inorganic nutrient data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

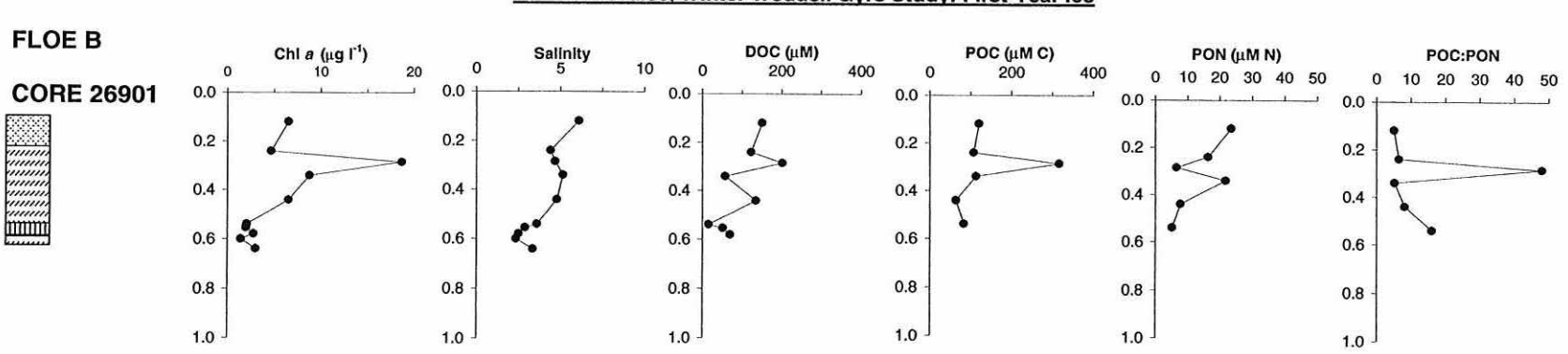

Fig. 5.9. Composite ice texture stratigraphy and vertical depth profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON) concentrations and particulate organic carbon to particulate organic nitrogen ratios (POC:PON) in a first-year ice core (26901) collected from Floe B. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

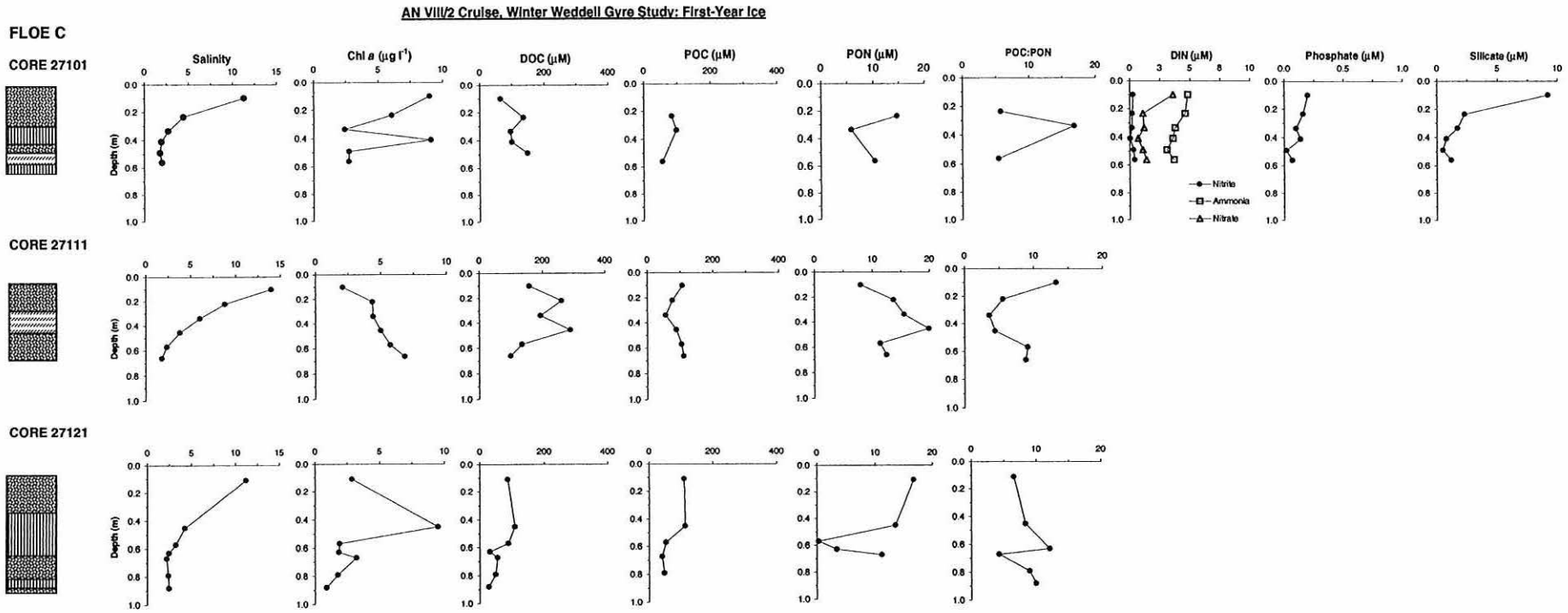

Fig. 5.10. Composite ice texture stratigraphy and vertical profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), particulate organic carbon to particulate organic nitrogen ratio (POC:PON), dissolved inorganic nitrogen (DIN), phosphate and silicate concentrations in first-year ice cores (27101, 27111, 27121) collected from Floe C. Samples were taken from a transect in pack ice of the Weddell Sea in winter 1989. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity and inorganic nutrient data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

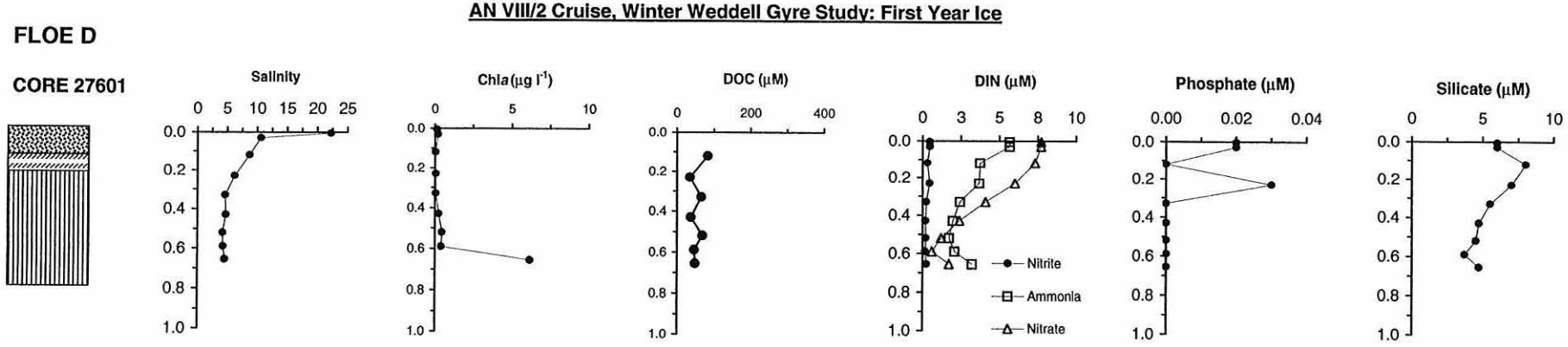

Fig. 5.11. Composite ice texture stratigraphy and vertical profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN), phosphate and silicate concentrations in a first-year ice core (27601) collected from Floe D. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity and inorganic nutrient data data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

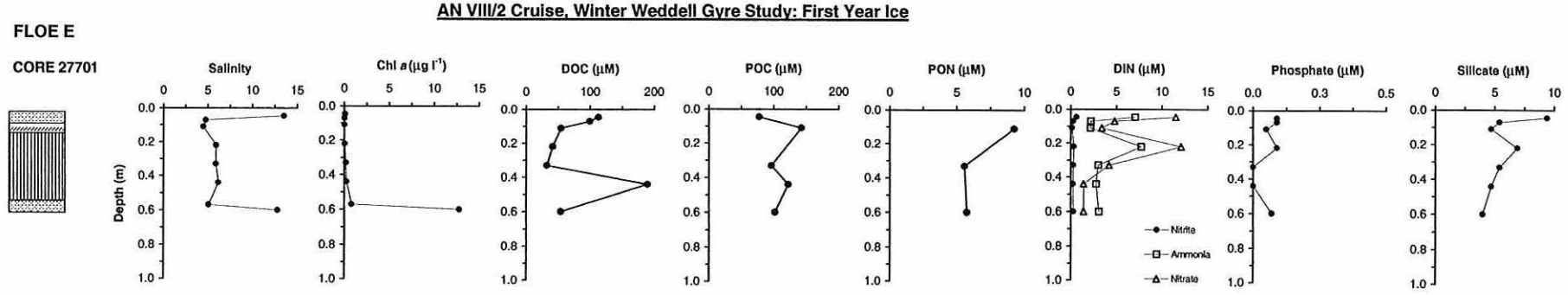

Fig. 5.12. Composite ice texture stratigraphy and vertical depth profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), dissolved inorganic nitrogen (DIN), phosphate and silicate concentrations in a first-year ice core (27701) collected from Floe E. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity and inorganic nutrient data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

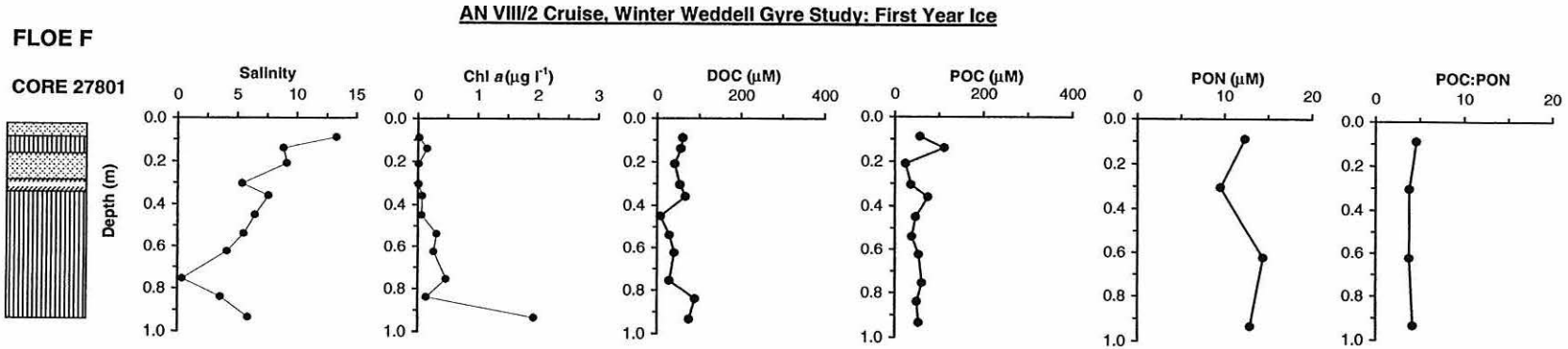

Fig. 5.13. Composite ice texture stratigraphy and vertical depth profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), particulate organic carbon (POC) particulate organic nitrogen (PON) concentrations and particulate organic carbon to particulate nitrogen ratios (POC:PON) in a first-year ice core (27801) collected from Floe F. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity data courtesy of H.Eicken. Ice texture legend as in Fig. 5.6.

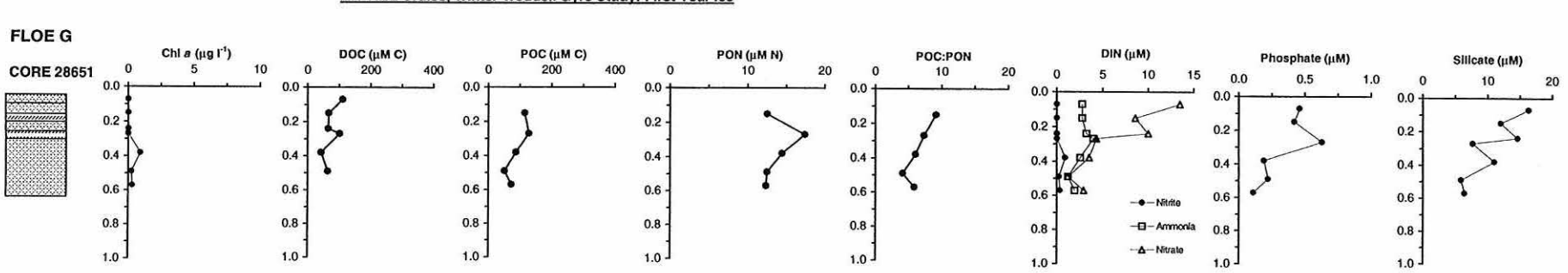

Fig. 5.14. Composite ice texture stratigraphy and vertical depth profiles of chlorophyll *a* concentration, salinity, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON) concentrations, particulate organic carbon to particulate organic nitrogen ratio (POC:PON), dissolved inorganic nitrogen (DIN), phosphate and silicate concentrations in a first-year ice core (28651) collected from Floe G. Samples were taken from a transect in pack ice of the Weddell Sea in winter. Textural characteristics were derived from analyses of thick sections under polarised light. Ice texture, chlorophyll *a*, salinity and inorganic nutrient data courtesy of H. Eicken. Ice texture legend as in Fig. 5.6.

DOC concentrations in first-year ice showed less variability and lower values than in second-year ice, averaging 83 ± 52 μM and ranging from 16 to 290 μM (Fig. 5.8) The top half of the first-year ice had approximately 10 times less DOC than observed in second-year ice cores. However, in the bottom 50 cm, the range and distribution of DOC concentration is similar in both first- and second-year ice, e.g. Floe H (cores 26001-26005; Fig. 5.7).

As observed from Table 5.3 and individual cores profiles (Figs. 5.6 and 5.7) there was a well defined gradient in the texture of ice in the second-year floe, suggesting that the upper portion of second-year core was older than the lower portion, consisting mainly of congelation ice, which is more similar in characteristics to the portions of ice floes observed belonging to first-year ice. Factors such as geographical location, ice growth modality and seasonality may play a major role in causing such difference. Preliminary analyses showed overall lack of homogeneity of variance and normality, therefore a Mann-Whitney test was performed to test for differences between median DOC concentrations in ice core sections (see Table 5.4).

The results obtained showed a significant difference between median DOC concentration of first-year cores and second-year cores ($p < 0.01$, Table 5.4). A second Mann-Whitney test was run to test if the DOC concentration in the upper 0.6 m of the ice cores is the same as the DOC concentration in the lower portion of the second-year cores (the cut-out point used was the change in ice texture profile from predominantly congelation to mixed/frazil in second-year ice consistently at 0.6 m, see Figs. 5.6 and 5.7).

Table 5.4. Matrix of Mann-Whitney test results for the differences in median dissolved organic carbon (DOC) concentrations between first-year ice core sections and second-year ice core sections, second-year upper ice core sections (0-0.6 m) and second-year lower ice core sections (0.6-1.2m) of sea ice cores from the winter Weddell Sea. The analysis also tested for differences between lower and upper sections of second-year ice.

	First-year ice	Second-year ice (0-0.6 m)
Second-year ice	$p < 0.01$	
Second-year ice (0-0.6 m)	$p < 0.01$	
Second-year ice (0.6-1.2 m)	$p > 0.05$	$p < 0.01$

The results obtained showed significant differences between DOC concentrations in upper, retextured area of the cores and the lower portion, characterised by congelation ice, of the second-year cores, approximately by a 2:1 ratio ($p < 0.01$, Table 5.4). Differences were also tested between the lower portion (0.6-1.2 m) of the second-year cores versus the first-year ice cores and no significant difference ($p > 0.05$) was found in terms of DOC concentration (Table 5.4). Finally a further Mann-Whitney test shows that the upper portions of the second-year ice cores are significantly different from the first-year ice, indicating a strong DOC enrichment in the older cores ($p < 0.01$, Table 5.4). A non-parametric Kruskal-Wallis was utilised for testing the null hypothesis that the mean DOC concentrations are the same between the individual first-year ice cores. The results obtained allow us to reject the null hypothesis at $p < 0.05$ and show that there are significant differences in DOC between cores, reflecting the spatial differences in ice types, texture and potential biological activity that impinge on the DOC concentration (Table 5.5).

Table 5.5. Kruskal-Wallis test results for the differences in median DOC concentration (µM) distribution in the individual first-year sea ice cores sampled from Weddell Sea pack ice floes in winter (AN VIII/2, September-October 1989). Abbreviations used are n = number of samples, df = degrees of freedom.

Ice core code	Median DOC Concentration (µM)	n	df	p
26801	53	6	8	0.002
26901	70	10		
27101	99	6		
27111	177	6		
27121	55	7		
27601	48	7		
27701	55	7		
27801	47	11		
28651	68	7		

Brine volumes of ice core sections were not measured directly, therefore it was calculated to give an indication of the porosity of the ice and an estimate of DOC concentration within the brine according to the empirical equations of Cox and Weeks (1983) using *in situ* measurements of temperature and salinity (see section 5.3). The second-year ice floes contained a higher brine volume (mean of 93 ± 82 ml, range 19-483 ml), in comparison with 73 ± 39 ml in the first-year ice cores, varying from 33-202 ml (see Table 5.3). The results may have been affected by the

strong temperature difference between cores and the warmer older ice. Maximum brine volumes in both ice cores categories (respectively 202 and 483 ml in first- and second-year ice) were restricted to the surface layers at the ice-snow interface, where seawater can infiltrate (Ackley and Sullivan, 1994). The DOC content within the cores brine was determined on the basis of the calculated brine volumes and measured bulk DOC concentrations (Table 5.3). Mean DOC content encountered in second-year ice brine was >1979 ± 1360 μM and varied between 230 to 7500 μM. First-year core brines were not as enriched in DOC, which averages >1370 ± 960 μM and ranged between 270 to 4840 μM (Table 5.3).

POC concentrations were variable in both first- and multi-year ice categories, but were higher on average in second-year ice, averaging 131 ± 72 μM (ranging tenfold from 30 to 330 μM, Table 5.3). In first-year ice cores the average POC concentration was 40% lower, with a mean POC content of 87 ± 55 μM, however the range was similar to second-year ice (24-374 μM), showing an isolated maximum value of 374 μM. PON concentrations were comparable within the two ice age types with a mean of 11.9 ± 5.0 μM (3.4-23.6) and 10.1 ± 5.6 μM (range 2.8-26.7) in first- and multi-year sea ice respectively (Table 5.3).

POC:PON ratios were different between first- and second-year ice as shown in vertical sea ice core profiles. The mean POC:PON ratios of the particulate phases for all samples was 14.6 ± 14 (Table 5.8) a value twice greater than the classical Redfield ratio and an indication of potential presence of broken down, detrital material, storage of high-C compounds (e.g. lipids, carbohydrates) within algal cells and nitrogen depletion. There was significantly greater enrichment of C-rich organic particles (POC:PON 18.5 ± 16.8, range 3-76) within the second-year ice, indicative of nutrient depletion. Conversely, in first-year ice POC:PON averaged 9.5 ± 28.7 (range 3.6 to 203) closer to the Redfield ratio and indicating cells were relatively more replete in inorganic nitrogen nutrients. Results of inorganic nutrients are on the basis available for three of the second-year cores 26101, 26103, 26105 (Floe H, Fig. 5.7) and from first-year cores 26801, 27101, 27601, 27701, 28651, (Figs. 5.8, 5.10, 5.11, 5.12, 5.14).

Among inorganic nutrients respectively nitrate and ammonium were the dominant inorganic nitrogen species, whereas nitrite was negligible in all cores, indicating low bacterial activity (see Figs. 5.7, 5.8, 5.10, 5.11, 5.12, 5.14). Nitrate was observed to be more replete in first-year sea ice cores, with a mean of 4.2 ± 3.6 μM and varied from 0.6 to 13.5 μM (Table 5.3). The maximum nitrate concentrations observed were in the upper layers of the youngest sea ice core (28651, Floe G, Fig. 5.14) sampled in mid October in the eastern coastal area of the Weddell Sea transect (Fig. 5.2). In second-year sea ice nitrate concentrations averaged 2.6 ± 2.3 μM and varied between 0.5 to 8.8 μM (Table 5.3), showing exhaustion in correspondence to high phytoplankton abundance (chl *a*) and high dissolved and particulate organic carbon pools (Fig. 5.7, cores 26103 and 26105). Ammonium in second-year sea ice was comparatively more abundant than in first-year ice, the average being in excess of 4.0 ± 2.4 μM, with a range between 1.4 to 10.1 μM (Table 5.3). The trend observed from the data of cores 26101 to 26105 was of a greater concentration of ammonium ions where nitrate was depleted (see Fig 5.7). In first-year ice the average concentration of ammonium was 3.5 ± 1.5 μM and varied between 1.2 to 7.7 μM (see Table 5.3). The mean phosphate concentration in first-year ice was low (0.11 ± 0.14 μM) and the maximum did not exceed 0.6 μM (Table 5.3). A fivefold higher mean concentration of phosphate was found in second-year ice, averaging 0.61 ± 0.42 μM and ranging between 0.09 to 1.92 μM (Table 5.3). Silicate concentrations were in a similar range both in terms of means and maxima in first-year ice (5.9 ± 3.6 μM, ranging from 0.5 to16.2) and second-year ice (5.9 ± 3.5 μM, varying from 1.2 to 16.2 μM) (Table 5.3).

Inorganic nutrient concentrations were plotted against salinity to identify whether their behaviour was conservative during the freezing process (due to physical dilution between seawater and freshwater) or nutrient concentrations are affected by other biological or chemical processes (Dieckmann et al., 1991; Thomas et al., 1998; Kennedy et al., 2002). The concentration of inorganic and organic nutrients, in the underlying seawater at each site, were not recorded for the area at the time of ice formation. Therefore dilution lines were extrapolated using literature data representing minimum and maximum inorganic nutrient concentrations in surface

ice-free waters of the Weddell Sea at the time of ice formation (Dieckmann et al., 1991; Thomas et al., 1998; Wedborg et al., 1998; Kennedy et al., 2002; Table 5.6).

Table 5.6. Ranges of organic matter and inorganic nutrient concentrations extracted from the literature and used in the calculation of physical dilution lines of individual nutrients. Concentrations refer to ice-free Antarctic open waters studies.

Variable	Minimum (μM)	Maximum (μM)	Reference
DOC	45	60	Wedborg et al., (1998)
POC	10	20	Wedborg et al., (1998)
Nitrate	28	32	Kennedy et al., (2002)
Silicate	59	73	Dieckmann et al., (1991)
Phosphate	1.9	2.1	Dieckmann et al., (1991)
Ammonium	0	1	Thomas et al., (1998)
Nitrite	0	0.25	Thomas et al., (1998)
DIN	28	33.25	Thomas et al., (1998)

Figure 5.15 (a, c, e, g, i, k) shows the distribution of inorganic nutrients as a function of salinity in first-year ice cores (core codes 26801, 27101, 27601, 27701, 28651). It can be noted that silicate and phosphate concentrations were mostly depleted compared to the levels foreseen by the dilution lines based on minimum and maximum concentrations in surface polar waters in late summer before the formation of sea ice (silicate, 59 to 73 μM; phosphate, 1.9 to 2.1 μM, Table 5.6). There was a good correlation of silicate with salinity, despite depletion in relation to physical dilution, whereas very low levels of phosphate (<0.3 μM) are observed, distributed in the young sea ice irrespective of salinity, showing elevated consumption (Fig. 5.15e). Ammonium and nitrite were greatly in excess of the maximum levels expected from the dilution extrapolations at a salinity of 34 (see Fig. 5.15g), indicating a net production within the first-year ice from the time of the ice formation. Nitrate is apparently the only inorganic nutrient in the range closest to the dilution lines estimated from minimum and maximum values (nitrate, 28 to 32 μM, Table 5.6) in surface waters. However, some consumption of nitrate has taken place in particular at salinity below 6 (see Fig. 5.15a).

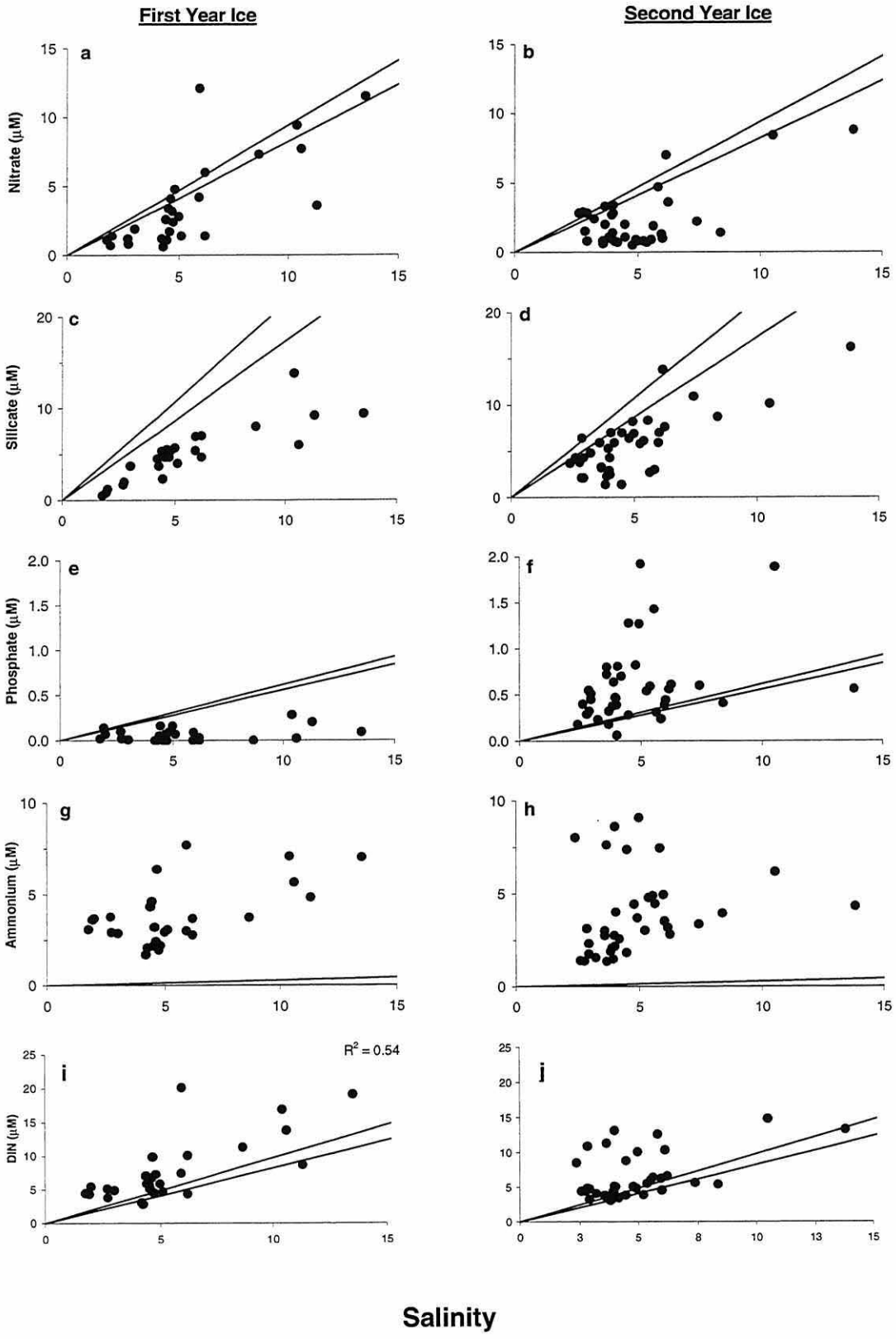

Fig. 5.15. Comparison of inorganic nutrient concentrations (a, b: nitrate; c, d: silicate; e, f: phosphate; g, h: ammonium; i, j: DIN) as a function of salinity in first-year ice (a,c,e,g,i) and second-year (b,d,f,h,j) sectioned sea ice cores collected in winter pack ice of the Weddell Sea sampled during the research cruise ANT VIII/2. The solid lines indicate the range of concentrations expected from physical dilution of surface seawater of the Weddell Sea on the basis of minimum and maximum ranges of values extracted from the literature (see Table 5.6).

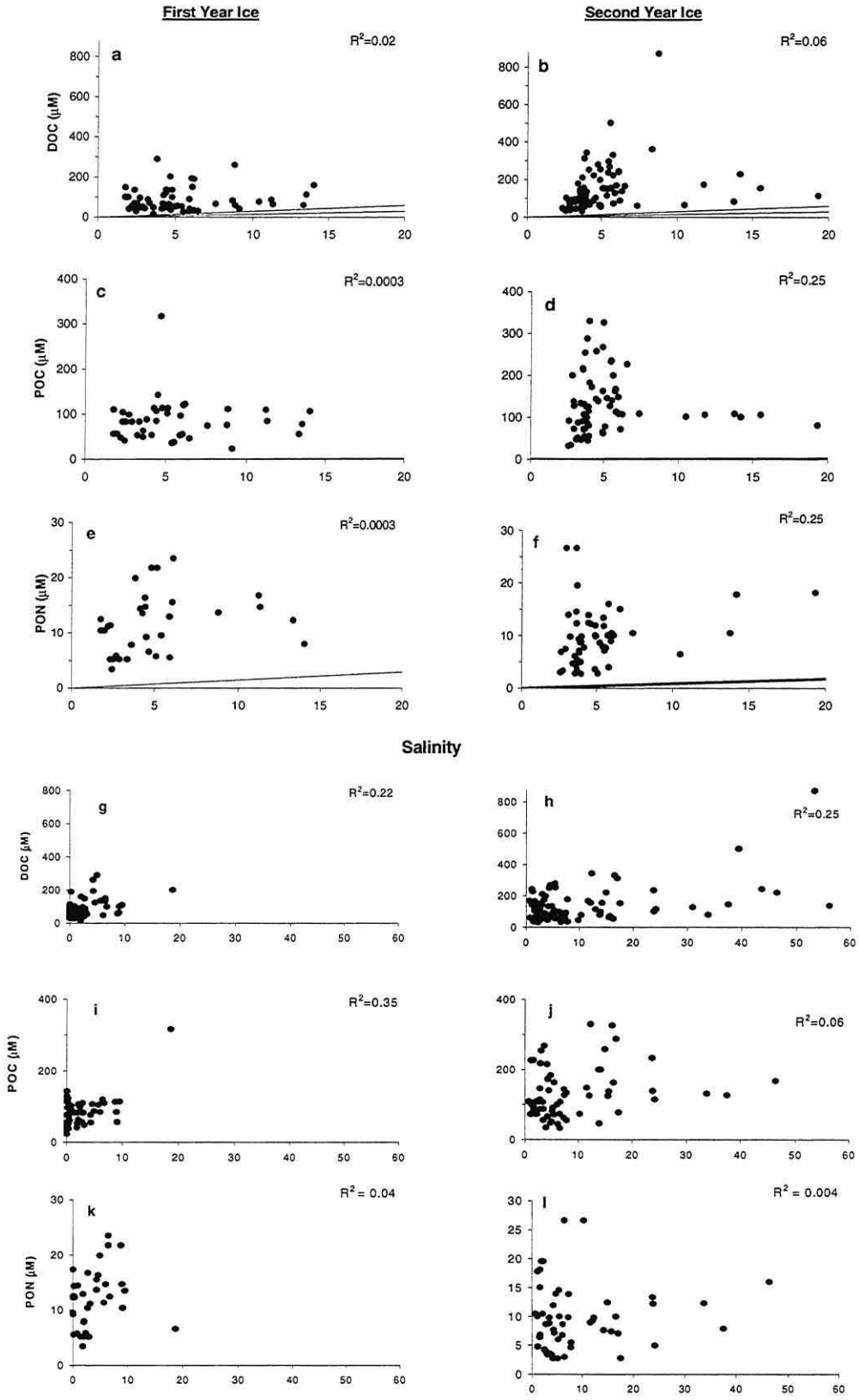

Fig. 5.16. Dissolved and particulate organic carbon (DOC, POC) and particulate organic nitrogen (PON) concentrations as a function of salinity (a,c,e) and chlorophyll *a* (g,i,k) in first-year ice core sections (n = 34), and as a function of salinity (b,d,f) and chlorophyll *a* (h,j,l) in second-year (n = 39) ice cores sampled from winter pack ice of the Weddell Sea, research cruise ANT VIII/2. The solid lines indicate the range of concentrations expected from physical dilution of surface seawater of the Weddell Sea. Values used were extracted from the literature on the basis of minimum and maximum ranges.

In Figure 5.15 (b,d,f,h,j,l) nitrate, silicate, phosphate, ammonium, nitrite and total dissolved inorganic nitrogen (DIN) concentrations are plotted as a function of salinity in second-year ice cores. Nitrate concentration at salinities below 8 shows depletion in comparison to the expected levels observed in surface seawater (Fig. 5.15a). However, there are a few isolated sections of the upper portions of the ice cores where nitrate is above the dilution line, potentially where input of surface seawater or melting snow replenished nutrient concentrations. As opposed to first-year ice, in second-year ice silicate shows lower levels of correlation with salinity, but values are found closer to the range of concentrations expected from the dilution lines (Fig. 5.15d). Phosphate concentrations lie above the range predicted from physical dilution, indicating extremely high levels of production compared to the exhaustion observed in first-year ice (Fig. 5.15f). Ammonium is clearly far in excess of the range of surface seawater values at salinity of 34. In particular the highest ammonium concentrations (>7 μM) were found at the bottom of the ice cores (at salinity <5) and a separate cluster of ammonium values (<5 μM) was mostly found within the upper sections of the ice cores. Thomas et al., (1998) found a similar ammonium enrichment in summer second- and multi-year pack ice of the Amundsen Sea, Antarctica. Similarly, nitrite is in excess of the dilution lines, but the regression line does not indicate correlation with salinity, as opposed to a stronger correlation in first-year ice.

The relationship between organic matter and salinity was examined as shown in Fig. 5.16. It can be noted that in both first- and second-year melted ice cores DOC, POC and PON are all in excess of concentrations predicted on the basis of minimum and maximum Antarctic surface water values (Fig. 5.16a,b,c,d,e,f, Table 5.6). The plots show substantial accumulation and production of organic matter fractions regardless of salinity. Similarly, the concentrations of organic matter are plotted as a function of the chl *a* concentrations in first- (Fig. 5.16g,i,k) and second-year ice (Fig. 5.16h,j,l). There is no apparent trend of DOC, POC and PON with chl *a* in second-year or first-year ice. The origin of DOC may not be strictly linked with phytoplankton abundance in the ice, but may derive from other sources such as excretion and breakdown of internal cellular contents due to lysis and its degradation may be limited by factors such as temperature on enzymatic hydrolysis. POM is also abundant in first-year ice even at very low levels of chl *a*, indicating that the nature

may be varied and include heterotrophic organisms or remnants of biological activity entrapped within the ice (Thomas et al., 2001). No discernible correlation is observed between DOC and POC in either first- or second-year ice cores (Fig. 5.16e,f,g,h).

A correlation analysis was carried out on the data for first- and second-year ice to explore the relationship between the variables and the resulting Pearson correlation coefficients are presented in matrices for first- and second-year ice categories (Table 5.7a and 5.7b). DOC and POC concentrations were highly correlated in both first-year sea ice (Pearson $r = 0.388$, $p < 0.01$) and second-year sea ice cores (Pearson $r = 0.608$, $p < 0.01$). The concentration of DOC in second-year ice was related to salinity, whereas DOC concentration was not significantly correlated with salinity in first-year ice (Table 5.7a). POC generally coincided with chl *a* in second-year ice profiles, but particularly in the first-year ice. In second-year ice an inverse relationship exists between POC concentrations and NO_3 concentrations, indicating that the inorganic nutrient was incorporated into biomass. The relationship between the nitrate and phosphate inorganic nutrients usually highly correlated did not hold in the second-year ice. Sea ice core variables measured are presented in Table 5.8 and a correlation matrix shows the Pearson product moment correlation coefficients between each pair of variables (see Table 5.9). The overall mean DOC concentration in all ice cores (122 μM) is > 11% higher than the total mean POC (108 μM). The concentration range of bulk DOC ranged fiftyfold, from 16 to 872 μM. Not only does DOC show a similar mean magnitude as POC, but it exhibits an overall highly positive correlation with the POC pool (Pearson $r = 0.568$, $p < 0.01$, Table 5.9).

Table 5.7. Two correlation matrices showing the Pearson product moment correlation coefficient between each pair of variables measured from (**a**) first-year sea ice core sections (n = 34) and (**b**) second-year sea ice core sections (n = 39) collected along a transect in winter of 1989 across pack ice of the Weddell Sea, Antarctica during the RV *Polarstern* research cruise ANT VIII/2. Level of significance * = $p < 0.01$, • = $p < 0.05$. Abbreviations used are Chl *a*, DOC, POC, PON = chlorophyll *a*, dissolved organic carbon, particulate organic carbon, particulate organic nitrogen.

a	DOC	POC	PON	Chl *a*	Salinity	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NO_2^-
POC	0.388*								
PON	0.374•	0.059							
Chl *a*	0.468*	0.593*	0.191						
Salinity	0.157	0.035	0.241	-0.069					
PO_4^3	0.255	0.328	0.649•	0.015	0.126				
$Si(OH)_4$	0.095	0.440	0.590•	-0.301	0.622*	0.755*			
NO_3	0.090	0.364	0.449	-0.367	0.658*	0.525*	0.790*		
NO_2^-	0.175	0.014	0.171	-0.273	0.667*	0.248	0.483*	0.732*	
NH_4^+	0.048	-0.068	0.171	0.087	0.537*	0.044	0.190	0.522*	0.563*
b	DOC	POC	PON	Chl *a*	Salinity	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NO_2^-
POC	0.608*								
PON	-0.087	-0.181							
Chl *a*	0.495*	0.246*	0.191						
Salinity	0.240•	0.035	0.241	-0.020					
PO_4^3	0.277	0.589	0.649•	0.142	0.294				
$Si(OH)_4$	0.293	0.132	0.590•	-0.471•	0.576*	0.394•			
NO_3	-0.278	-0.365•	0.449	-0.421•	0.357*	-0.057	0.521*		
NO_2^-	-0.146	-0.187.	-0.193	-0.165	-0.135	-0.135	-0.109	0.350•	
NH_4^+	0.016	0.231	0.171	-0.020	0.140	0.225	0.563	0.287	-0.109

Table 5.8. A summary of the mean ± standard deviation (SD), range of values (minimum and maximum) and number of observations (n) for variables measured from all the sea ice cores collected along a transect across pack ice of the Weddell Sea, Antarctica during the 1989 RV *Polarstern* research cruise ANT VIII/2. Abbreviations used are Chl *a* = chlorophyll *a*, DOC = dissolved organic carbon, POC = particulate organic carbon, PON = particulate organic nitrogen.

	n	Mean	Minimum	Maximum	± SD
Ice thickness (m)	18	0.95	0.42	2.27	-
Salinity	196	5.5	0.4	26.6	4
Chl *a* ($\mu g\ l^{-1}$)	192	5.6	0.01	56.1	10
DOC (μM)	186	122	16	872	100
POC (μM)	153	108	11.9	374	67
PON (μM)	153	10.8	2.8	26.7	5
POC:PON (molar)	153	14.6	1.6	76.3	14
Silicate (μM)	85	5.6	0.5	16.2	3.5
Nitrate (μM)	85	3.3	0.5	13.5	3.0
Ammonia (μM)	85	3.9	1.4	10.1	2.0
Phosphate (μM)	85	0.3	0	1.9	0.4

Table 5.9. A correlation matrix showing the Pearson product moment correlation coefficients between all variables measured from sea ice core sections. Levels of significance: * = $p < 0.01$, ♦ = $p < 0.05$. Abbreviations used are Chl *a*, DOC, POC, PON = chlorophyll *a*, dissolved organic carbon, particulate organic carbon, particulate organic nitrogen.

	DOC	POC	PON	Chl *a*	Salinity	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NO_2^-
POC	0.568*								
PON	0.053	-0.187♦							
Chl *a*	0.533*	0.342*	-0.010						
Salinity	0.194♦	0.105	0.148	-0.030					
Phosphate	0.407*	0.547*	-0.195	0.259♦	-0.052				
Silicate	0.212♦	0.296♦	0.149	-0.242♦	-0.565*	0.315*			
Nitrate	-0.180	-0.193	0.203	-0.365*	0.507*	-0.056	0.616*		
Nitrite	-0.062	-0.048	0.017	-0.161	0.496*	-0.135	0.225♦	0.496*	
Ammonia	0.109	0.223	-0.101	0.108	0.402*	0.188	0.186	0.361*	0.634*

5.5 Discussion

The range of physical and biological parameters was markedly different between younger, first-year ice and older, second-year ice. Differences reflect mode of ice formation, the timing of sampling, spatial zonation and communities present. At the time of the study in September/October, late austral winter/early spring, the ice provided a snapshot of the end of the winter period when ablation has not yet occurred. The estimated age of first-year cores is of around 4-5 months since ice growth typically begins in June in the eastern Weddell Sea (Gleitz et al., 1998). The second-year ice floes in the north-western Weddell Sea have a longer history prior to sampling, as they have survived one summer warming. This ice may have been exposed to deformation events, including restructuring and internal refreezing processes, and biological activity. There was very little variability in ice core thickness of the second-year ice, but it was characteristically defined by two different layers. In second-year ice there was an upper, older part, subject to a first freezing event and then withstanding a second summer melting and a lower, younger layer mostly formed of congelation ice, i.e. resulting from slow and non-turbulent growth, similar to the new ice in the coastal area of the southern Weddell Sea. This appears to be a common pattern in older polar ice, in particular that characterised by congelation ice growth, also observed by Thomas et al., (1995) and Gleitz et al., (1998).

The amount of retexturing within the cores appears an important factor in determining distribution of dissolved and particulate compounds and in summer, brine is strongly affected by biological activity (Gleitz et al., 1995). Reasons for the high production may be linked to the life-history of the cores. Salinity was more uniform in second-year ice due to desalination as a result of brine drainage and warming, a process typical in ice which has lasted summer melting. However, there were signs of seawater floods on the ice surface, due to overlying snow pressure, resulting in characteristic orbicular or polygonal ice texture of high salinity at the top of the cores. In contrast, the higher salinity found in the first-year cores is expected given the more recent formation. Brine volume is important as it is linked to core permeability, as a function of temperature and salinity, which enables supply of nutrients into the ice (Arrigo et al., 1997) and represent the space available to

organisms and compounds in solution (Günther and Dieckmann, 2001). The authors argue that brine volumes over 70 ml render the sea ice permeable. Brine volumes in both first- and second-year ice were above this threshold and therefore the ice is open to potential nutrient exchange. The second-year ice core was also warm at the surface and this may have increased the porosity in comparison to first-year ice cores.

From the patterns in DOC distribution and concentration it is clear that there is a strict link with textural composition. The striking feature which emerges from second-year cores is the clear cut zonation between the upper and lower half of the vertical core profiles, in terms of both ice crystal type and organic carbon (DOC and POC) content. In the lower half, second-year ice cores are exclusively composed of congelation ice, likely to have grown in the winter season prior to sampling (Eicken et al., 1991). Due to its thickness and conditions, the rate of growth of second-year ice must also be slower than the first-year ice. In the lower portion there are signs of consistently low concentration of DOC (<100 μM) and POC (<100 μM) (Fig. 5.7).

Instead, large accumulation of DOC (>100 μM to 800 μM) was found within the upper half of second-year ice, also supporting elevated POC concentrations (>200 μM) and extremely dense algal assemblages (up to 50 μg chl *a* l^{-1}) (Fig. 5.7). Within this upper ice area the textural composition was complex and there was evidence of infiltration and freeboard layers reflecting the deformation events during the previous summer. The high peaks of algal biomass may be remnants of the previous summer production. It has been shown that the internal layers are more productive both in the Antarctic and Arctic due to nutrients input (Horner et al., 1988; Ackley and Sullivan, 1994; Thomas et al., 1998). The winter season is usually characterised by decreased irradiation, temperature and higher salinity which would be thought unfavourable to biological activity (Eicken, 1992a). However *in situ* bacterial assemblages metabolism continues through winter in sea ice down to –15 °C (Helmke and Weyland, 1995). Interestingly, growth of ice algae has been shown to occur down to –5.5 °C with a corresponding salinity of 95 and lower temperature and higher salinities of winter ice are also tolerated up to –10 °C and salinity of 145 surviving for 6 weeks (Bartsch, 1989; Spindler, 1994). According to the temperature in the present sea ice cores no physiological inhibition may have taken place, since

minimum ice temperature reached was –6.8 °C at the ice-snow surface of first-year ice (see core 27601, Fig. 5.4).

The first-year ice cores exhibited shorter length, indicating a more recent formation than the second-year cores, and were composed mainly of frazil ice and of congelation ice only in the eastern coastal region. The DOC peaks were higher in older ice where ice composition is typically mixed granular, in a freeboard layer, indicative of intrusion of surface seawater, which can bring fresh nutrients within an otherwise closed system. Helmke and Weyland (1995) indicated that in Weddell Sea ice the initial settlement of bacteria colonies is closely linked to genetic ice classes and in older ice, characterised by mixed ice or frazil ice texture, there are greatest bacteria numbers and over increasing ice age comprised increasing proportions of viable cells and psychrophilic bacteria. It is known that seawater infiltration can provide new nutrients, increasing production (Ackley and Sullivan, 1994). Second-year cores sampled appear to have received a supply of fresh nutrients either at the ice-water interface during the previous summer warming and/or at the ice-snow interface as a result of seawater infiltration snow depression. Snow cover can contribute to seawater exchange as it can depress the underlying ice layer. In the study all second-year cores had a snow-depth to ice-thickness ratio of >0.38. The critical snow-depth to ice-thickness ratio over which seawater flooding will occur is 0.3 according to Jeffries et al., (1998) and 0.38 by Eicken et al., (1994), the difference in ratio due to differing snow density used. Only four first-year ice cores (codes 26801, 26901, 27101, 27111) were potentially flooded by seawater, having snow/ice ratios of >0.3. Equally, it could be noted that the temperature profiles in the western multi-year ice cores were variable but not as strong than the first-year ice cores in the eastern transect, thus enabling expansion of brine channels and facilitating the nutrient exchange process. The substantial snow cover on the multi-year cores, given its poor heat-conductivity also helped insulating the underlying older ice layers from strong temperature gradients.

The maximum DOC concentration in brine measured in this study exceeds by fiftyfold typical DOC concentration (40-50 μM) in surface waters of the Weddell Sea in austral summer (see Wedborg et al., 1998). Kähler et al., (1997) recorded similar DOC concentrations in spring and this study also confirms surface DOC

concentrations within this range in the Scotia Sea waters (see Chapter 3). In this study the mean concentration of DOC within brine of all ice cores of 1720 µM (200 to 7300 µM) lies within the calculated mean values reported for two summer pack ice expeditions in the Bellinghausen/Amundsen and Weddell Sea (mean 1800 µM, range 130-23300 µM, during ANT 11/3; mean 1570 µM, range 120-18450 µM during ANT 14/3), but the maximum value attained was 2.5-3 times lower than the summer maxima (Thomas et al., 2001). However, the present values are higher than values of autumn brine measured in the eastern Weddell Sea (Thomas et al., 2001). This would support the evidence for a maximal seasonal activity in the spring/summer season, when ice porosity is highest, and a decline in autumn/winter when temperature impinges on available volume of brine.

Carlson and Hansell, (in press) have measured extremely variable DOC values in the spring/summer season pack ice profiles, from 10 µM at the surface to concentrations in excess of 20000 µM in the bottom 5 cm of congelation ice in the Ross Sea. It is apparent that different mechanisms occur to determine DOC distribution in ice cores. The finding of this study is consistently high peaks of bulk DOC (up to 800 µM) in multi-year ice above or corresponding to the chl *a* maximum in the interior 0.6 m layer of the ice.

The observation that DOC concentrations are highest at the same depth as chl *a* in autumn multi-year ice of the western Weddell Sea (Fritsen et al., 1994), has indicated that snow has an effect in inducing flooding of the top layer. Melnikov (1998) has followed the early austral winter sea ice algae production (chl *a* levels 20-50 µg l^{-1}) in the western Weddell Sea in 1992 young, growing, first-year sea ice. The authors describe autumn algae in the upper 0.4 m layer of 1.2 m thick ice in association with ice which had a composition affected by flooded and frozen seawater intrusions.

The present observations agree with findings of high DOC in correspondence of high chl *a* in multi-year sea ice of the Amundsen Sea, Antarctica, (Thomas et al., 1998) albeit cores having been sampled in austral summer. This reflects a potential common pattern in DOC distribution when nutrient supply is high due to exchanges

with seawater and it shows that DOC is following a common algal zonation in multi-year ice. However this *per se* does not imply a correlation between the two variables, as the production mechanisms of DOC are still speculative and accumulation of DOC may derive from a variety of mechanisms.

Studies have shown that metazoans may affect the concentration of DOC pool by processes such as sloppy feeding and dissolution of faecal pellets (Lampert, 1978; Lampitt et al., 1990). Gradinger (1999) reports on meiofauna biomass in the same ice cores from ANT VIII/2. The relative abundances show a high proportion of foraminifera, followed by ciliates, turbellarians, copepods and nauplii larvae, averaging 0.4 mg C m^{-2} and indicating the potential impact of grazing rates. Schnack-Schiel et al., (2001) further indicated abundant and varied sympagic biomass in western Weddell Sea ice cores taken during ANT VIII/2. The findings of the latter authors showed that meiofauna was distributed at a similar depth-range (0.6-0.8 m) in multi-year cores sampled in the vicinity of the floe presented in this study where DOC is found enriched in conjunction with high phytoplankton abundance. This suggests a potential contribution by a variety of mechanisms, e.g. sloppy feeding processes, egestion and protozooplankton release of solutes and digestive enzymes inducing DOC production and increasing levels of nutrient regeneration (Daly, 1998). Moreover the sympagic heterotrophs can exert a top-down control on bacterial and protozoan populations potentially through grazing and predation, controlling the major users of DOC assimilation and regeneration enabling accumulation of DOC within the ice (Grossmann and Dieckmann, 1994; Gradinger and Zhang, 1997). Indeed nitrite concentrations were limited and indicative of low denitrification. However, it is known that reduced grazing may occur at low temperatures and it may be physically impaired due to the fine ramifications of brine channels (Krembs et al., 2000).

Regeneration processes are evident in second-year ice from nutrient profiles. Phosphate and ammonium exceeded the concentrations in the water column, according to the dilution lines, and in second-year ice both are found at high concentrations concurrent with high internal bands of DOC (see core 26103, Fig. 5.7). At the same time there was evidence of nitrate exhaustion at the same depth range. Culture work which has demonstrated that large phytoplankton production of

extracellular DOC may result from nutrient depletion (Goldman et al., 1992). Verity et al., (1988) found a small amount of DOC production by *Phaeocystis spp.* cells but larger excretion in nutrient-stressed cells than in nutrient replete cells.

It could be hypothesised that the highest production of DOC at a particular depth is related to the nutrient availability at the time. The nutrient availability is associated with currents and fluxes with the underlying water or from depression into the water by snow. The nutrient flux must occur where there is greater brine volume. In the second-year ice it seems that nutrients have been utilised as they are inversely proportional to the POC and PON. McMinn et al., (2000) have indicated that as the velocity of the under-ice currents increases, the production in the bottom-ice community is higher. The authors attribute a greater photosynthetic activity through an increase in nutrient flux to cells at the ice-water interface and a rapid and efficient removal of oxygen accumulated, which can inhibit photosynthesis and lead to algal mortality (Raven and Beardall, 1981; McMinn et al., 2000).

Sea ice POC concentrations exceed POC (62.5 μM) in ice-free waters by five times (Cota et al., 1992). Garrison and Close (1993) report POC and PON for young, first-year and older sea ice cores from the ice edge area of the Weddell Sea (~ 61° S, 48-40° W) for the previous winter season (June-July) of 1988. However, in this study the highest concentrations of POC (330-370 μM) in ice-core segments are in the low range for Antarctic ice. Compared with literature values of POC maxima, the POC concentrations from this study are sixfold lower than the 2000 μM average concentration in first-year and older winter sea ice (Garrison and Close, 1993), and <16-18 times smaller than maximum POC values (>6000 μM) recorded in Weddell Sea summer sea ice by Kennedy et al., (2002).

The POM material was collected from ice in the late winter season, when algae have been exposed to low irradiance levels, reduced nutrient input or uptake limitation with consequent photosynthesis and biomass production at its lowest. At the height of winter the reduced light supply and photo-acclimation by algae. If cells have experienced nutritional limitation then this brings on increased POC at the same time that ATP in the cells decreases (Hewes et al., 1990).

Grossi et al., (1987) report POC:chl *a* ratios of 33 to 795 in platelet ice and 133 to 6063 in congelation ice of McMurdo sound. Garrison and Close (1993) report high POC:chl *a* varying from 7 to 62 in winter sea ice cores of the north-western Weddell Sea (average of 28). POC:chl *a* ratios usually decrease with increasing irradiance and decreasing temperature (Geider et al., 1997). In winter ice cells experience a natural decrease in irradiation and the snow accumulation is known to reduce light transmission in ice (Grossi et al., 1987). However, dark-adapted cells would markedly increase the content of chl *a* per cell relative to C (Prézelin, 1981). Cellular compositions may also alter during residence in ice. Ice algae appear to adapt their pigmentation to the low light levels and in particular tend to increase the content of carotenoids and chl *c* to chl *a* ratio (Boczar and Palmisano, 1990; Lizotte and Sullivan, 1992; Robinson et al., 1995). This may have important consequences on POC:chl *a*.

Mock (1997) also noticed that during reduced light intensities sea ice algae tend to physiologically adapt by producing lipids, in particular glycolipids rather than phospholipids or triacylglycerols. Certain species of sea ice diatoms are able to adapt their membrane fluidity to low temperature by increasing their amount of unsaturated fatty acids as temperature decreases, according to the theory of homeoviscous adaptation (Palmisano and Garrison, 1993). Bacteria have also been observed to alter viscosity of membranes, i.e. show homeoviscous adaptation and polar bacteria in response to lowering of temperature increase of internal stores of polyunsaturated fatty acids (Chattopadhyay, 2000).

The most striking feature is the equal partitioning among the pools of DOC and POC in the majority of the ice cores analysed. Also the high correlation between the two organic pools is high and consistent. In the water column partitioning between dissolved and particulate pools is notably different. There are new perspectives on colloidal matter taking a new role within the ice.

Thomas et al., (1998) have described rotten sea ice as a biological soup, but more recently the soup appears to thicken, (see Azam, 1998) who talks of plot thickening indicating the gel like structures are produced in seawater. The same type of compounds have been observed in the ice (Krembs et al., 2001) and have been

observed in the Ross Sea where *Phaeocystis* is abundant (Hong et al., 1997). The compounds are defined as transparent exopolymer particles (TEP), which may serve as a smoothing agent for improved mobility and as a protectant from pressure. Raymond et al., (1994) pointed out that pitting may be induced by ice active substances released by sea ice algae (Raymond, 2000). Assuming DOC is actively secreted as a cryoprotectant then it should be in higher concentrations in sea ice in the winter season.

Archive samples were analysed for DOC and POC and despite continuous storage at -30 to -20 °C and careful handling of the sub-samples, the age of the cores could be addressed as a limitation to the study. However results are in a range similar to samples processed within a shorter time-span. The POC:PON ratios show that they are within expected values for fresh material and there is low variability within the replicate cores. On the other hand, it is not possible to identify the small scale temporal evolution and fluxes during the period for DOC production and absorption. The greatest limitation stands in the sample size, as for instance there are a number of second-year cores but sampled from only one floe. It could be suggested that a greater number of floes will give a greater picture of DOC and POC distribution in second-year ice.

5.6 Conclusions

The analyses performed in this study have provided new quantitative evidence of spatial and temporal distribution of DOC and POC in cores of first- and second-year Weddell Sea ice in late winter to early spring. Cores collected from different floes show that there is high DOC and POC content in internal layers of older floes which have experienced changes in physical variables through melting and re-freezing. This reflects the different physical, chemical and biological influences within the ice. In summary, the major findings were as follows: consistently high concentrations of DOC, in excess those in surface waters were found in the internal assemblages of second-year ice cores in floes of the semi-compact Weddell Sea pack ice (7-8/10) at the same depth as high phytoplankton abundance. Peaks of DOC were in conjunction with signs of retexturing in the ice matrix, i.e. freeboard and infiltration layers as a result of summer warming events. Estimated DOC within the brine is consistent with

previous measurements in Antarctic pack ice areas in both summer and autumn seasons. DOC does not dominate the total organic pool as it does within Antarctic waters, as there is a proportional distribution of POC and DOC. Within the ice DOC and POC were in excess of that predicted, if only physical processes had driven the incorporation into the ice. Potential controlling factors are the grazing impact by sympagic meiofauna detected by other authors on the same ice core samples and nutrient limitation.

CHAPTER 6

EXPERIMENTAL INCORPORATION OF DISSOLVED ORGANIC MATTER IN SEA ICE

6.1 Introduction

In Chapter 5 the dissolved organic carbon (DOC) distribution was determined *in situ* in winter pack-ice cores, showing the enrichment of DOC and particulate organic carbon (POC) in second-year ice. Theoretically, inorganic nutrients are initially incorporated conservatively into sea ice (Weeks and Ackley, 1982). However this has not previously been tested for dissolved organic matter (DOM) or individual substrate classes, (e.g. carbohydrates, amino acids) in sea ice, although DOM can be found in very high concentrations in the sea ice matrix (Thomas et al., 1995, 1998).

This chapter reports the results of two experiments investigating the incorporation of dissolved organic compounds into newly forming sea ice under controlled laboratory conditions. Laboratory simulations are useful and accepted tools in identifying temporal trends and responses of either natural assemblages of organisms or cultured species to controlled varying physico-chemical conditions (nutrients, salinity, temperature, water motion, ice texture) (Weissenberger, 1998; review by Brierley and Thomas, 2002). Given the high costs of fieldwork in polar regions, the logistic difficulties and often restrictions caused by adverse weather conditions, there are clear advantages in the use of experimental simulations of sea ice. Understanding the physics, chemistry and biology of sea ice and their interactions in experimental conditions is therefore an active area of Antarctic research (Grossmann and Gleitz, 1993; Eicken, 1998; Haas et al., 1999).

A range of studies have been carried out to show the internal microstructure of the sea ice matrix and brine channel geometry and the significance for sympagic organisms (Weissenberger et al., 1992; Cottier et al., 1999; Krembs et al., 2000). Weissenberger (1998) extended the work to a larger scale using a mesocosm (200 m^3) to maintain a living sea ice community for a total of 19 weeks to follow the

succession of species with ice growth. Similarly, Krembs et al., (2001) used existing large-scale facilities intended for testing models of ships to successfully investigate incorporation and succession of algae and bacteria in sea ice.

The aim of this chapter is to address and test the conservative behaviour of DOC and a variety of individual compounds during the initial stages of sea-ice formation. Distribution of phytoplankton-extracted DOM, glucose, glycine was recorded in brine, ice and underlying water phases in almost virtual absence of living organisms. Changes in organic compound concentration in ice, brine and underlying water were followed in comparison to salinity and inorganic nutrients during two freezing periods at different stages of ice growth.

The chapter is organised into the following sections: a brief introduction to experimental work in sea ice (section 6.1), followed by the specific experimental design and methodology (section 6.2), a results section reporting findings from two consecutive experiments of different duration (section 6.3.1 and section 6.3.2), and a discussion (section 6.4) in context with previous literature. Section 6.5 presents the main conclusions and limitations of the present work.

6.2 Methods

Two experimental studies were conducted in the indoor Arctic Environmental Test Basin at the Hamburg Ship Model Basin (HSVA) in Hamburg, Germany, from 9 November to 1 December 1998 (for further details of the present work see Haas et al., 1999; Giannelli et al., 2001).

Artificial seawater was obtained by adding Instant Ocean salts (Aquarium Systems Ltd., Ohio, Weissenberger and Grossmann, 1998; Krembs et al., 2001) to tap water. Five polyethylene 1 m^3 enclosures were filled with 1000 l of artificial sea water and placed in an indoor deep-freeze water tank (30m x 6m x 1m, see Fig. 6.1a). All experimental enclosures were situated within the calm area of the tank, where no water current action was generated (Fig. 6.1b).

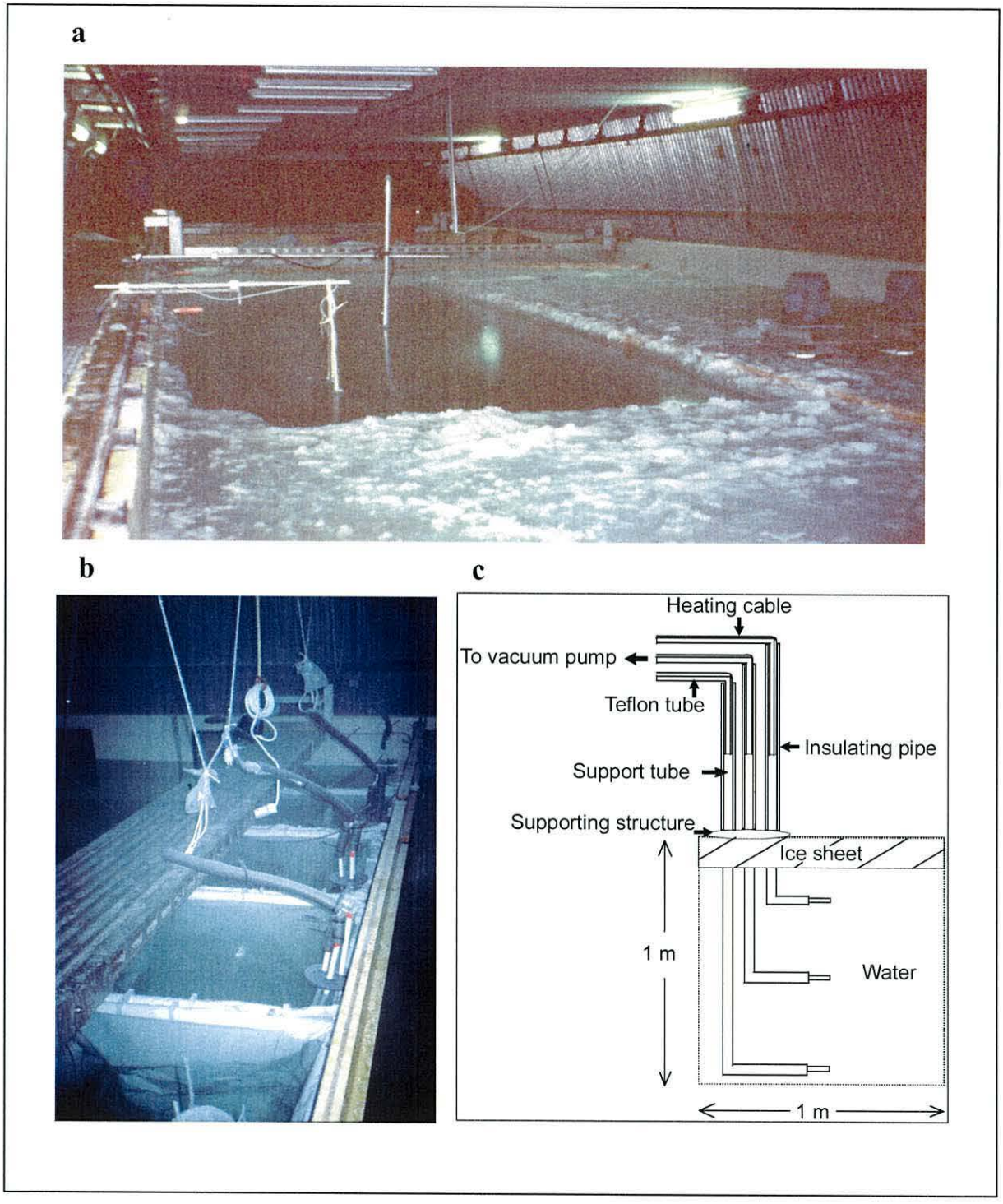

Fig. 6.1. **a**) Photograph of the indoor Arctic Environmental Test Basin at the Hamburg Ship Model Basin (HSVA), Hamburg, Germany. **b**) View of the five polyethylene enclosures filled with artificial seawater used in the experiment. The devices employed to sample the water from different depths are visible at the side of each enclosure. Electrical appliances visible were used to avoid freezing of the water during sampling. **c**) A cross-sectional diagram of the sampling apparatus used in each of the tanks for collecting water samples from under the solid ice sheet (surface), 50 cm depth (middle) and from 90 cm depth (bottom). Note that the uppermost tube was adjusted during the experiment to sample water immediately below the growing ice cover.

Differing loadings of DOM were added in experiment 1 and experiment 2 to the five enclosures prior to freezing (see Table 6.1) and the contents mechanically stirred in order to obtain a homogenous solution. Compounds were used in treatments in an effort to simulate a realistic composition of phytoplankton-released DOM. This ensured that a wide range of organic compounds would be present, representing a wide spectrum of biological lability and physico-chemical characteristics.

Table 6.1. Composition and concentration of dissolved organic matter (µM C) added to the artificial seawater in each of the experimental enclosures numbered 1 to 5 at the beginning of the first and second experimental phase at the indoor Arctic Environmental Test Basin, Hamburg, Germany. *DOC extracted from algal cultures.

Enclosure	Experimental Addition	Initial concentration (µM C)	
		Experiment 1	Experiment 2
1	DOC*	180	486
2	Glucose	272	349
3	Glycine	2.84	4.74
4	Glucose	276	455
	DOC*	320	758
5	Glycine	3.82	5.24
	DOC*	448	343

Microalgal-extracted DOM was used from harvested unialgal cultures of the pennate diatom *Skeletonema costatum* (Bacillariophyceae), maintained in non-axenic conditions in 0.2 µm-filtered and UV-treated natural sea water enriched with Conway medium. The diatom cells were separated from the seawater medium by reverse flow filtration and ruptured to release internal cellular DOM contents by a rapid change in temperature from ambient to –70 °C (K. Flynn, pers. comm., 1998). Both algal and medium extracts were filtered through pre-combusted (500 °C, 3 h) 25 mm Whatman GF/F glass fibre filters and the filtrate preserved at –20 °C until analysis.

During the first experiment formation of sea ice was initiated by lowering the air temperature to approximately –15 °C (see Fig. 6.2). A fog of ice-crystals was sprayed on the surface of the water to act as nuclei for the initiation of ice growth

(Evers and Jochmann, 1993). Ice growth occurred under calm conditions. After five days ice growth was terminated by raising the air temperature to >0 °C (Fig. 6.2). The first experiment (Exp. 1) lasted for a total period of 120 h. At the beginning of experiment 1 initial mean surface salinity in the enclosures was 32.9 ± 0.1 (Table 6.2).

Table 6.2. The temporal evolution of mean water salinity (± standard deviation, n = 5) measured in the same five enclosures over the first experimental phase. Experiment 1 lasted 120 h and experiment 2 lasted up to 336 h. Sampling of the ice took place after 120 h in all enclosures in Experiment 1.

Freezing period (h)	0	24	48	72	96	120*
Water salinity ± SD	32.9 ± 0.1	33.8 ± 0.1	34.4 ± 0.1	35.0 ± 0.1	35.7 ± 0.2	36.6 ± 0.3

The solid phase (ice) was sampled separately from the liquid phase (underlying water). During the first experiment the liquid phase was sampled daily whereas ice sampling occurred on the last day of the experimental phase (day 5) in order to avoid disturbance of the water column induced by sampling. At the end of Experiment 1 all ice was removed from each of the enclosures. More artificial seawater was added to the remaining water and the resulting mean salinity was 34.5 ± 0.3 (Experiment 2, Table 6.3). A second and new experimental cycle of ice growth was initiated by lowering the air temperature to –20 °C on 18 November (see Fig. 6.2). During experiment 2 water sampling took place at 2-3 day intervals and ice coring took place on different days according to different enclosures (see Table 6.3).

Table 6.3. The temporal evolution of mean water salinity (± standard deviation, n = 5) measured in the same five enclosures over the second experimental phase. Experiment 2 lasted up to 336 h. Sampling of the ice took place after on different days in Experiment 2. Symbols are as follows: ° ice sampling in enclosures 2 and 3, • ice sampling in enclosure 4, $^{\nabla}$ ice sampling in enclosure 1, ♦ ice sampling in enclosure 5.

Time (h)	0	72	144	216°	240•	312$^{\nabla}$	336♦
Water salinity ± SD	34.5 ± 0.3	35.2 ± 0.4	37.3 ± 0.4	40.4 ± 0.04	40.9 ± 0.2	43.1 ± 0.2	43.5

Custom-made sampling devices were used to perform the water sampling. Devices were positioned in one corner of the enclosure and water samples taken at three

depths in the 1 m water column of each enclosure (Fig. 6.1b and Fig. 6.1c). Water was vacuum pumped at approximately 0.6 bar from immediately under the ice-water interface (surface), from 50 cm (middle) and 90 cm depth (bottom) (Fig. 6.1c). Water samples were collected from these depths since a sharp density gradient was expected to occur in the water column. Water samples were pumped into 250 cm^3 Duran bottles through Teflon tubing (4 mm internal diameter), to which a 50 Volt heating cable was tied to prevent internal freezing, and both encased in PVC pipes (2 cm internal diameter).

The consolidated ice thickness in each of the experimental enclosures was recorded daily with a meter stick (Stoecker et al., 2000). During the experimental period enclosures were covered with polystyrene covers to avoid potential contamination or condensing liquid from the equipment and overlying platform. Ice coring took place in each enclosure by a manually-driven titanium corer (8 cm internal diameter) with minimal handling to prevent brine drainage and potential contamination to the ice. Eight or nine individual cores were cored from each of the enclosures.

After drilling, each core was immediately sawed in 5 cm-long sections with a clean stainless steel fret-saw. At the end of experiment 1 ice cores were divided in an upper (0-5 cm) and lower (5-10 cm) half. At the end of experiment 2, which lasted longer than experiment 1, ice cores were divided in three to four 5 cm sections according to the final ice depth reached in each enclosure. Each ice section was placed into clean Teflon containers with apposite drainage grids. Liquid brine was mechanically separated from the ice sections matrix through centrifugation of ice core segments at 900 rpm at –2 °C for 3 minutes in a refrigerated Beckmann rotor centrifuge (Weissenberger et al., 1992; Grossmann and Gleitz, 1993). After centrifugation, ice core sections were bulk stored into sealed PVC containers and thawed in the dark at 4 °C. The volume of both the extracted brines and the ice meltwater were determined gravimetrically.

Sub-samples from brine and ice melt water were taken for the determination of salinity, inorganic nutrients, total DOC, monosaccharides, dissolved free amino acids and bacterial abundance. Salinity of the brine and melted ice was measured with a digital conductivity probe (WTW, Weilheilm, Germany, precision of ± 0.2%). All

samples were filtered through pre-combusted (500 °C, 3 h) Whatman GF/F filters and aliquots of the filtrate were flame sealed in 30 cm^3 pre-combusted glass ampoules (500 °C, 3 h) for analysis of DOC, glucose and glycine (see Chapter 2 for analytical methods) and preserved at –20 °C until analysis.

Filtered water sub-samples were stored in 60 cm^3 polyethylene bottles and preserved at –20°C for inorganic nutrient determination (nitrate, nitrite, ammonium, phosphate and silicate) on a standard Technicon Autoanalyser (Kattner and Becker, 1991) with relative errors of ± 2-5% (Lara et al., 1997; analyses courtesy of G. Kattner). Before filtration 20 ml sub-samples for bacterial abundance determination were fixed with 2 ml of 20% buffered formalin (1% final concentration), preserved in 30 cm^3 polyethylene vials and stored in the dark at 4 °C until slide preparation (Porter and Feig, 1980). The calculated brine salinity (S_b) was determined by measuring the *in situ* temperature (T, courtesy of C. Haas; Haas et al., 1999) and was derived from a modified equation (C. Haas, pers. comm.) on the basis of original equations by Assur (1960):

$$S_b = 9.65 - 14.8\ T$$

The calcualted brine salinity and volumes were compared with the measured brine salinity and volume.

6.3 Results

6.3.1 Experiment 1

6.3.1.1 Physical Characteristics

The first experimental period lasted 120 h from 9 November to 14 November and air temperatures recorded from thermistors suspended 1.5 m above the ice surface averaged –14.4 ± 0.6 °C (see Fig. 6.2). Ice growth began immediately after seeding in all enclosures and at the end of the experiment ice sampled had an average thickness of 10.7 ± 0.9 cm across all enclosures, corresponding to an ice formation rate of 2.1 ± 0.5 cm day^{-1} (Fig. 6.3). Below a thin layer of granular ice, the ice had a

columnar crystal texture typical for young ice grown under calm conditions (Weeks and Ackley, 1982; Haas et al., 1999). The ice developed a characteristic pore structure consisting of brine channels and inter-linked brine layers (Haas et al., 1999). At the end of the experiment, after 5 days (120 h) of ice growth, the water salinity of the enclosures increased by a mean of 3.7 ± 0.5 (SD) due to brine expulsion from the growing ice sheet into the water (Fig. 6.4).

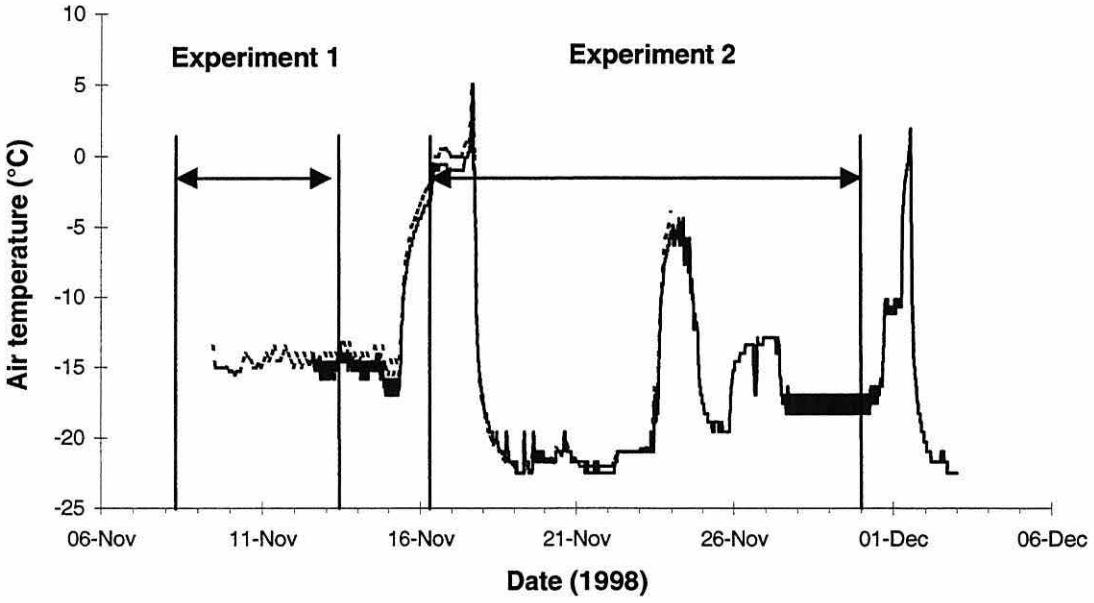

Fig. 6.2. Daily air temperature measured above the experimental enclosures in the indoor Arctic Environmental Test Basin at the Hamburg Ship Model Basin, Germany. The two arrows indicate starting and end point of the first experimental phase, from 9 to 14 November 1998 and the second experimental phase, spanning from 17 November to 1st December 1998. The data were provided by C. Haas, Alfred Wegener Institute.

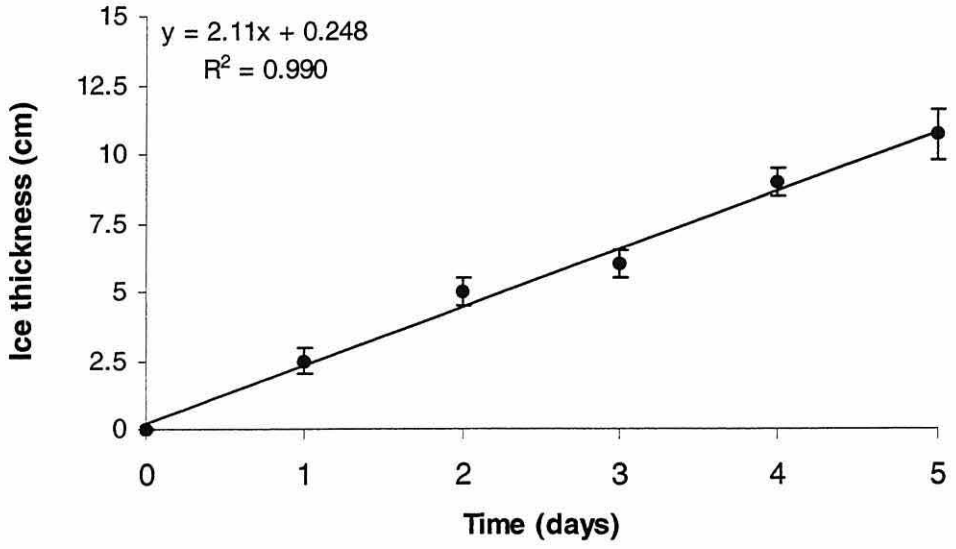

Fig. 6.3. Average ice thickness (cm) ± standard deviation as a function of time (days) in all enclosures (n = 5) during the first experimental phase. Solid line indicates linear regression between ice thickness and time.

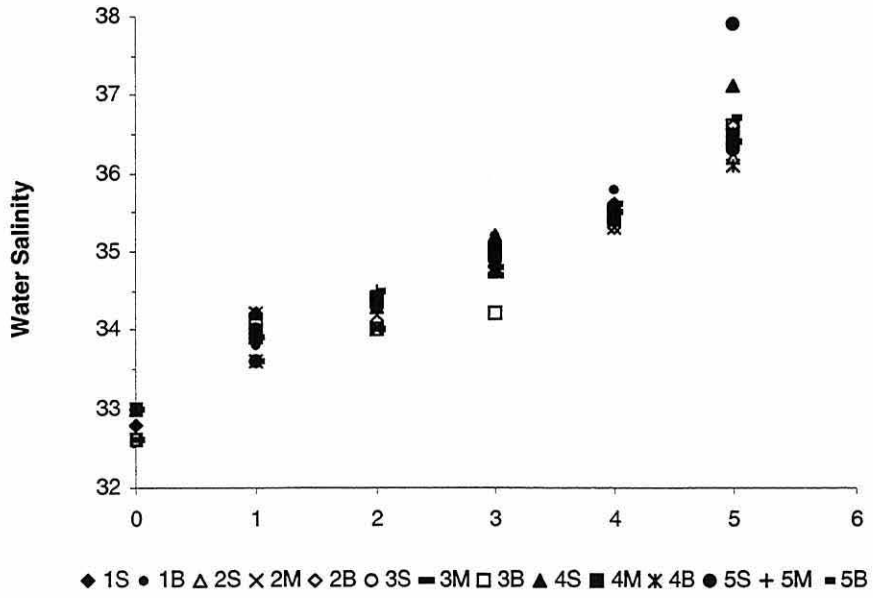

Fig. 6.4. Water salinity as a function time in the three different sampling positions of enclosures 1 to 5 during the first experimental phase. Letters used are S = surface water sampling, M = middle water sampling and B = bottom water sampling. Numbers 1 to 5 represent the enclosures from which water samples were collected.

The ice had a C-shaped salinity profile typical for young ice growth (C. Haas pers. comm., Weeks and Ackley, 1982). Raised salinities of 11 to 15 were determined in the top and bottom of the core and lower salinities of 6 to 8 in the middle of the ice cores (Haas et al., 1999).

Table 6.4. Comparison of measured and calculated ice and brine properties obtained from ice cores sections at the end of experiment 1 (means ± 1 standard deviation). The ice layer during the first experiment reached a thickness of 10 ± 0.9 cm after five days of growth. [1]Assur (1960), [2]Cox and Weeks (1983) and [3]Haas et al., (1999).

Ice Cores Sections (cm)	Measured brine salinity	Calculated brine salinity[1]	Centrifuged brine volume (%)	Calculated brine volume (%)[2]	Residual ice salinity	Calculated bulk ice salinity	Measured Bulk Ice Salinity[3]
0-5	62.3 ± 0.8	80.9	10.1 ± 1.1	8.7	3.5 ± 0.1	9.4 ± 0.6	8.4
5-10	42.3 ± 0.6	53.6	18.7 ± 0.9	19.5	4.1 ± 0.7	11.2 ± 0.3	11.2

Due to the colder ice temperatures, measured salinities of the obtained brines were approximately 50% higher in the top 5 cm compared to the bottom 5 cm sections (Table 6.4), in rough agreement with values calculated from empirical equations (Assur, 1960). The obtained brine volume amounted to 11% and 23.5% of the total sample volume in the top and bottom 5 cm sections (Table 6.4), also in close agreement with theoretical values calculated from bulk ice salinity and temperature (Cox and Weeks, 1983). Despite centrifugation, the top and bottom sections of the ice cores had a mean residual salinity of 3.5 and 4.1, showing that not all brine could be centrifuged out of the ice (Table 6.4). The salinity and volume of centrifuged ice and brine samples were combined to calculate the bulk salinity of the ice, which varied between 9 and 11 in the higher and lower portion of ice sampled. The calculated values are in good agreement with direct measurements of bulk ice salinity (Haas et al., 1999, Table 6.4), thus the table can give an impression of the accuracy which could be achieved with the experiments.

6.3.1.2 Inorganic Nutrients

The distribution of nitrate, phosphate and silicate measured in the ice, brine and water of the experimental enclosures is presented in Fig. 6.5 A,B,C. If nutrients and/or DOM are concentrated or expelled due to purely physico-chemical processes

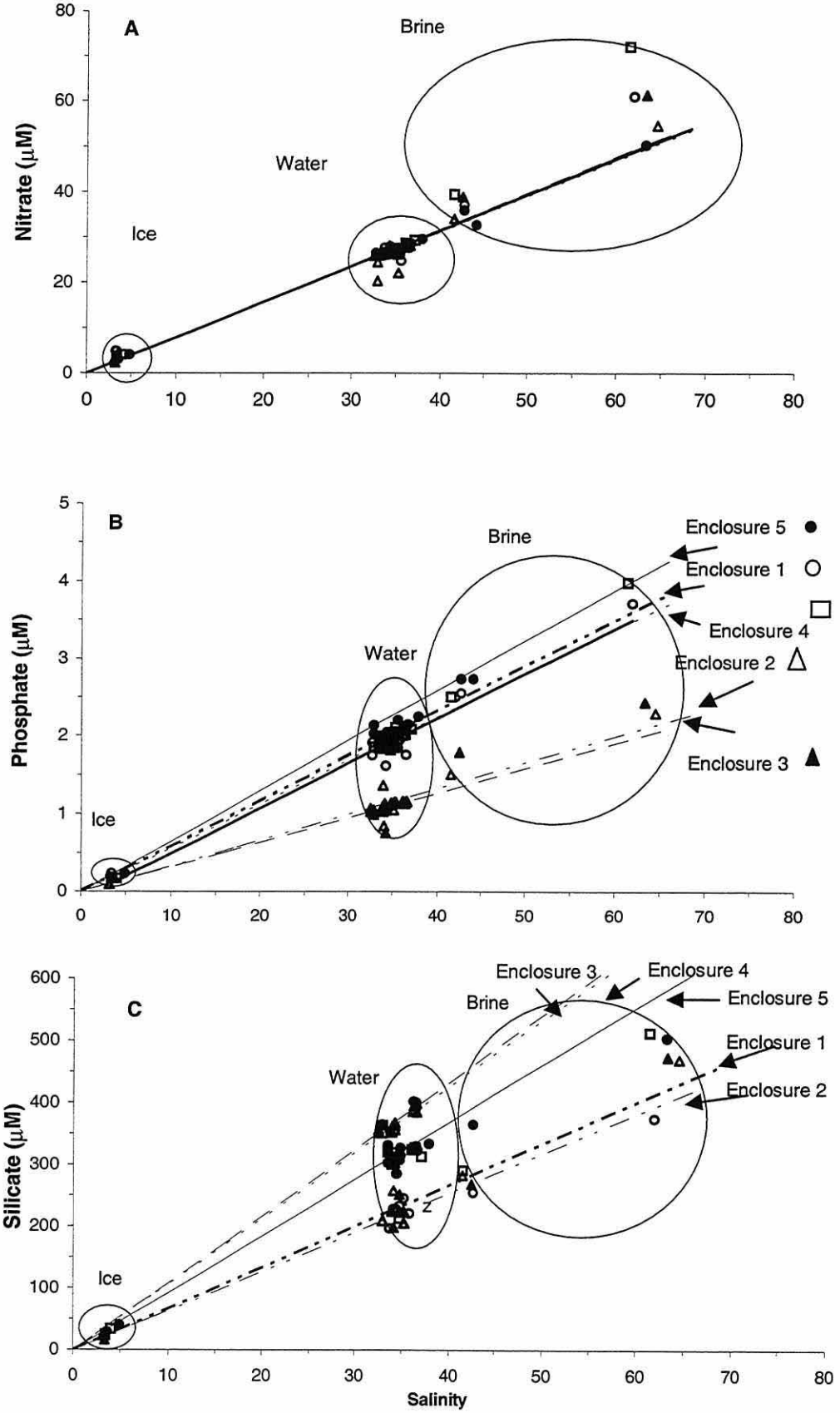

Fig. 6.5. Nitrate (A), phosphate (B) and silicate (C) concentration as a function of salinity in water and centrifuged brine and ice during experiment 1. The solid lines represent the dilution lines extrapolated from the initial surface water values at the start of the experiment. Note that the dilution lines in Fig. 6.5A are similar because of similar starting concentrations of nitrate in the enclosures. This was not the case for phosphate and silicate.

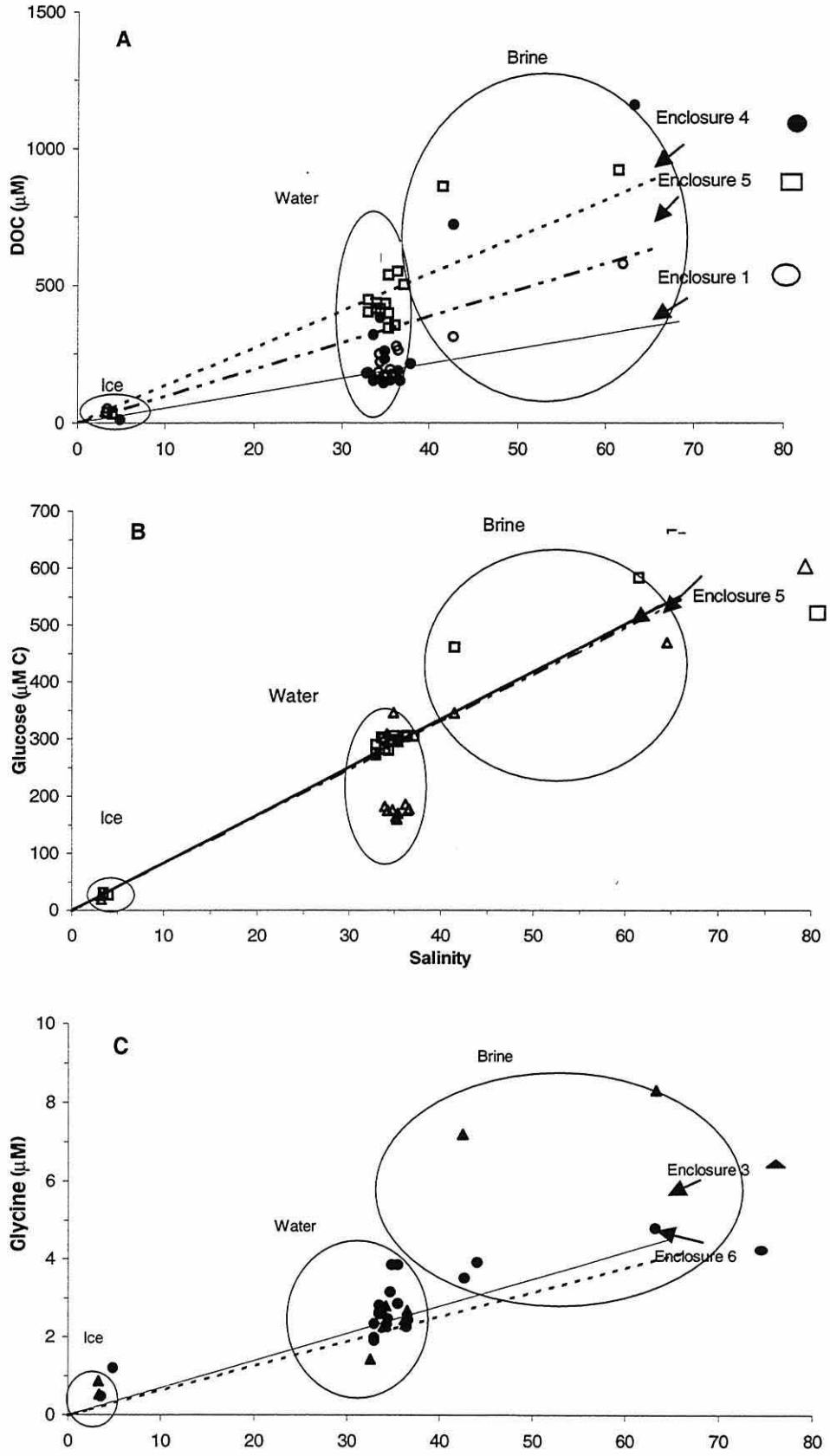

Fig. 6.6. DOC (A), glucose (B) and glycine (C) concentration as a function of salinity in water and centrifuged brine and ice during experiment 1. The solid lines represent the dilution lines extrapolated from the initial surface water values at the start of the experiment. Note that the dilution lines in Fig. 6.6B are similar because of similar starting concentrations of glucose in the enclosures.

during ice formation, concentrations should be a direct function of the salinity. This is true for the underlying water into which brine has been introduced from the developing ice cover. A mathematical representation of this behaviour can be achieved through plotting a chemical variable against a conservative parameter such as salinity to provide a theoretical dilution line (see Mantoura and Morris, 1983; Miller, 1999). Dilution lines provide a measure of the conservative behaviour for comparison with the measured concentration (Dieckmann et al., 1991). Nitrate changes displayed conservative behaviour (Fig. 6.5A). However, at salinity greater than 40 there was a significant enrichment of nitrate in the top and bottom brines collected from almost all enclosures, in excess to that predicted from the dilution line (Fig. 6.5). Because the starting concentrations of nitrate were virtually the same in all enclosures (26.4 ± 0.4 μM), the dilution lines for each enclosure were indistinguishable at a resolution beyond the analytical error.

Phosphate was also linearly related to salinity in all enclosures and was approximately within the range predicted by the dilution lines (Fig. 6.5B). The starting phosphate concentrations were different between enclosures and separate dilution lines have been drawn for each enclosures. In enclosures 2 and 3, where no algal-DOM was added, phosphate concentration (1.08 μM) was 55% of the initial mean concentration recorded in the other three enclosures (1.96 μM). Silicate was also linearly related to salinity in all enclosures and followed physical enrichment as predicted by the dilution lines (Fig. 6.5C). Silicate showed a similar trend to phosphate in that it has differing initial concentrations in two of the enclosures.

6.3.1.3 Dissolved Organic Carbon

DOC in enclosure 1 had an initial concentration of 180 μM, enclosures 5 and 6 had values of 320 and 448 μM respectively (Table 6.1). Over the experimental period there was a homogenous distribution of DOM in the waters of enclosures 1 and 5 at all depths in contrast to enclosure 6. In the brine of the surface section of the consolidated ice there was a characteristic and substantial enrichment of DOC with maximum concentrations (578 μM, 923 μM, >1158 μM in enclosures 1, 5 and 6 respectively). These values were consistently up to tenfold those in centrifuged ice

and threefold those in the water (Fig. 6.6A). The brine from the top section was always most enriched in DOC in comparison to the bottom and less saline section. DOC was found to be up to four times higher in brine than in the underlying water.

DOC distributions in ice, water and brine are more scattered relative to the dilution line than both nitrate and phosphate (see Fig. 6.5). DOC in enclosures 5 and 6 was concentrated within the brine reaching concentrations up to 200-300 μM higher than values expected from dilution line predictions (Fig. 6.6A). DOC in the brine of enclosure 6, where it was particularly highly concentrated, showed a maximum difference from the dilution line of 500 μM enrichment.

6.3.1.4 Glucose

Glucose when added as a single compound (enclosure 2) and in association with algal-extracted DOM (enclosure 5) had an initial concentration of 272 and 276 μM (see Table 6.1). Over the experimental period there was a homogenous distribution of glucose in the water of enclosures 2 and 5 at all depths. In both enclosures the brine in the top section of the consolidated ice retained elevated glucose concentrations (469 μM and 584 μM in enclosures 2 and 5 respectively), double the concentrations in the artificial seawater and twenty times greater than those in centrifuged melted ice (Fig. 6.6B). The brine from the top section was always most enriched in glucose in comparison to the bottom and less saline section. Glucose distribution in ice, water and brine is relatively adherent to the dilution line (see Fig. 6.6B).

6.3.1.5 Glycine

Glycine in enclosure 3 and 6 had an initial concentration of approx. 1.4 μM and 1.9 μM in enclosures 3 and 6 (see Table 6.1). Over the experimental period there was a scattered distribution of glycine in the waters at all depths. In the brine of the top section of the consolidated ice, glycine was found in elevated concentrations (7-8 μM and 3-4 μM in enclosures 3 and 6 respectively), approximately almost double concentrations in the artificial seawater in enclosure 6 and threefold those in ice in

enclosure 3 (Fig. 6.6C). The brine from the top section was consistently most enriched in glycine in comparison to the bottom, less saline section both in enclosures 3 and 6. Glycine distribution in ice, water and brine appears enriched to the dilution line in both enclosures, particularly when added as a single compound (see Fig. 6.6C), due to its deviation from the applied dilution line by over 4 µM.

6.3.1.6 Budgets

Nutrient and DOC budgets were calculated on the basis of water volumes and measured salinity in each enclosure and compared with the actual measurements (Table 6.5). Knowing the initial and final salinity and assuming it behaves conservatively it is possible to calculate the volume of unfrozen water at the end of the experiment. This in turn can be used to calculate the expected change in concentration of the inorganic nutrients and organic compounds and compare the calculated values with the measured values. Measured and calculated levels of nitrate and phosphate in all surface waters are within the same range, differences being within the analytical error. DOC measured values for enclosure 1 were in excess of the calculated value by 74 µM, enclosure 5 shows a value exact to the predicted value and in enclosure 6 153 µM are unaccounted for (Table 6.5). This gives a further indication of the excess DOC found in brine compared to water. Glycine is found in excess of the predicted values, particularly when added as a single compound (enclosure 3), in contrast to glucose, which does not show a discernible difference between calculated and measured concentration as a single compound but a depletion of 47 µM in the enclosure with algal-extract addition.

Table 6.5. Measured nitrate, phosphate, dissolved organic carbon (DOC), glycine and glucose concentration of the enclosures in the water phase and the predicted values on the basis of conservative behaviour in experiment 1. Calc. = calculated, n.r = not recorded.

Enc	Nitrate (µM)		Phosphate (µM)		DOC (µM)		Glycine (µM)		Glucose (µM)	
	Calc.	Measured	Calc.	Measured	Calc.	Measured	Calc.	Measured	Calc.	Measured
1	29.4	28.3	2.1	2.0	204	278	n.r	n.r	n.r	n.r
2	27.1	28.4	1.1	1.2	n.r	n.r	n.r	n.r	n.r	n.r
3	29.1	28.2	1.2	1.1	n.r	n.r	1.58	2.44	438.8	432.9
5	29.2	29.4	2.1	2.1	504	504	n.r	n.r	n.r	n.r
6	30.2	29.7	2.5	2.3	368	215	2.19	2.26	541.8	494.5

6.3.1.7 Bacterial Abundance

Bacteria were consistently found in concentration range of 1-8 x 10^6 cells l^{-1} in ice, water and brine during the first experiment (Fig. 6.7). There was no evidence that bacteria were being differentially distributed between water, ice and brine (Fig. 6.7). Bacterial densities were not correlated in any way with nutrients or DOC, suggesting that they do not have any influence on the nutrient or DOC dynamics in the system.

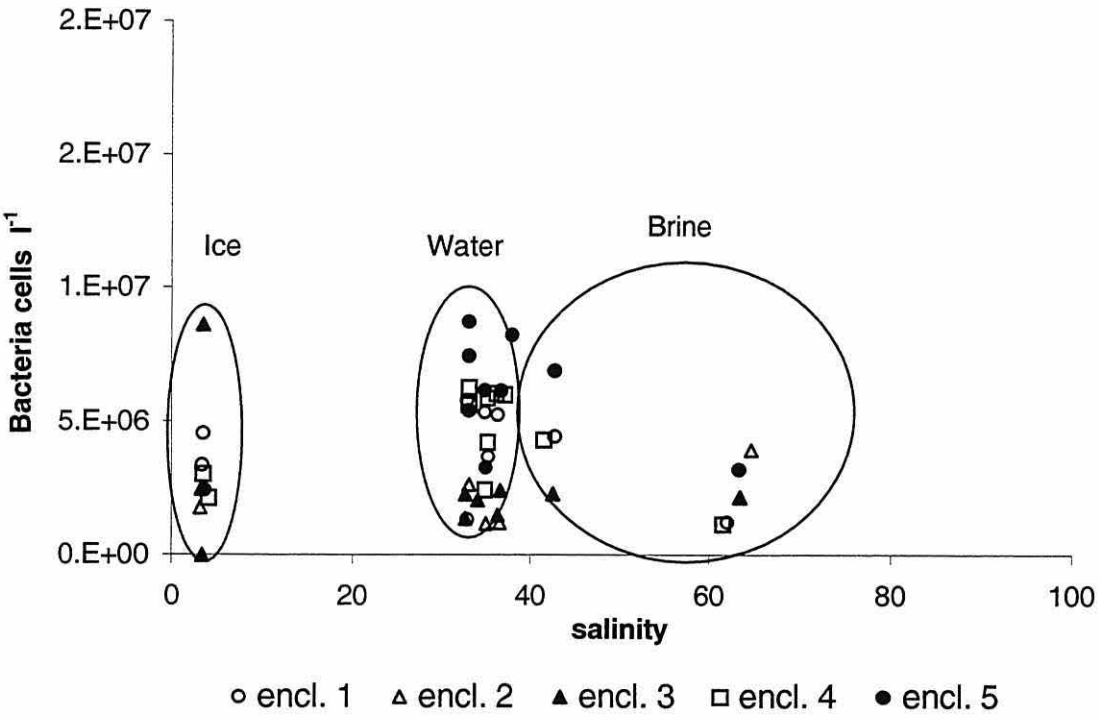

Fig. 6.7. Bacterial abundance as a function of salinity in water, brine and centrifuged ice during experiment 1. Open circles represent enclosure 1; open triangles represent enclosure 2; closed triangles represent enclosure 3; open squares represent enclosure 4 and closed circles enclosure 5.

6.3.2 Experiment 2

6.3.2.1 Physical Characteristics

During the second experimental phase air temperature averaged –16.9 ± 4.9 °C (see Fig. 6.2). After 336 h the ice cover thickness in the enclosures reached a maximum

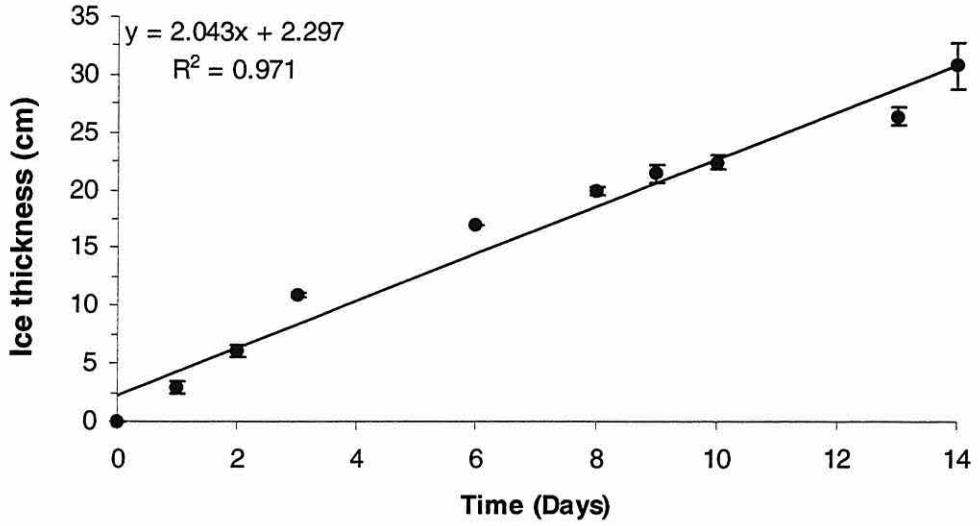

Fig. 6.8. Average ice thickness (cm) standard deviation as a function of time in all enclosures (n=5) during the second experimental phase. Solid line indicates linear regression between ice thickness and time.

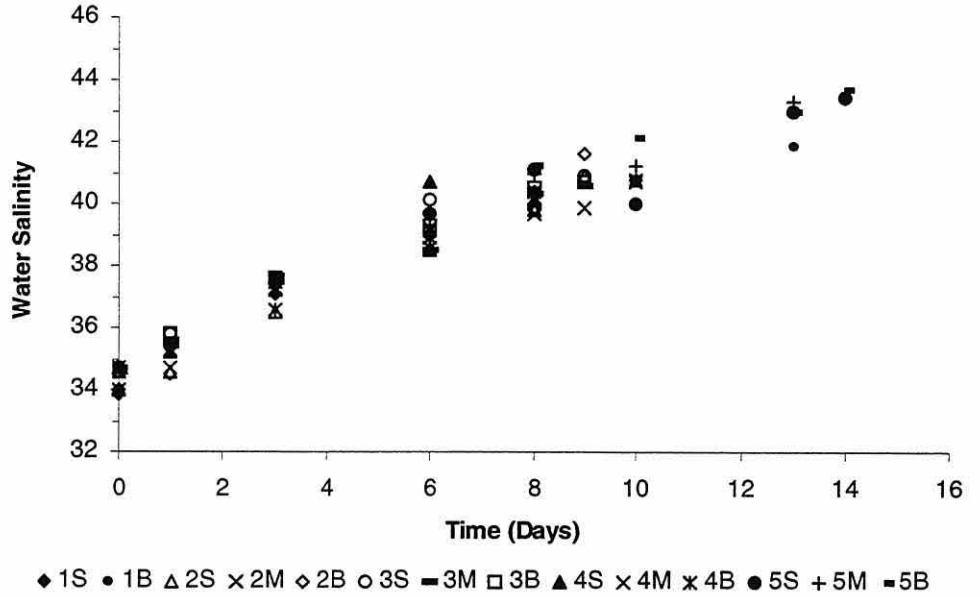

Fig. 6.9. Water salinity as a function time in the three different sampling positions of enclosures 1 to 5 during the second experimental phase. Letters used are S = surface water sampling, M = middle water sampling and B = bottom water sampling. Numbers 1 to 5 represent the enclosures from which water samples were collected.

of 30.8 ± 2 cm, indicating an ice formation rate of 2.0 ± 0.6 cm day^{-1} (Fig. 6.8). Ice sampling took place on different days in each enclosure, resulting in different end-point ice thickness (see Table 6.6). As in experiment 1, below a thin layer of granular ice, the ice had a columnar crystal texture typical of young ice grown under calm conditions (Weeks and Ackley, 1982), and a pore structure consisting of brine channels had developed (Haas et al., 1999).

After 144 h freezing the salinity of the water had increased by an average of 2.3 ± 0.3 and after 336 h by 9.1 supporting the fact that some brine expulsion occurs at the ice-water interface driven by the progressive cooling of ice and increasing pressure within the ice (Fig. 6.9). Similarly to experiment 1, the salinity profile in the ice followed a C-shaped form reported previously for young first-year sea ice (Weeks and Ackley, 1982). Because of the colder ice temperatures, measured salinity of the centrifuged brines was almost double at the top of the ice sheet (82.4) compared to the bottom sections (approximately 41) towards the ice-water interface (see Table 6.6). However they appear to be below values calculated from empirical equations (Assur, 1960).

Table 6.6. Comparison of measured and calculated ice and brine properties obtained from up to 6 ice cores sections at the end of experiment 2. The ice layer during the second experiment reached a thickness of 30.8 ± 2 (SD) cm after 14 days of growth. [1]Assur (1960).

Ice Cores Sections (cm)	Measured brine salinity	Calculated brine salinity[1]	Centrifuged brine volume (%)	Residual ice salinity	Calculated bulk ice salinity
0-5	82.4 ± 12.1	215.1	5.8 ± 1.4	4.1 ± 0.1	8.4 ± 0.3
5-10	78.8 ± 13.0	182.1	4.1 ± 0.4	3.8 ± 0.4	6.8 ± 0.2
10-15	64.3 ± 7.0	149.0	6.1 ± 0.9	2.8 ± 0.5	5 ± 0.2
15-20	48.9 ± 2	226.0	14.6 ± 5.8	2.5 ± 0.4	11.6 ± 6.4
20-25	41.7	82.9	10.	2.8	6.4
25-30	47.7	49.9	28.5	2.8	13.1

The brine volumes increased from 5.6 to 22.9% of the total sample volume along the vertical profile from the top to bottom of the ice (Table 6.6). It should be noted that, in contrast to experiment 1, ice temperature profile data were not available, thus calculated brine salinity has been estimated assuming that there was a linear

temperature gradient from the air to the underlying water (Haas pers. comm.; Arrigo et al., 1993). Centrifuged ice samples had a residual salinity of 2.5 to 4.1, showing that not all brine could be centrifuged out of the ice (Table 6.6).

The influence of sampling positioning in the water column of the enclosures was investigated by means of a one-way analysis of variance, after preliminary tests of normality and homogeneity of variance on the data proved significant ($p < 0.05$). Results show that overall the sampling depth had no significant effect on the variability of salinity or concentration of inorganic and organic compounds measured within each of the enclosures ($p > 0.05$, see summary Table 6.7).

Table 6.7. One-way analysis of variance (ANOVA) on concentrations of variables measured according to the three positions of sampling in the water column of each enclosure. Abbreviations used are Encl. = enclosure, n. r.= not recorded.

Measured Variable	Source of variation	Encl. 1	Encl. 2	Encl. 3	Encl. 4	Encl. 5
Salinity	Water Sampling depth (surface, middle, bottom)	0.873	0.969	0.942	0.948	0.774
DOC	Water Sampling depth (surface, middle, bottom)	0.802	n.r.	n.r.	0.749	0.734
Phosphate	Water Sampling depth (surface, middle, bottom)	0.811	0.340	0.633	0.820	0.758
Nitrate	Water Sampling depth (surface, middle, bottom)	0.799	0.889	0.849	0.820	0.500
Silicate	Water Sampling depth (surface, middle, bottom)	0.126	0.690	0.663	0.863	0.470
Glucose	Water Sampling depth (surface, middle, bottom)	n.r.	0.0990	n.r.	0.266	n.r.
Glycine	Water Sampling depth (surface, middle, bottom)	n.r.	n.r.	0.837	n.r.	0.342

6.3.2.2 Inorganic Nutrients

The initial nitrate concentration within water was consistent among enclosures (32.4 ± 0.5 µM) and significantly co-varied with salinity (see Fig. 6.10). Observed nitrate concentration did not significantly differ from the dilution lines in enclosures 1 to 5 ($p<0.05$, see Table 6.8). The slopes and intercepts of the predicted dilution lines were

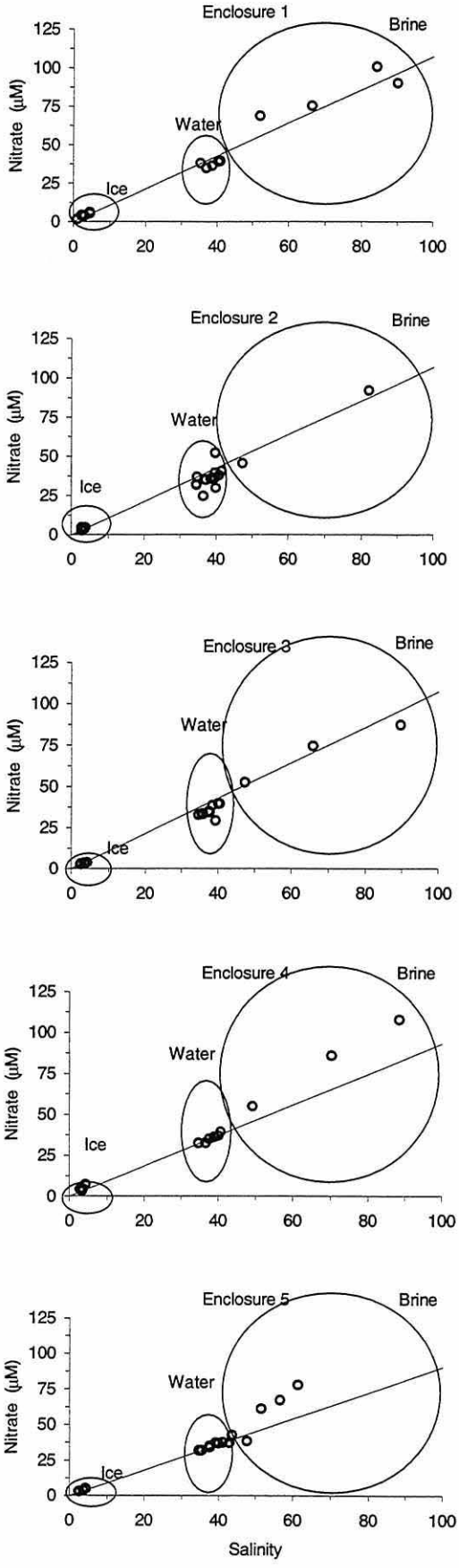

Fig. 6.10. Nitrate plots as a function of salinity of water, brine and centrifuged ice in enclosures 1 to 5 during experiment 2. The solid line represents the dilution line calculated from the surface water nitrate value at the start of the experiment.

within the upper and lower 95% confidence intervals of the measured data in all enclosures (Table 6.8). In enclosure 4, however, at salinity higher than 40 within the brine, nitrate was found at higher concentrations than those expected from the physical dilution line (Fig. 6.10).

Table 6.8. A summary of the statistical comparison in enclosures 1 to 5 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence intervals, CI) around the measured data slopes and intercept for nitrate concentrations regressed against salinity.

Enclosure	Dilution Line		Data	95% CI		Data	95% CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
1	1.071	$-6x10^{-15}$	1.080	0.896	1.264	-3.83	-11.936	4.276
2	1.068	$-1x10^{-14}$	1.040	0.908	1.711	-2.289	-7.331	2.753
3	0.942	$7x10^{-15}$	1.012	0.928	1.095	-1.272	-4.694	2.150
4	1.071	$-6x10^{-15}$	1.171	1.044	1.298	-3.95	-9.348	1.440
5	1.071	$-6x10^{-15}$	1.078	0.927	1.228	-2.546	-8.230	3.138

In contrast to nitrate, as observed in experiment 1, phosphate initial concentration was different between enclosures. In enclosures 2 and 3, where no algal DOM was added, phosphate was 0.85 ± 0.1 µM, whereas in the other enclosures it was almost double the concentration (1.5 ± 0.6 µM). The relationship between phosphate concentration and salinity is less apparent than for nitrate or silicate (Fig. 6.11). When comparing the regression line with the dilution it is possible to see that in enclosures 2, 3 the slope and intercepts of the phosphate theoretical dilution line are included within the 95% CI of the measured data (Table 6.9). However, at salinity greater than 70, phosphate data in tanks were not recorded in enclosures 2 and 3 (Fig. 6.11).

Table 6.9. A summary of the statistical comparison in enclosures 1 to 5 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence intervals, CI) around the measured data slopes and intercept for phosphate concentrations regressed against salinity.

Enclosure	Dilution Line		Data	95%CI		Data	95%CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
1	0.0568	-4×10^{-16}	0.043	0.036	0.049	0.245	0.025	0.515
2	0.0291	1×10^{-16}	0.026	0.016	0.036	-0.059	-0.390	0.272
3	0.024	0	0.023	0.021	0.025	-0.038	-0.113	0.037
4	0.0574	-9×10^{-16}	0.037	0.025	0.050	0.200	-0.268	0.668
5	0.0631	9×10^{-16}	0.051	0.042	0.061	0.142	-0.229	0.512

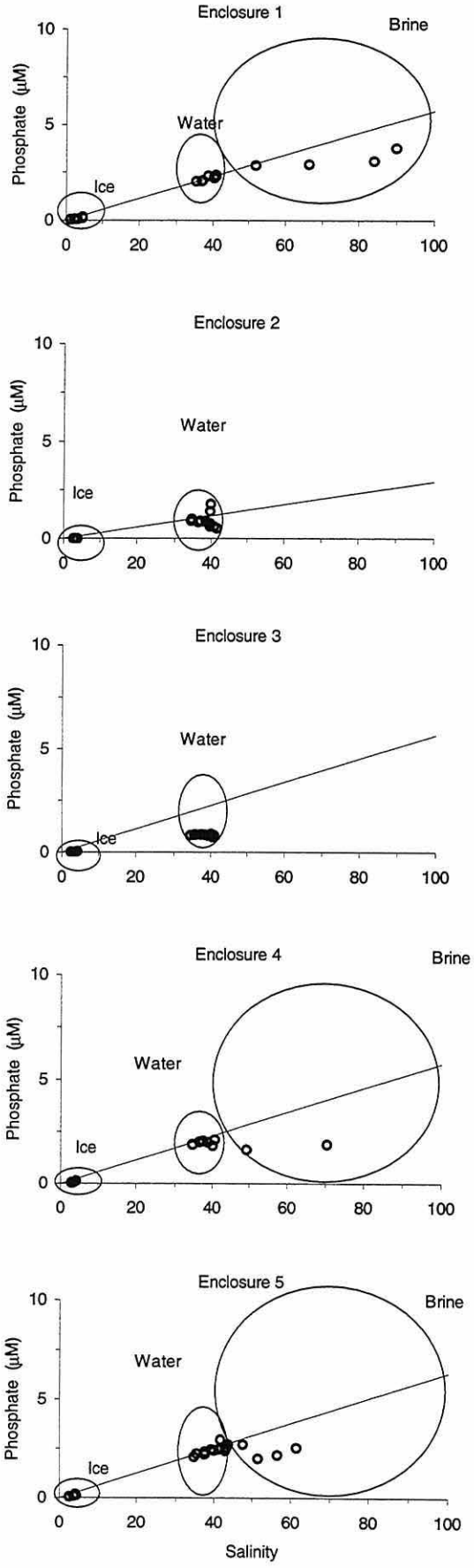

Fig. 6.11. Phosphate plots as a function of salinity, water, brine and centrifuged ice in enclosures 1 to 5 during experiment 2. The solid line represents the dilution line calculated from the surface water phosphate value at the start of the experiment.

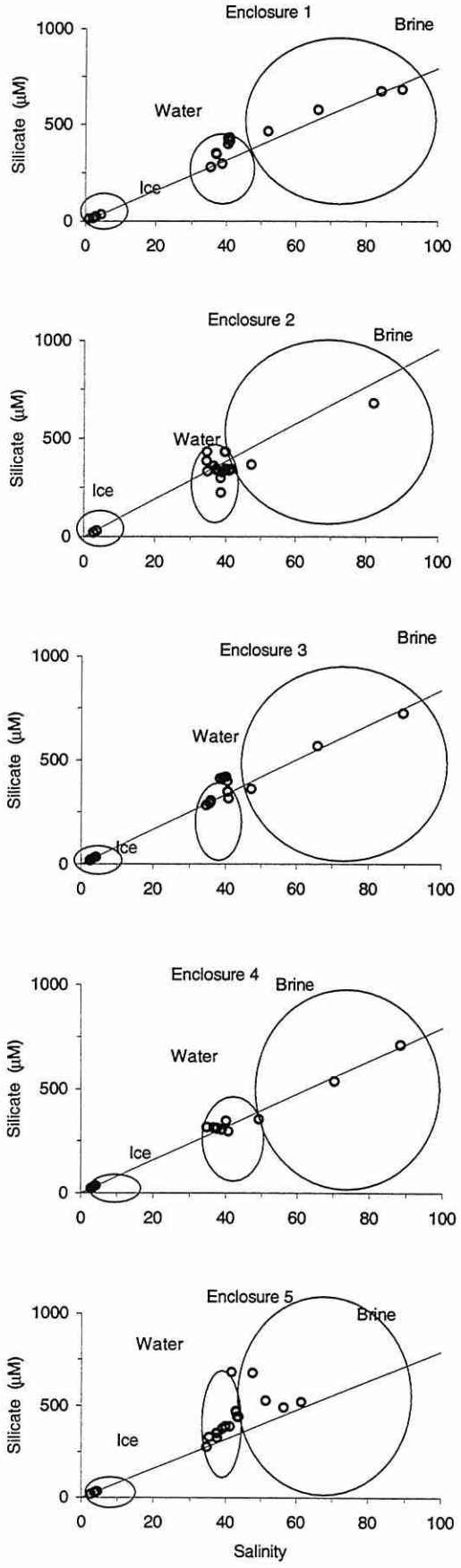

Fig. 6.12. Silicate plots as a function of salinity, water, brine and centrifuged ice in enclosures 1 to 5 during experiment 2. The solid line represents the dilution line calculated from the surface water silicate value at the start of the experiment.

Silicate was evenly distributed within the different enclosures. Concentration due to physical dilution was observed in enclosures 1, 2, 3 and 5 since the dilution lines were within the 95% confidence interval range of the regression of silicate concentrations against salinity (Fig. 6.12, Table 6.10). In enclosure 4 there was a significant departure of silicate distribution from the theoretical dilution line (Table 6.10). Enclosure 5 showed that in the brine of the lower sections of ice DOC was particularly enriched.

Table 6.10. A summary of the statistical comparison in enclosures 1 to 5 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence intervals, CI) around the measured data slopes and intercept for silicate concentrations regressed against salinity. Encl. = enclosure.

Encl.	Dilution Line		Data	95% CI		Data	95% CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
1	7.921	-9.00×10^{-14}	8.054	7.123	8.986	20.260	-20.860	61.680
2	9.576	0	8.525	7.110	9.940	19.830	-34.470	74.130
3	8.353	2.00×10^{-13}	8.400	7.507	9.287	13.080	-23.840	50.000
4	9.336	-2.00×10^{-13}	7.860	7.384	8.339	6.010	-14.330	26.350
5	9.360	-1.00×10^{-13}	10.320	8.326	12.319	-5.410	-82.390	71.570

6.3.2.3 Dissolved Organic Carbon

DOC initial concentration was 486, 758 and 343 µM in enclosures 1, 4 and 5 respectively (Table 6.1). Over the experimental period there was a similar distribution of DOC in the waters of all enclosures and at all depths. In the upper brine section of the consolidated ice there was a characteristic and substantial enrichment of DOC with maximum concentrations over 1500 µM. The DOC concentrations in brine of the enclosures were on average over twentyfold those in centrifuged ice and between three- to sixfold those in the underlying water in all enclosures (Fig. 6.13A).

Table 6.11. A summary of the statistical comparison in enclosures 1, 4 and 5 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence intervals, CI) around the measured data slopes and intercept for dissolved organic carbon concentrations regressed against salinity. Encl. = enclosure.

Encl.	Dilution Line		Data	95%CI		Data	95%CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
1	5.198	0	15.985	11.885	20.085	-179.86	-362.04	2.32
4	15.691	0	10.906	3.10	13.412	73.51	-34.63	181.65
5	5.1138	0	21.475	10.521	32.429	-206.1	-619.7	207.5

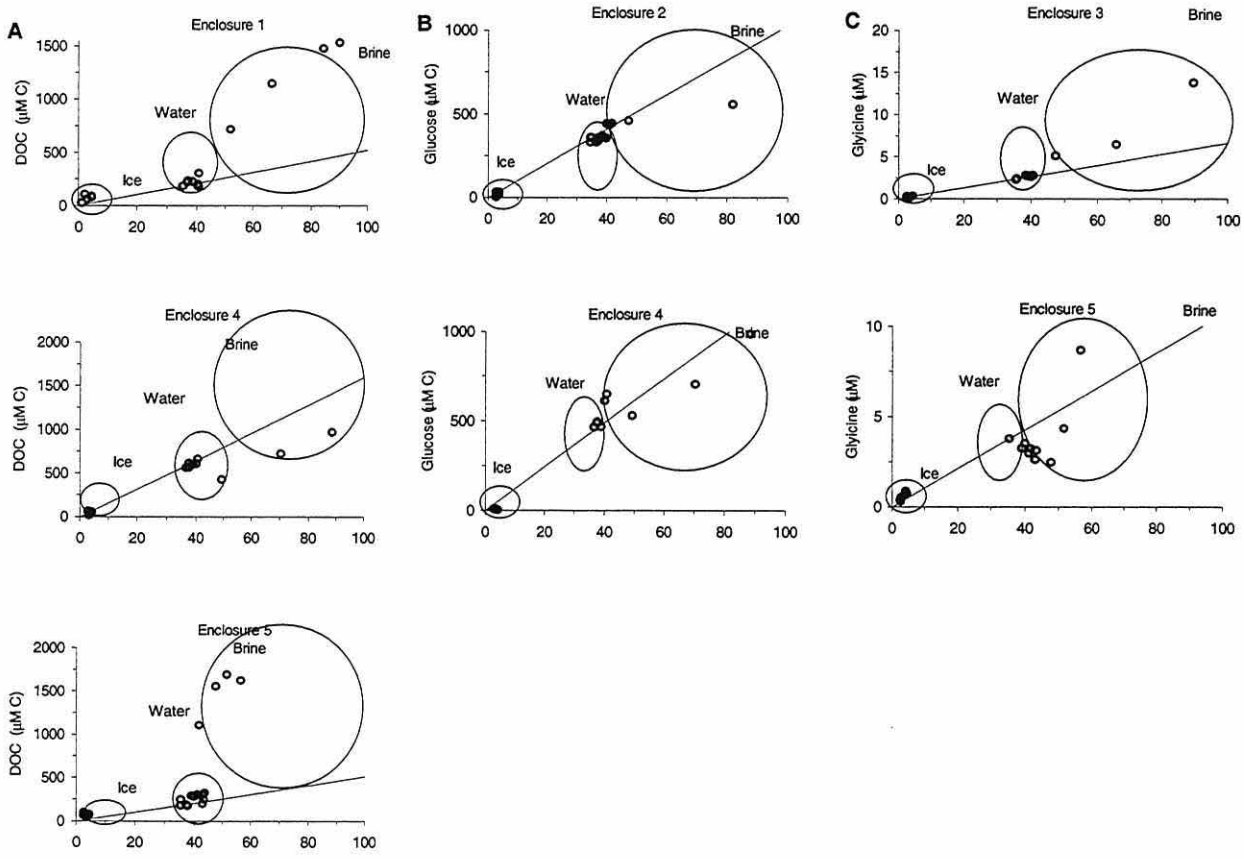

Fig. 6.13. A) Dissolved organic carbon (DOC), B) glucose and C) glycine plots as a function of salinity, water, brine and centrifuged ice in enclosures 1 to 5 during experiment 2. The solid line represents the dilution line calculated from the surface water values at the start of the experiment.

DOC distributions in ice, water and brine were more scattered relative to the dilution line than nutrients such as nitrate and silicate (see Fig. 6.13). A significant difference was found in all enclosures between the concentrations of DOC as a function of salinity and the theoretical dilution line (Table 6.11, $p > 0.05$). DOC was highly concentrated within the brine reaching concentrations up to 200-300 µM higher than values expected from dilution line predictions in enclosure 1 (Fig. 6.13). In particular DOC in enclosure 6, which was frozen for the longest time, showed a maximum enrichment in brine, reaching over 2000 µM in the top brine, a maximum difference from the dilution line of >1000 µM. However, in enclosure 5 DOC concentration was depleted in respect to the dilution line (Fig. 6.13).

6.3.2.4 Glucose

In contrast to experiment 1, the initial glucose concentration in enclosure 4 was over 100 µM higher than in enclosure 2 (Table 6.1). Over the experimental period there was a homogenous distribution of glucose in the waters of both enclosures and at all depths. In the brine of the top section of the consolidated ice there was a substantial enrichment of glucose: concentrations of 560 µM and 980 µM were recorded in the top section brine of enclosures 2 and 4 respectively. In enclosure 2, glucose in the upper brine was on average up to twentyfold the concentration in the centrifuged ice and up to the double concentrations in the water (Fig. 6.13B). Glucose showed a physical concentration in enclosure 4, where it was added with algal DOM (Table 6.12). In contrast, the slope and intercept of the dilution line for enclosure 2, where only glucose was added, were not within the 95% confidence intervals (CI) of slopes and intercepts of the measured data.

Table 6.12. A summary of the statistical comparison in enclosures 2 and 4 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence interval, CI) around the measured data slopes and intercept for glucose concentrations regressed against salinity.

Encl.	Dilution Line		Data	95% CI		Data	95% CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
2	10.268	0	8.189	6.901	9.478	38.620	-10.720	87.960
4	12.27	-3.0×10^{-13}	11.555	9.694	13.415	15.080	-65.20	95.360

However, in enclosure 4, brine of the upper sections of consolidated ice was relatively enriched in glucose, with values up to ninetyfold those in the centrifuged ice and double those in the water. The brine from the top sections was always most enriched in glucose in comparison to the bottom and less saline sections. Distribution in ice, water and brine are in general good correspondence to the dilution lines in both enclosures and in both experiments. However, in experiment 2, glucose in both enclosures 2 and 4 showed a depletion in the brine, reaching concentrations up to 200-400 µM lower than values expected from dilution line predictions.

6.3.2.5 Glycine

Initial glycine concentration was similar in enclosures 3 and 5 (>2 µM, see Table 6.1). Over the experimental period there was a more scattered distribution of glycine in the waters of both enclosures and at all depths. In the brine of the top section of the consolidated ice there was enrichment of glycine with maximum concentrations particularly in enclosure 3. These values were on average up to fortyfold those in the centrifuged ice and over threefold concentrations in the water (Fig. 6.13C). The brine and ice near the air interface were always most enriched in DOC in comparison to the bottom and less saline sections. In enclosure 5, where glycine was added together with DOC, despite high variability of concentrations, there was significant evidence of physical dilution within water, centrifuged ice and brine (Table 6.13) as the 95% confidence intervals of slope and intercept of the measured glycine concentrations were within the dilution line slope and intercept (Table 6.13).

Table 6.13. A summary of the statistical comparison in enclosures 3 and 5 between the slopes and intercepts calculated for the theoretical dilution lines and the variability (upper and lower 95% confidence interval, CI) around the measured data slopes and intercept for glycine concentrations regressed against salinity. Encl. = enclosure.

Encl.	Dilution Line		Data	95% CI		Data	95% CI	
	Slope	Intercept	Slope	Lower	Upper	Intercept	Lower	Upper
3	0.0662	-4.00×10^{-16}	0.1299	0.09822	0.16158	-1.3686	-2.698	-0.039
5	0.1068	-9.00×10^{-16}	0.11211	0.06805	0.15617	-0.3014	-1.9404	1.3376

6.3.2.6 Budgets

Budgets for inorganic nutrients and DOC were determined using water volumes and measured salinity in each of the enclosures and compared with the recorded measurements (Table 6.14). Knowing the initial and final salinity and assuming it behaves conservatively it is possible to calculate the volume of unfrozen water at the end of the experiment. This in turn can be used to calculate the expected change in concentration of the inorganic nutrients and organic compounds and compare the calculated values with the measured values. The data referring to measured and calculated nutrients are shown in Table 6.14. Nitrate measured was in excess to the calculated value, however, within levels of analytical error. Measured phosphate concentration was also within agreement with calculated values, with the exception of enclosures 3 and 5, where phosphate was in excess by 20-25%. In terms of DOM, DOC was markedly below calculated end-point water values, indicating that there was a concentration effect within the ice sheet, whereas glycine is approximately within the same range and glucose, as in experiment 1, shows around 40µM to be unaccounted for in enclosure 5.

Table 6.14. Measured nitrate, phosphate, dissolved organic carbon (DOC), glucose and glycine contents of the enclosures in water and the predicted values calculated on the basis of conservative behaviour in experiment 2. Enc. = enclosure, Calc = calculated.

Enc.	Nitrate (µM)		Phosphate (µM)		DOC		Glucose (µM)		Glycine (µM)	
	Calc.	Measured	Calc.	Measured	Calc.	Measured	Calc.	Measured	Calc.	Measured
1	40.0	39.8	2.34	2.34	584.7	398.7	n.r	n.r	n.r	n.r
2	37.64	38.22	0.98	0.97	n.r	n.r	418.80	432.87	n.r	n.r
3	38.63	39.59	1.04	0.78	n.r	n.r	n.r	n.r	2.79	2.81
4	38.39	39.85	2.21	1.76	1023	638.81	534.55	494.48	n.r	n.r
5	40.01	42.67	2.61	2.57	429.54	251.65	n.r	n.r	3.28	3.12

6.3.2.7 Bacterial Abundance

Bacteria were in variable concentrations: in enclosures 2 and 3 densities never exceeded 3 x 10^6 cells l^{-1} in ice, water and brine (Fig. 6.14). There was evidence that bacteria were in higher densities in enclosures 1, 4 and 5. Bacterial concentrations in

the brine sections of enclosures 4 and 5 were between 1 and 2 x 10^7 cells l^{-1}. Bacterial density was significantly correlated with DOC (Pearson correlation coefficient r = 0.404, p <0.05) and nitrate in all enclosures (r = 0.330, p <0.05, n = 76, see Table 6.15).

Table 6.15. Pearson product moment correlation coefficients matrix between bacterial abundance, dissolved organic carbon (DOC) and inorganic nutrient (nitrate, phosphate and silicate) concentrations during experiment 2. Symbols indicate level of significance:* = p <0.01, • = p <0.05:, n.s = not significant.

	Bacteria Abundance	DOC	Nitrate	Phosphate
DOC	0.404•			
Nitrate	0.330•	0.713*		
Phosphate	0.128 n.s	0.440*	0.733*	
Silicate	0.232 n.s	0.663*	0.910*	0.767*

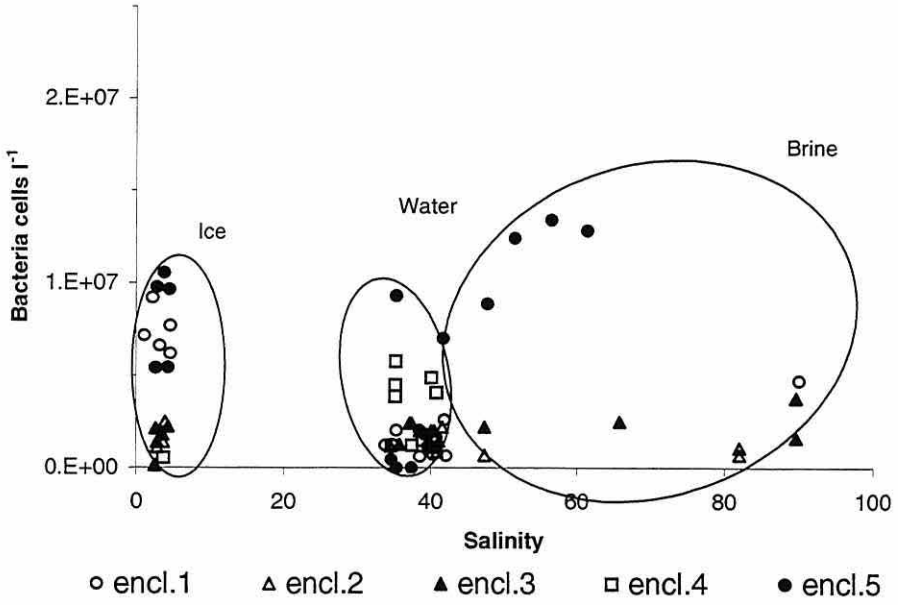

Fig. 6.14. Bacterial abundance as a function of salinity in water, brine and centrifuged ice during experiment 2. Open circles represent enclosure 1; open triangles represent enclosure 2; closed triangles represent enclosure 3; open squares are enclosure 4 and closed circles represent enclosure 5.

6.4 Discussion

The two experiments were relatively consistent in terms of their physical parameters and overall consistency was observed across the enclosures, producing characteristics that can be considered a realistic representation of formation of young columnar sea ice at different time scales. New ice growth was initiated under quiescent conditions in both experiments, resulting in a mostly columnar ice texture, which is typical of slow growth at the bottom of an ice layer at the ice-water interface under hydrodynamically stable conditions (see Eicken and Lange, 1989). Congelation ice is commonly found in multi-year sea drifting pack ice and the generally thicker land-fast ice of both Arctic and Antarctic regions, reaching >1-2 metres in thickness and being characterised by steep temperature and salinity gradients (Kottmeier and Sullivan, 1988; Arrigo et al., 1995). Congelation ice may also be found in the vicinity of large areas of open water (polynyas) up to several square kilometres within the pack ice forming as a result of upwelling warm water and/or prevailing offshore winds.

During both experiments the ice freezing rate was approximately 2 cm day^{-1}. The growth rate of congelation ice is typically slow, approximately 1 mm h^{-1} in natural quiescent conditions and the texture consists of large, columnar-grained crystals resulting from the slow removal of latent heat from under the ice-sheet (Weeks and Ackley 1982; Clarke and Ackley, 1984). The observations are in close agreement with recent experimental evidence by Krembs et al., (2001) who indicated that columnar ice formed at a rate of approximately 1.8 cm day^{-1} and with field studies of congelation ice showing its formation has a rate of <10 cm day^{-1} (Gleitz et al., 1998). The degree of physical turbulence and wind action influences the mode of ice formation and the type of distribution of both biotic and abiotic constituents of seawater.

Brine rejection occurred at the ice-water interface during both congelation processes, increasing the enclosures sub-ice water salinity by approximately 4 from 32.8 to 37 after approximately 120 h of freezing. However, no significant vertical salinity stratification was observed in the water column of the enclosures either in the first or second experiment. A first observation which can be made concerns the scale of the

volume chosen in the experimental design. The scale may be too small to discern differences in concentrations of the compounds in the water column sampling positions, which were placed 40 cm from each other. In particular in the second experiment, due to the increasing thickness of the ice, surface water sampling immediately under the ice was increasingly closer to the middle water sampling position. Secondly, the methodology of sampling water used may have been inefficient and have induced mixing between levels of sampling. Due to the nature of the enclosures, made of polyethylene, water mixing may have occurred as a result of the influence of the adjacent current area, despite partial separation through a wooden divider, or internal haline circulation caused by brine expulsion may have induced similar concentrations of components at the water depths.

During the second experimental phase the freezing process was made to last for a longer period, leading to a maximum ice thickness two to three times greater than the first experiment. However, a higher variability in air temperature regime was recorded in the second experiment in comparison to experiment 1. Our observation was that brine volume is around 20% in the bottom ice layers both in experiments 1 and 2, and the trend shown is that of being consistently smaller on the ice surface and increasing at depth towards the ice-water interface, where also bulk salinity is highest. The observations are in line with theoretical aspects of ice physics, which define that volume of the brine changes in relation to temperature and bulk salinity of the ice, whilst brine salinity is solely dependent on ice temperature (Assur, 1958; Frankenstein and Garner, 1967). The higher brine volumes at the ice water interface also enable an exchange process with the underlying water due to the warmer ice temperature and porosity. Although it has been observed that more brine is extractable from columnar ice in comparison to granular ice, the residual ice salinity confirms that brine may remain isolated in pockets and bubbles with little or no communication with other brine masses and cannot be released by the centrifugation process alone at the temperature at which the ice is kept (Niedrauer and Martin, 1979; Weissenberger et al., 1992; Krembs et al., 2000). Krembs et al., (2001) however have reached almost complete brine drainage in centrifuged ice with a longer centrifugation time (up to 20 minutes) at a lower temperature and a higher rotor speed of 1500 rpm.

Results for nitrate for both the first and second experimental phase show a broad conservative behaviour during ice growth and brine rejection. There is consistency of physical forcing on nutrient incorporation in newly formed sea ice, as seen in field studies on young sea ice cores (see Dieckmann et al., 1991). Phosphate concentrations within enclosures 2 and 3 are consistently half those in enclosures 4 and 5 in both experimental phases. It could be an indication that the algal-extracted inoculum contained excess phosphate which modified the nutrient content. Silicate shows a similar broad range in initial water concentration, possibly confirming that the addition of the algal extract influenced the nutrient distribution. In the first experiment bacteria numbers were in constant proportions among enclosures and did not display any correlation with nutrient or organic matter contents. In contrast, during the second experiment bacteria were present in far greater numbers in enclosure 1, 4 and 5, whose common factor is the addition of algal-extracted DOM. In absence of grazers bacteria may be metabolically stimulated by the interaction of a bottom-up control other than inorganic nutrients, such as substrate and the temperature regime during the experiment (see Hoch and Kirchman, 1993). However, bacterial numbers are one magnitude lower than typical seawater concentrations and no bacterial production was measured identifying whether bacterial communities were actively growing. Therefore it is assumed they had no impact on the change in nutrient concentrations. Although air temperature mean value was similar between experiments, in the first phase little temperature fluctuation was observed, whilst in the second phase there was a temperature increase from –20 to 5 °C recorded after 120 h, which lasted for no longer than 48 h (Fig. 6.2). During the temperature increase the warming of the air may have contributed to increase the ice cores porosity.

Overall these first results by use of experimental enclosures in simulated polar conditions and with the near exclusion of biological processes, reflect the evidence for conservative behaviour of inorganic nutrients in the brine pockets of sea ice. Different initial concentrations of algal-extracted DOC within the first experiment suggest a different quality of substrate. This makes a comparison between the first and second experiment difficult, but results show the incorporation of a range of starting seawater DOM concentrations. The partially large differences of DOC to the applied dilution lines may indicate a potential selective retention of DOC in the brine

interstices. The implication for natural conditions is that DOC is initially physically constrained into the ice interstices in relatively large quantities and available to the organisms entrapped.

In the first experiment DOC was found to be up to three-four times higher in brine than in the underlying water, which indicates a general basic agreement of our experimental findings with field samplings (Thomas et al., 2000; Herborg et al., 2001). Glucose also varied in concentrations within enclosures. Glucose was also observed to be double in brine than in the underlying water and glycine follows a similar trend, however in the second experiment it showed a depletion to predicted values, as opposed to glycine. Herborg et al., (2001) observed that the average concentration of monosaccharides to be over 5 times in summer Weddell Sea ice cores relative to open water and to be the major contributor to carbohydrate composition. It appears that the dominant control on initial DOC, glucose and glycine incorporation in ice is salinity distribution, however according to the nature of DOM the enrichment may vary, as observed from clear deviations from the dilution lines.

Among individual classes it appears that adsorption of amines and amino acids by marine sediments has also been found to be greater than other small water-soluble compounds such as glucose, but not as great as hydrophobic compounds, such as large molecular weight lipids and hydrocarbons (Wang and Lee, 1993). In the first and second experiment glycine is particularly abundant in the brine sections and appears in excess to the applied dilution line in comparison to glucose, confirming such concentration due to physical properties of single compounds. Also glycine is exceeding the dilution line in the brine in the first experiment, whereas no other compound was found to exceed the predicted values in brine. Amino acids and simple sugars showed enrichment in platelet ice in comparison to undetectable levels in the sub-ice water column (Arrigo et al., 1995). However they were differentially distributed along the vertical ice core profiles.

The novelty of this experimental approach lies in using a large scale-facility and manipulate and control a variety of environmental conditions to investigate the chemistry and physical responses of organic compounds in simulated sea ice

achieving a required ice texture. This type of study is also economically and logistically viable, enabling continuous sampling and may be used to support micro- or mesocosm and modelling studies. However, due to the limited data set it is clear that further experiments are needed to verify these findings. Future investigation of DOM in experimental ice studies, such as the incorporation of individual organic compounds under turbulent or calm conditions, may further elucidate the DOC accumulation into brine and ice. For instance lipids (e.g. fatty-acids), are compounds high in carbon, biosynthesised as storage reserves by sea-ice algae particularly under nutrient-limitation conditions and may maintain fluidity for metabolic processes (Fahl and Kattner, 1993; Gleitz et al., 1996). Weissenberger (1998) argued the ice/water ratio in small scale (<200 m^3) experimental enclosures may not fully represent the natural sea-ice/water ratio, therefore the use of larger mesocosms and frozen natural assemblages samples may provide a further test of the incorporation of organic compounds.

6.5 Conclusions

The distribution of inorganic nutrients and a variety of dissolved organic compounds during the initial stages of the freezing show that the inorganic nutrients are physically conservatively enriched within the ice. However the incorporation of DOC in young ice was more variable and in excess of expected concentrations from a purely physical dilution.

In the first experiment there are signs of physical concentration of DOC, whereas in the second experiment DOM does not entirely follow the physical concentration mechanism. This will reflects the different physical chemical and biological effects within the ice.

CHAPTER 7

GENERAL CONCLUSIONS

The aim of this study was to determine spatial and temporal variations in organic matter concentrations in different phases of the Southern Ocean: oceanic and coastal water column profiles, time series observations at a representative coastal site and through direct measurement of organic carbon from pack ice. The process of dissolved organic carbon (DOC) incorporation into sea ice was experimentally tested during the transition from water into newly forming ice in quasi-abiotic conditions. This chapter summarises some of the main conclusions which can be drawn from the studies carried out on DOC, dissolved organic nitrogen (DON), particulate organic carbon and nitrogen (POC and PON) both *in situ* and from laboratory simulations. The overall objective was to study the biogeochemistry of DOC in the Southern Ocean and to study the physical and biological variables affecting DOC production and distribution in the marine environment. It is clear that the production is of biological nature but that the physical factors constraining DOC in the Southern Ocean are of great importance.

The distribution and dynamics of dissolved and particulate organic matter (DOM and POM) were investigated in HNLC (high nutrient low chlorophyll) surface waters during two visits at a shelf and oceanic station off the sub-Antarctic island of South Georgia (South Atlantic) during the austral spring of 1997. The oceanic station was characterised by the ongoing development of a spring bloom, whilst on shelf non-bloom conditions prevailed and may reflect the tail end of a bloom or have been influenced by the presence of macrophyte degradation products by the coastal ice. Despite greater primary production at the oceanic site than at the shelf site, DOC (38-60 μM) and DON concentrations (3-13 μM) were in a similar range at both sites, and show that 70-80% of the total organic carbon (TOC) pool was partitioned as DOC and DON was approximately 20% of the dissolved nitrogen pool. However the tight correlation observed between POC and PON was not found for the DOC and DON pools. The residence time of DOC was calculated in the order of several weeks to months and it is concluded that DOC was mostly semi-labile or refractory.

The bacterial heterotrophic production to primary production percentage ratios were low, evidence showing a weak coupling of bacteria depending on dissolved organic compounds released by the microalgae. The result is supported by similar observations of low (<10%) BP:PP in Antarctic areas (Bird and Karl, 1999). Top-down control, represented by grazing pressure from protozoans at the oceanic site appears an important factor in controlling bacterial growth and full utilisation of dissolved substrates. Another constraint on the conclusions which can be drawn from the data that the coastal area of South Georgia hosts a variety of macrophytes which in shallow waters may become degraded by the ice and the runoff released suspended material in the water column upon melting.

The principal aim of the study at the Rothera Time Series (RaTS) site, western Antarctic Peninsula, was to follow the temporal evolution of organic carbon year-round in surface waters at bi-weekly/monthly intervals from 1997 to 2001. It is apparent that DOC in the Antarctic Peninsula coastal waters shows a strong seasonal signal as in other coastal areas of the Antarctic and global oceans (Williams, 1995; Scott et al., 2000). During autumn and winter under the pack ice DOC is present in low and constant concentrations, with the lowest levels just above values recorded in the deep Pacific Ocean (>1000 m, 35-39 μM, Carlson and Ducklow, 1995). This reflects the refractory nature of winter DOC. Subsequently in spring DOC concentrations increase and become maximal in the summer months, in correspondence with the increases in temperatures and complete melting of the sea ice. Maximal concentrations of DOC were three times those observed during a spring bloom in coastal waters. It was observed that the DOC pool was the principal component of the organic carbon fraction throughout the seasons and the largest POC contribution was observed in spring and summer, but not exceeding 40% of TOC. The results suggest that the seasonal cycle of DOC and POC varied to some extent in relation to phytoplankton abundance and decline. The pack ice upon melting releases sympagic communities and particulate matter which can provide the seed for the initiation of intense phytoplankton blooms under stable water column conditions and increasing irradiation, as observed at the RaTS site (>20 μg chl *a* l^{-1}). A constraint on the conclusions is the lack of data on the coupling of the input from benthic production and potential early release of macrophyte beds material degraded and macerated by the ice in the shallow waters of Ryder Bay.

Complementary data on salinity may help assess the contribution of the ice melt and compositional data of the dissolved material at the molecular level would help identify the major contributing source at the site. The inter-annual variation observed in DOC may be due to natural variability, however other factors may be underlying such observations and trigger the increase in DOC and chl *a* concentrations at the site, such as increased micro- or macronutrient availability. Parallel studies on interannual variation in phytoplanktonic and microbial production and respiration together with inorganic nutrient dynamics may elucidate the controlling factors. Overall seasonality emerges as a crucial factor to the Southern Ocean system and disruption to it may affect the biogeochemical cycle of carbon. Recent research points to a 1 °C increase in air temperature at Signy Island over the last 15 years reflected in changes in the island lakes ecology and a 2 °C rise recorded over the past 50 years in the Antarctic Peninsula coastal region (Loeb et al., 1997; Quayle et al., 2002). If the factors triggering melting of sea and glacial ice changed in a sensitive environment such as coastal Antarctica the consequences may alter quality and quantity of DOC produced. Dierssen et al., (2002) point to glacial meltwater as having an important role in the western coast of the Antarctic Peninsula, rendering waters less saline and warmer and impacting sea ice formation. It may be a source of concern that with anthropogenic influences, i.e. greater emission of carbon dioxide and potential global warming, there may be effects on the Southern Ocean with alterations in biogeochemical cycles and consequently on cycling of the DOC pool. Measurements of DOC and POC dynamics in conjunction with communities and physical factors at this time may represent a baseline on which to compare future observations. Similarly other factors induced by climatic change may also impinge on the equilibrium of species composition, for instance by UV radiation affecting smaller size classes or inducing production of protective compounds.

One of the main aims of the study of sea ice was to identify the distribution of DOC and POC in pack ice collected from a transect along semi-closed pack ice floes of the Weddell Sea in late winter to early spring of 1989 (Augstein et al., 1991). The ice cores sampled were distinguished between first and second year ice due to differences in their ice texture and physical characteristics (Eicken et al., 1991, Eicken, 1998). Second year ice cores belonged to the same floe and showed strong

similarity in their physical and chemical characteristics. Conversely, the first year ice cores show larger variability as they represent individual floes along the Weddell Sea. The highest organic carbon concentrations were in the upper half of second-year ice, in correspondence to high phytoplankton abundance and layering of ice textures. Although corroborating similar observations (Smith et al., 1997), other authors have observed poor correlations of DOC with ice algae abundance and have indicated grazing and excretion are major sources of DOC (Thomas et al., 1995, 1998, 2001). It also appears that the age of the sea ice and its history are important factors in determining the amount of biological activity and hence organic carbon distribution within the ice. DOC and POC concentrations are higher than those expected from physical dilution at the time of the ice formation both in first- and second-year ice. Overall DOC was strongly correlated to the POC present in the ice. Second-year ice may have resisted one or more melting processes and through infiltration from overlying snow pressure or increased porosity may have received a supply of fresh inorganic nutrients and new organisms, leading to an enrichment in biological activity. The older ice is a more open system which has received nutrients sufficient to meet the demands of the algae to reach high abundance (50 μg chl *a* l^{-1}) as opposed to a semi-enclosed system of first-year ice. Although brine was not directly extracted at the time of ice collection the estimated brine volumes show that second year ice is more porous than first year ice and contains a greater brine volume and DOC concentrations. These results are consistent with observations of higher porosity giving rise to potential exchange with the surrounding seawater, inducing nutrient replenishment (Thomas et al., 2001; Kennedy et al., 2002). In terms of inorganic nutrients, some nutrient depletion was observed in first year ice in terms of silicate and phosphate. Conversely, in second year ice only silicate and nitrate were found to be depleted, but not exhausted. The large excess of ammonium and phosphate concentrations would indicate higher regeneration processes in second year ice. Silicate uptake observed would suggest the uptake by diatoms; however its regeneration is slower compared to other nutrients and its availability therefore limiting to the algal communities and controlling speciation, as opposed to nitrate influencing species abundance (see Dieckmann et al., 1991; Günther and Dieckmann, 2001). In conclusion DOC and POC concentrations in the pack ice cores analysed, characterised by presence of sea ice biological assemblages (Augstein et al., 1991; Nöthig et al., 1991; Schnack-Schiel et al., 2001), are in

excess of levels expected from purely physical dilution from concentrations in the seawater at the time of freezing, indicating alteration of pools of organic carbon and nitrogen after ice formation, regardless of ice age and position.

Unlike observations from the Weddell Sea and other polar oceanic and coastal environment, where organic carbon is mostly partitioned as DOC rather than POC (<10% TOC) (Wheeler et al., 1996; Wedborg et al., 1998; Carlson et al., 2000), a characteristic equal partitioning of organic carbon as DOC and POC was observed in the sea ice. DOC does not appear to follow inorganic nutrient distribution and it may be originating from a variety of mechanisms such as phytoplankton exudation, grazing and excretion. The high concentrations observed and recent observations in polar ice (Raymond et al., 2000; Krembs et al., 2000, 2001) point in the direction of functional or physiological purposes, for example to create a biofilm suitable for adherence to ice crystals, repel predation and help preventing freezing (cryoprotection) or, conversely, stimulating melting around cells according to changes in the physico-chemical conditions.

The role of DOC in sea ice has been recognised, since it represents a productive habitat, hosting a rich and active sympagic community of planktonic organisms during seasonal ice formation (Weeks and Ackley, 1982; Horner, 1985). Inorganic nutrients in seawater are concentrated during congelation into sea ice as a direct function of salinity, showing a conservative behaviour (Weeks and Ackley, 1982; Weissenberger et al., 1992). Similarly, ice algae and bacteria are found to be enriched in newly formed ice in comparison to the water column due to physical harvesting of ice crystals as they rise through the water column (Garrison et al., 1993; Weissenberger and Grossmann, 1998). The main objective of the experimental study was to address physical incorporation of a variety of dissolved organic compounds found in natural seawater into newly forming sea ice in virtual absence of organisms under calm conditions of growth. In summary, relatively little DOC was found within the solid ice matrix, whereas elevated concentrations were measured within the centrifuged liquid brine which fills the spaces of pores and channels of the sea ice. In particular higher concentrations of dissolved organic matter (DOM) were observed in the top layers. The DOC expelled in the underlying seawater was homogenously mixed and its distribution did not vary according to the

water depth. However, a constraint to the data obtained may be the size of the enclosures used: generally the water to ice ratio in the polar ocean is bigger and a larger mesocosm may give rise to a different distribution of ions within the seawater. The results from the controlled physical studies show dissolved organic compounds to be incorporated and concentrated within the ice according to physical forcing mechanisms in the early stages of ice formation, although not in all experiments. Although bacteria were present, their low concentrations and uniform distribution within ice, water and brine suggests no influence on the DOC dynamics within the simulated sea ice system. A study using large scale ice tank facilities overall is a useful and economic tool to help identifying processes which are logistically difficult and require costly resources to follow in the field. A follow-up experimental program using laboratory simulations may explore the incorporation of other DOM substrates (e.g. lipids, humic or fulvic acids) or molecular-weight size cut-off into sea ice. Moreover, it is unclear whether colloidal DOM may be scavenged into the sea ice as it occurs with algae and it may be useful to test this during turbulent conditions as opposed to quiescent conditions. Further high resolution investigations within the ice may show the small scale distribution of dissolved organic compounds.

This study has provided some baseline information on the spatial and temporal distribution of DOM and POM nitrogen in key productive ice-free and ice-covered areas of the Southern Ocean. In summary, DOC during an oceanic sub-Antarctic bloom exhibited low concentrations and relatively little change in time, with turnover times indicative of a dominant semi-labile and refractory nature. Within the seasonal ice zone in the eastern Antarctic Peninsula DOC was higher in concentration during intense blooms and it was strongly seasonal, where the sea ice congelation and ablation system dominates. A characteristic increase of seasonal DOC and phytoplankton abundance was observed within the four-year time series. DOC was observed the greater fraction of total organic carbon in oceanic, and to a lesser extent in coastal waters, where POC increases during phytoplankton blooms. Direct measurements of DOC in Weddell Sea ice show it is enriched in upper sections of second-year pack ice, which showed elevated phytoplankton abundance and was open to receiving inorganic nutrient inputs through snow or freezing-melting cycles in comparison to first-year ice. The transition from first-year to

second-year ice, the flushing of nutrients and the ice type and texture and the sympagic assemblage appear related to the extent to which the DOC accumulates within the ice. Through experimental sea ice simulation studies inorganic nutrients and DOM have been shown to mostly be conservatively incorporated in newly formed congelation sea ice in virtual absence of biota.

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APPENDIX 1. JR25 DOM AND POM

Chapter 3. DOC, DON, POC and PON data from RRS *James Clark Ross* Research Cruise JR25.

VISIT	STATION	DATE	CTD CAST	DEPTH (m)	DOC (µM)	DON (µM)
1	oceanic	29.10.97	ctd #065	1	55	10.0
1	oceanic	29.10.97	ctd #065	12	54	5.4
1	oceanic	29.10.97	ctd #065	21	59	6.6
1	oceanic	29.10.97	ctd #065	50	49	8.5
1	oceanic	29.10.97	ctd #065	200	46	7.6
1	shelf	31.10.97	ctd #077	8	53	11.4
1	shelf	31.10.97	ctd #077	43	58	13.0
1	shelf	31.10.97	ctd #077	65	44	9.5
1	shelf	31.10.97	ctd #077	90	59	11.0
1	shelf	31.10.97	ctd #077	120	51	6.5
1	shelf	31.10.97	ctd # 080	8	82	16.0
1	shelf	31.10.97	ctd # 080	28	62	10.3
1	shelf	31.10.97	ctd # 080	65	82	17.9
1	shelf	31.10.97	ctd # 080	90	137	23.7
1	shelf	31.10.97	ctd # 080	120	64	11.5
2	shelf	3.11.97	ctd #105	5	51	5.3
2	shelf	3.11.97	ctd #105	15	48	5.1
2	shelf	3.11.97	ctd #105	36	61	5.7
2	shelf	3.11.97	ctd #105	48	48	5.5
2	shelf	3.11.97	ctd #105	120	57	4.8
2	shelf	3.11.97	ctd #105	150	81	-
2	oceanic	4.11.97	ctd #119	3	49	8.1
2	oceanic	4.11.97	ctd #119	6	62	8.8
2	oceanic	4.11.97	ctd #119	38	52	8.9
2	oceanic	4.11.97	ctd #119	80	51	8.1
2	oceanic	4.11.97	ctd #119	150	58	9.4
2	oceanic	5.11.97	ctd #142	9	61	-
2	oceanic	5.11.97	ctd #142	15	48	4.2
2	oceanic	5.11.97	ctd #142	20	53	3.9
2	oceanic	5.11.97	ctd #142	60	51	3.0
2	oceanic	5.11.97	ctd #142	80	47	3.2
2	oceanic	5.11.97	ctd #142	120	47	3.5

VISIT	STATION	DATE	CTD CAST	DEPTH (m)	POC (µM)	PON (µM)
1	oceanic	28.10.97	ctd #031	3	7.9	2.8
1	oceanic	28.10.97	ctd #031	50	5.8	1.4
1	oceanic	28.10.97	ctd #031	63	10.6	3.8
1	oceanic	28.10.97	ctd #031	200	6.6	2.4
1	oceanic	28.10.97	ctd #040	3	15.6	5.5
1	oceanic	28.10.97	ctd #040	10	14.1	5.1
1	oceanic	28.10.97	ctd #040	63	13.8	4.9
1	oceanic	28.10.97	ctd #040	100	5.99	5.2
1	oceanic	28.10.97	ctd #040	200	4.9	1.7
1	oceanic	29.10.97	ctd #065	1	28.3	2.3
1	oceanic	29.10.97	ctd #065	12	25.2	2.6
1	oceanic	29.10.97	ctd #065	50	16.9	1.9
1	oceanic	29.10.97	ctd #065	200	4.6	0.7
1	shelf	31.10.97	ctd #077	8	11.5	1.8
1	shelf	31.10.97	ctd #077	16	3.9	0.7
1	shelf	31.10.97	ctd #077	50	5.8	1.0
1	shelf	31.10.97	ctd #077	90	6.3	0.8
1	shelf	31.10.97	ctd #077	120	3.2	-
1	shelf	31.10.97	ctd # 080	8	13.5	1.4
1	shelf	31.10.97	ctd # 080	28	20.7	1.7
1	shelf	31.10.97	ctd # 080	65	8.3	1.4
1	shelf	31.10.97	ctd # 080	90	6.5	0.8
1	shelf	31.10.97	ctd # 080	120	5.1	0.6
2	oceanic	4.11.97	ctd #119	3	9.2	1.9
2	oceanic	4.11.97	ctd #119	6	9.9	1.9
2	oceanic	4.11.97	ctd #119	29	8.6	1.8
2	oceanic	4.11.97	ctd #119	38	38.1	2.5
2	oceanic	4.11.97	ctd #119	80	29.9	1.5
2	oceanic	5.11.97	ctd #142	150	5.6	0.9
2	oceanic	5.11.97	ctd #142	9	27.2	2.9
2	oceanic	5.11.97	ctd #142	20	60.0	3.1
2	oceanic	5.11.97	ctd #142	60	30.2	2.8
2	oceanic	5.11.97	ctd #142	80	28.6	2.8
2	oceanic	5.11.97	ctd #142	120	6.0	0.6
2	shelf	8.11.97	ctd #158	6	10.9	3.8
2	shelf	8.11.97	ctd #158	11	15.4	2.8
2	shelf	8.11.97	ctd #158	20	12.3	1.2
2	shelf	8.11.97	ctd #158	46	22.1	1.3
2	shelf	8.11.97	ctd #158	80	7.9	2.6
2	shelf	8.11.97	ctd #158	120	9.7	1.0
2	shelf	8.11.97	ctd #162	10	4.4	0.8
2	shelf	8.11.97	ctd #162	20	3.6	0.6
2	shelf	8.11.97	ctd #162	40	4.3	0.6
2	shelf	8.11.97	ctd #162	80	4.0	0.8
2	shelf	8.11.97	ctd #162	120	3.3	0.7

APPENDIX 2. ROTHERA DOC AND POM

Chapter 4. DOC, POC and PON data from the Rothera Time Series (RaTS) Site.

DATE	DOC (µM)	POC (µM)	PON (µM)
05.01.1997	55	-	-
05.04.1997	-	12.6	-
03.05.1997	92	14.1	-
04.06.1997	75	12.0	0.1
06.07.1997	83	8.0	-
08.08.1997	54	13.5	0.1
06.09.1997	50	7.1	-
06.10.1997	58	5.8	-
05.11.1997	48	6.7	0.1
18.11.1997	49	15.3	0.1
05.12.1997	38	27.0	-
06.01.1998	57	31.7	-
20.01.1998	55	28.1	-
04.02.1998	141	45.9	4.2
17.02.1998	62	46.5	5.7
15.03.1998	71	30.3	-
04.04.1998	59	10.6	-
01.05.1998	70	4.6	-
20.06.1998	54	4.8	-
04.07.1998	98	7.8	-
04.08.1998	77	12.9	-
05.09.1998	60	14.2	-
03.10.1998	72	8.3	-
05.11.1998	65	6.4	-
18.11.1998	105	8.5	-
05.12.1998	80	16.3	-
21.12.1998	103	13.5	2.6
06.01.1999	102	20.0	4.3
19.01.1999	158	21.4	4.3
03.02.1999	171	23.6	4.9
17.02.1999	100	44.2	6.7
05.03.1999	105	6.1	-
07.04.1999	105	6.5	-
05.05.1999	102	7.3	-
18.08.1999	128	14.3	1.4
08.10.1999	86	7.6	-
15.11.1999	82	6.0	-
06.12.1999	101	43.0	10.3
22.12.1999	82	8.3	1.3
05.01.2000	148	45.7	10.4
26.01.2000	143	23.3	4.6
09.02.2000	-	42.6	5.9
20.02.2000	96	24.1	5.7
01.03.2000	135	25.9	6.1
22.04.2000	72	15.4	1.7
23.05.2000	79	15.1	1.3
19.07.2000	62	8.2	-
07.12.2000	89	30.5	4.7

02.01.2001	95	29.2	3.7
17.01.2001	103	-	6.2
01.02.2001	109	31.7	4.3
28.02.2001	187	47.7	6.4

APPENDIX 3. ANT VIII/2 DOC AND POM

Chapter 5. DOC, POC and PON data from sea ice cores collected during RV *Polarstern* research cruise ANT VIII/2, Winter Weddell Gyre Study.

SEA-ICE CORE CODE	DEPTH (m)	DOC (µM)
AN 8/2 26001	12-24	363
AN 8/2 26001	24-27	872
AN 8/2 26001	27-33	502
AN 8/2 26001	33-43	244
AN 8/2 26001	43-48	138
AN 8/2 26001	48-61	129
AN 8/2 26001	61-66	115
AN 8/2 26001	66-74	93
AN 8/2 26001	74-87	67
AN 8/2 26001	87-100	79
AN 8/2 26001	100-113	45
AN 8/2 26001	113-126	39
AN 8/2 26001	126-139	38
AN 8/2 26003	0-11	229
AN 8/2 26003	11-22	166
AN 8/2 26003	22-27	210
AN 8/2 26003	27-36	345
AN 8/2 26003	36-41	314
AN 8/2 26003	41-50	237
AN 8/2 26003	50-59	148
AN 8/2 26003	59-69	103
AN 8/2 26003	69-78.5	109
AN 8/2 26003	78.5-87.5	95
AN 8/2 26003	87.5-98.5	83
AN 8/2 26003	98.5-108	82
AN 8/2 26003	108-119	104
AN 8/2 26005	0-13	115
AN 8/2 26005	13-18	94
AN 8/2 26005	18-22	153
AN 8/2 26005	22-26	234
AN 8/2 26005	26-33	328
AN 8/2 26005	13-18	274
AN 8/2 26005	18-32	194
AN 8/2 26005	22-26	298
AN 8/2 26005	26-33	344
AN 8/2 26005	33-40	298
AN 8/2 26005	40-50	222
AN 8/2 26005	50-54	116
AN 8/2 26005	54-59	92
AN 8/2 26005	59-62	79
AN 8/2 26005	62-74	92
AN 8/2 26005	74-83	64
AN 8/2 26005	83-92	61
AN 8/2 26005	92-102	65
AN 8/2 26005	102-112	37
AN 8/2 26005	112-124	31
AN 8/2 26101	0-10	83

AN 8/2 26101	10-20	61
AN 8/2 26101	20-27	168
AN 8/2 26101	27-37.5	153
AN 8/2 26101	37.5-46	168
AN 8/2 26101	46-53	155
AN 8/2 26101	53-63	87
AN 8/2 26101	63-75	89
AN 8/2 26101	75-85	127
AN 8/2 26101	85-98	73
AN 8/2 26101	98-111	59
AN 8/2 26101	111-124	47
AN 8/2 26103	0-0.095	241
AN 8/2 26103	0.095-0.21	142
AN 8/2 26103	0.67-0.795	179
AN 8/2 26103	0.795-0.9	89
AN 8/2 26103	0.9-1.02	99
AN 8/2 26103	1.02-1.14	94
AN 8/2 26103	1.14-1.225	99
AN 8/2 26103	0.635-0.67	66
AN 8/2 26103	0.57-0.635	156
AN 8/2 26103	0.21-0.26	268
AN 8/2 26103	0.26-0.33	253
AN 8/2 26103	0.33-0.445	280
AN 8/2 26103	0.445-0.475	307
AN 8/2 26105	0-12.5	64
AN 8/2 26105	12.5-22	55
AN 8/2 26105	27-32	147
AN 8/2 26105	32-38	133
AN 8/2 26105	38-42	134
AN 8/2 26105	50.5-59	81
AN 8/2 26105	59-65	71
AN 8/2 26105	65-68	82
AN 8/2 26105	42-50	
AN 8/2 26105	68-77.5	36
AN 8/2 26105	77.5-87.5	57
AN 8/2 26105	0.875-0.95	78
AN 8/2 26105	0.95-1.04	46
AN 8/2 26105	1.04-1.14	33
AN 8/2 26105	1.14-1.24	45
AN 8/2 26801	0-10	77
AN 8/2 26801	10-20	48
AN 8/2 26801	20-26.5	44
AN 8/2 26801	26.5-31	52
AN 8/2 26801	31-42	54
AN 8/2 26901	0-12	151
AN 8/2 26901	12-24	123
AN 8/2 26901	24-28.5	202
AN 8/2 26901	28.5-34	58
AN 8/2 26901	34-44	135
AN 8/2 26901	44-54	16
AN 8/2 26901	54-58	52
AN 8/2 26901	58-64	70
AN 8/2 27101	0-10	65
AN 8/2 27101	10-23.5	137

AN 8/2 27101	23.5-33.5	97
AN 8/2 27101	33.5-41	101
AN 8/2 27101	41-49	149
AN 8/2 27101	49-56	41
AN 8/2 27111	0-10	160
AN 8/2 27111	10-22	261
AN 8/2 27111	22-34	194
AN 8/2 27111	34-45.5	290
AN 8/2 27111	45.5-57	136
AN 8/2 27111	57-66	101
AN 8/2 27121	0-11	87
AN 8/2 27121	34-45	110
AN 8/2 27121	45-57	89
AN 8/2 27121	57-63	31
AN 8/2 27121	63-67	56
AN 8/2 27121	67-79	50
AN 8/2 27121	79-88	29
AN 8/2 27601	3-12	83
AN 8/2 27601	12-23	34
AN 8/2 27601	23-33	65
AN 8/2 27601	33-43	37
AN 8/2 27601	43-52	68
AN 8/2 27601	52-59	46
AN 8/2 27601	59-64	48
AN 8/2 27701	0-4.5	113
AN 8/2 27701	4.5-7	99
AN 8/2 27701	7-11	55
AN 8/2 27701	11-22	43
AN 8/2 27701	22-33	33
AN 8/2 27701	33-44	190
AN 8/2 27701	44-57	55
AN 8/2 27701	22-27	198
AN 8/2 27801	75.5-84	47
AN 8/2 27801	84-93.5	90
AN 8/2 28601	0-12	75
AN 8/2 28601	12-22.5	56
AN 8/2 28601	22.5-33	42
AN 8/2 28601	33-43	79
AN 8/2 28651	0-7	112
AN 8/2 28651	15-24	111
AN 8/2 28651	24-27	66
AN 8/2 28651	27-38	102
AN 8/2 28651	38-49	43
AN 8/2 28651	49-57	64
AN 8/2 28651	7-15	68
AN 8/2 28661	0.5-9	97
AN 8/2 28661	9-18	66
AN 8/2 28661	18-27	85
AN 8/2 28661	27-35	74
AN 8/2 28661	35-43	129

SEA-ICE CORE CODE	DEPTH (m)	POC (µM)	PON (µM)
AN8/2 26003	0-11	101.6	17.82
AN8/2 26003	11-21	227.1	15.05
AN8/2 26003	22-27	254.9	3.47
AN8/2 26003	27-36	330.4	9.82
AN8/2 26003	36-41	288.5	7.11
AN8/2 26003	41-50	233.6	13.39
AN8/2 26003	50-59	127.4	7.96
AN8/2 26003	59-69	139.5	12.28
AN8/2 26003	69-78	91.5	6.08
AN8/2 26003	78.5-87.5	87.2	1.26
AN8/2 26003	87.5-98.5	48.3	13.95
AN8/2 26003	98.5-108	87.9	9.81
AN8/2 26003	108-119	92.6	6.88
AN8/2 26005	0-13	82.1	18.14
AN8/2 26005	13-22	106.7	-
AN8/2 26005	22-33	163.2	10.02
AN8/2 26005	33-40	236.0	11.84
AN8/2 26005	40-50	168.3	16.01
AN8/2 26005	50-54	115.5	5.00
AN8/2 26005	54-59	128.0	-2.63
AN8/2 26005	59-74	73.6	26.68
AN8/2 26005	74-83	66.5	11.95
AN8/2 26005	83-92	63.	9.89
AN8/2 26005	92-102	30.4	18.83
AN8/2 26005	102-124	73.0	19.55
AN8/2 26101	0-27	109.3	10.47
AN8/2 26101	27-37.5	146.7	8.69
AN8/2 26101	37.5-46	149.0	8.98
AN8/2 26101	46-53	200.8	7.68
AN8/2 26101	53-63	144.0	13.91
AN8/2 26101	63-75	55.8	8.86
AN8/2 26101	75-85	107.3	4.29
AN8/2 26101	85-111	114.3	4.00
AN8/2 26101	111-124	51.1	-
AN8/2 26103	0-9.5	72.8	10.03
AN8/2 26103	9.5-21	226.6	4.81
AN8/2 26103	21-26	140.8	7.17
AN8/2 26103	26-33	173.1	7.73
AN8/2 26103	33-44.5	0.04	-
AN8/2 26103	44.5-47.5	326.8	1.66
AN8/2 26103	47.5-57	78.8	2.85
AN8/2 26103	57-63.5	126.1	9.32
AN8/2 26103	63.5-67	125.4	1.06
AN8/2 26103	67-79.5	134.2	4.70

AN8/2 26103	79.5-90	108.1	-
AN8/2 26103	90-102	44.9	8.71
AN8/2 26103	102-114	52.3	1.60
AN8/2 26103	114-122.5	47.0	-
AN8/2 26105	0-12.5	102.3	6.46
AN8/2 26105	12.5-22	100.5	6.81
AN8/2 26105	22-27	268.0	3.57
AN8/2 26105	27-32	217.4	1.43
AN8/2 26105	32-38	215.0	2.82
AN8/2 26105	38-42	183.9	0.63
AN8/2 26105	42-50	258.2	12.48
AN8/2 26105	50.5-59	131.7	12.34
AN8/2 26105	59-65	138.5	7.45
AN8/2 26105	65-68	200.6	0.10
AN8/2 26105	68-77.5	55.6	5.49
AN8/2 26105	77.5-87.5	71.6	14.58
AN8/2 26105	87.5-95	99.3	3.31
AN8/2 26105	87.5-95	63.9	2.19
AN8/2 26105	1.04-1.14	32.9	3.00
AN8/2 26105	1.14-1.24	35.0	3.32
AN8/2 26901	0-12	120.3	23.55
AN8/2 26901	12-24	107.2	16.39
AN8/2 26901	24-28.5	316.9	6.61
AN8/2 26901	28.5-44	113.2	21.79
AN8/2 26901	44-54	63.9	7.83
AN8/2 26901	54-64	83.3	5.20
AN8/2 27101	0-23.5	84.7	14.71
AN8/2 27101	23.5-33.5	98.4	5.84
AN8/2 27101	33.5-56	56.8	10.42
AN8/2 27111	0-10	106.6	8.00
AN8/2 27111	10-22	76.3	13.69
AN8/2 27111	22-34	55.8	15.58
AN8/2 27111	34-45	88.2	19.90
AN8/2 27111	45.5-57	88.9	11.76
AN8/2 27111	45.5-57	119.7	10.96
AN8/2 27111	57-66	110.7	12.46
AN8/2 27121	0-11	109.9	16.77
AN8/2 27121	35-45	113.5	13.55
AN8/2 27121	45-57	53.5	0.34
AN8/2 27121	57-67	41.5	3.43
AN8/2 27121	67-79	48.2	11.18
AN8/2 27701	0-7	78.1	0.20
AN8/2 27701	7-22	142.9	9.25
AN8/2 27701	22-33	96.5	5.57
AN8/2 27701	33-44	122.6	-2.92
AN8/2 27701	44-57	102.0	5.76

AN8/2 27801	0-9	56.5	12.33
AN8/2 27801	9-14	111.5	-
AN8/2 27801	14-21	23.7	-
AN8/2 27801	21-30.5	36.1	9.53
AN8/2 27801	30.5-36	75.0	-
AN8/2 27801	36-45	47.0	-
AN8/2 27801	45-54	38.3	0.97
AN8/2 27801	54-62.5	53.9	14.39
AN8/2 27801	62.5-75.5	61.3	-
AN8/2 27801	75.5-84	49.5	0.59
AN8/2 27801	84-93.5	53.7	12.92
AN8/2 28651	0-7	222.4	10.44
AN8/2 28651	7-15	115.3	12.52
AN8/2 28651	15-27	128.7	17.42
AN8/2 28651	27-38	87.9	14.45
AN8/2 28651	38-49	51.5	12.50
AN8/2 28651	49-57	72.5	12.35

APPENDIX 4. INTERICE II DOM AND INORGANIC NUTRIENTS

Chapter 5. Silicate, phosphate, nitrate, glucose, glycine, DOC and bacterial abundance data from the INTERICE II experiment.

Experiment 1

ENC.	DATE	Sample	POSITION	DEPTH (cm)	Si (µM)	PO_4^{3-}(µM)	NO_3^- (µM)	DOC (µM)	GLUCOSE (µM)	GLYCINE (µM)	BACTERIA (cells l^{-1})
1	9.11.98	Water	Surface			1.91	26.60				6.E+06
1	10.11.98	Water	Surface	>3	227.90	1.92	26.98	184			
1	11.11.98	Water	Surface	>5.5	228.40	1.83	28.02	221			1.E+08
1	12.11.98	Water	Surface	>6.5	233.40	2.05	27.43	172			5.E+06
1	13.11.98	Water	Surface	>9.5		1.91	24.88	194			
1	14.11.98	Water	Surface	>11.6	401.84	1.99	28.33	278			5.E+06
1	9.11.98	Water	Bottom	90		1.75	25.92	180			1.E+06
1	10.11.98	Water	Bottom	90	196.70	1.86	27.71				0.E+00
1	11.11.98	Water	Bottom	90	355.48	1.61		250			
1	12.11.98	Water	Bottom	90	245.80	1.91	27.67	168			4.E+06
1	13.11.98	Water	Bottom	90	221.44	1.95		176			
1	14.11.98	Water	Bottom	90	400.49	1.76	27.71	263			0.E+00
1	14.11.98	Brine		0-5	374.05	3.71	60.96	579			1.E+06
1	14.11.98	Brine		5-10	255.15	2.55	37.20	313			4.E+06
1	14.11.98	Ice		0-5	20.45	0.23	4.80	51			5.E+06
1	14.11.98	Ice		5-10	22.81	0.19	4.88	39			3.E+06
2	9.11.98	Water	Surface			0.99	24.57		272.44		3.E+06
2	10.11.98	Water	Surface	>3	198.10	1.13	26.71		308.64		
2	11.11.98	Water	surface	>5.5	356.10	1.12	28.19		175.25		
2	12.11.98	Water	Surface	>6.5	205.80	1.05	26.29		164.47		1.E+06
2	13.11.98	Water	Surface	>9.5		1.16	27.62		169.43		
2	14.11.98	Water	Surface	>11.6	385.31	1.17	28.37		185.96		

2	9.11.98	Water	Middle	50		1.00						
2	10.11.98	Water	Middle	50	258.00		26.93					
2	11.11.98	Water	Middle	50	351.45	1.37	26.87		181.91			
2	12.11.98	Water	Middle	50	222.70	1.14	27.34		345.85			
2	13.11.98	Water	Middle	50	223.45	1.13	22.16		160.00			
2	14.11.98	Water	Middle	50	397.17	1.16	28.36		175.03			1.E+06
2	9.11.98	Water	Bottom	90	208.92	1.05	25.98					
2	10.11.98	Water	Bottom	90	222.90	1.16	26.96					
2	11.11.98	Water	Bottom	90	362.62	0.85	27.42					
2	12.11.98	Water	Bottom	90	251.30	1.12	27.62		175.67			
2	13.11.98	Water	Bottom	90	204.65	1.15	27.68		160.71			
2	14.11.98	Water	Bottom	90	398.98	1.15	28.37		177.30			
2	14.11.98	Brine		0-5	468.58	2.29	54.64		468.72			4.E+06
2	14.11.98	Brine		5-10	282.80	1.51	34.12		344.82			
2	14.11.98	Ice		0-5	22.93	0.09	2.84		25.64			2.E+06
2	14.11.98	Ice		5-10	24.17	0.09	2.30		19.45			2.E+06
3	9.11.98	Water	surface		351.27	1.03				1.42		1.E+06
3	10.11.98	Water	surface	>5.5	224.55	1.11	26.42			2.27		2.E+06
3	11.11.98	Water	surface	>6.5	367.59	0.76	28.02			2.29		
3	14.11.98	Water	surface	>11.6	394.29	1.14				2.44		6.E+05
3	11.11.98	Water	middle	50	302.06	1.05	27.17			2.79		1.E+06
3	14.11.98	Water	middle	50	394.60	1.13				2.32		0.E+00
3	9.11.98	Water	bottom	90	355.08	1.07	26.00					2.E+06
3	10.11.98	Water	bottom	90		1.08	26.56			2.27		3.E+06
3	11.11.98	Water	bottom	90	300.48	1.03	27.16			2.64		2.E+06
3	14.11.98	Water	bottom	90	384.60	1.17	28.24			2.68		
3	14.11.98	Brine		0-5	268.74	1.79	38.92			7.20		2.E+06
3	14.11.98	Brine		5-10	472.52	2.43	61.40			8.31		2.E+06
3	14.11.98	Ice		0-5	23.16	0.18	2.58			0.53		0.E+00
3	14.11.98	Ice		5-10	16.54	0.10	2.68			0.87		9.E+06
4	9.11.98	Water	surface		350.23	1.85	25.96	448	275.69			
4	10.11.98	Water	surface	>3	318.96	1.84	26.72	436	281.50			

4	11.11.98	Water	surface	>5.5		2.05	27.11	345	295.46		
4	12.11.98	Water	surface	>6.5	313.21	2.09	29.42	504	304.28		
4	13.11.98	Water	surface	>9.5					301.43		
4	14.11.98	Water	surface	>11.6							
4	9.11.98	Water	middle	50	363.23	1.86	26.05	403	290.06		6.E+06
4	10.11.98	Water	middle	50		1.85	26.36	416	300.42		6.E+06
4	11.11.98	Water	middle	50		1.88	26.94	414			
4	12.11.98	Water	middle	50		1.85	27.42	434	304.82		
4	13.11.98	Water	middle	50		2.11	27.45	538			6.E+06
4	14.11.98	Water	surface	50	327.69	2.02	28.65	552	305.06		2.E+06
4	9.11.98	Water	bottom	90							4.E+06
4	10.11.98	Water	bottom	90	320.12	1.87	26.25		302.20		
4	11.11.98	Water	bottom	90		1.87	26.94	401	280.00		6.E+06
4	12.11.98	Water	bottom	90	213.16	1.82	26.76		298.75		6.E+06
4	13.11.98	Water	bottom	90		2.02	26.90	398	297.86		
4	14.11.98	Water	bottom	90	324.33	2.00	28.71	355	303.94		2.E+06
4	14.11.98	Brine		0-5	511.77	3.98	72.15	923	584.02		3.E+06
4	14.11.98	Brine		5-10	290.54	2.50	39.49	863	461.61		4.E+06
4	14.11.98	Ice		0-5	25.11	0.18	3.70	38	31.08		1.E+06
4	14.11.98	Ice		5-10	34.09	0.17	4.10	33	27.27		
5	9.11.98	Water	surface		364.46	2.13	26.30			1.91	5.E+06
5	10.11.98	Water	surface	>3	303.26	1.96	25.95	320		2.64	9.E+06
5	11.11.98	Water	surface	>5.5	312.27	2.04	27.07	383		2.33	7.E+06
5	12.11.98	Water	surface	>6.5	326.63	2.02	27.18	259			
5	13.11.98	Water	surface	>9.5		2.73	32.73			3.92	3.E+06
5	14.11.98	Water	surface	>11.6	333.16	2.25	29.71	215			6.E+06
5	9.11.98	Water	middle	50	363.48	2.03	26.36			2.34	
5	10.11.98	Water	middle	50	330.76	1.95	26.39	153		2.81	6.E+06
5	11.11.98	Water	middle	50	285.46	2.04	26.50	156			8.E+06
5	12.11.98	Water	middle	50	314.35	2.05	27.65	230		3.85	
5	13.11.98	Water	middle	50		2.21	27.15			3.85	
5	14.11.98	Water	middle	50	329.30	2.11	28.39	189		2.26	

5	9.11.98	Water	bottom	90				182	1.99	2.E+06
5	10.11.98	Water	bottom	90	319.57	1.99	26.18		2.59	7.E+06
5	11.11.98	Water	bottom	90	306.08	1.94	27.25	157	2.48	3.E+06
5	12.11.98	Water	bottom	90	307.07	2.01	27.39	145	3.16	
5	13.11.98	Water	bottom	90		1.84		156	2.85	
5	14.11.98	Water	bottom	90	322.64	2.15	28.64	153	2.44	
5	14.11.98	Brine		0-5	503.23		50.34	1159	4.80	
5	14.11.98	Brine		5-10	364.57	2.73	35.99	722	3.52	
5	14.11.98	Ice		0-5	29.29	0.16	3.04		0.47	
5	14.11.98	Ice		5-10	40.77	0.23	4.04	12	1.20	

Experiment 2

ENC.	DATE	Sample	POSITION	DEPTH (cm)	Si (µM)	PO_4^{3-}(µM)	NO_3^- (µM)	DOC (µM)	GLUCOSE (µM)	GLYCINE (µM)	BACTERIA cells l^{-1}
1	18.11.98	Water	Surface	>3.5	280.40	2.01	37.92	184			2.02E+06
1	20.11.98	Water	Surface	>11.1	346.34	2.055	34.945	235			*
1	24.11.98	Water	Surface	>20.2	399.30	2.205	39.335	201			1.49E+06
1	27.11.98	Water	Surface	> 23	431.41	2.34	39.385	177			1.45E+06
1	20.11.98	Water	Bottom	90	350.16	2.045	35.055	222			6.20E+05
1	23.11.98	Water	Bottom	90	296.98	2.31	36.335	228			7.02E+05
1	24.11.98	Water	Bottom	90	431.00	2.265	39.08	193			1.64E+06
1	27.11.98	Water	Bottom	90	415.18	2.28	39.74	306			6.61E+05
1	30.11.98	Ice		0-5	35.66	0.17	5.18	79			7.70E+06
1	30.11.98	Ice		5-10	35.31	0.135	6.09	88			6.20E+06
1	30.11.98	Ice		10-15	24.37	0.075	3.945	64			6.64E+06
1	30.11.98	Ice		15-20	16.28	0.07	4.305	106			9.21E+06
1	30.11.98	Ice		20-25	13.42	0.045	1.75	28			7.18E+06
1	30.11.98	Brine		0-10	683.94	3.75	90.19	1531			4.72E+06
1	30.11.98	Brine		10-15	673.41	3.08	100.95	1478			5.06E+07
1	30.11.98	Brine		15-20	576.93	2.91	75.285	1149			7.26E+07
1	30.11.98	Brine		20-25	464.84	2.86	68.78	716			7.03E+07
2	17.11.98	Water	Surface		292.78	0.88	31.365				
2	18.11.98	Water	Surface	>3.5	431.00		31.985		360.3		1.20E+06
2	20.11.98	Water	surface	>11.1	359.62	0.845	24.665		331.0		
2	23.11.98	Water	surface	>17.5	297.99	0.9	35.945		372.2		2.00E+06
2	25.11.98	Water	surface	>20.2	431.00	1.39	52.225		356.8		
2	26.11.98	Water	surface	>22.2	337.81	0.615	38.215		432.8		8.97E+05
2	18.11.98	Water	Middle	50	332.30	1.01	37.05		356.3		
2	20.11.98	Water	Middle	50	338.59	0.89	35.055		338.2		2.43E+06
2	23.11.98	Water	Middle	50	224.25	0.88	35.945		359.1		
2	25.11.98	Water	Middle	50	431.00	0.795	36.18				
2	26.11.98	Water	Middle	50	344.56	1.77	29.965		441.0		

2	18.11.98	Water	Bottom	90	384.50	0.92	32.145	329.4		
2	20.11.98	Water	Bottom	90	342.56	0.905	35.2	358.4		
2	23.11.98	Water	Bottom	90	327.19		36.42	361.3		
2	25.11.98	Water	Bottom	90	431.00	0.63	39.48	356.1		
2	26.1198	Water	Bottom	90	344.56	0.525	40.62	443.4		2.21E+06
2	26.11.98	Ice		0-5	30.34	0.01	4.73	32.9		2.50E+06
2	26.11.98	Ice		5-10	29.76	0.01	3.84	14.9		1.39E+06
2	26.11.98	Ice		10-15	22.13	0.01	2.83	5.1		1.12E+06
2	26.11.98	Ice		15-20	22.79	0	4.56	32.6		1.40E+06
2	26.11.98	Brine		0-10	680.26		92.16	558.7		1.10E+06
2	26.11.98	Brine		10-15				423.5		7.02E+05
2	26.11.98	Brine		15-20	365.20		45.68	458.9		6.82E+05
3	17.11.98	Water	Surface		282.23	0.82	32.81			
3	18.11.98	Water	Surface	>3.5	299.04	0.86	33.72		2.37	1.28E+06
3	20.11.98	Water	Surface	>11.1		0.86	34.78			
3	23.11.98	Water	Surface	>17.5	418.94	0.89	39.69		2.67	2.00E+06
3	26.11.98	Water	Surface	>22.2	315.72	0.82				
3	18.11.98	Water	Middle	50	293.19	0.84	33.4		2.3	2.00E+06
3	20.11.98	Water	Middle	50		0.87	34.85			2.43E+06
3	23.11.98	Water	Middle	50	409.44	0.85	38.65		2.81	
3	26.11.98	Water	Middle	50	347.68	0.73			2.81	2.43E+06
3	18.11.98	Water	Bottom	90	304.39	0.85	33.28		2.41	2.51E+06
3	20.11.987	Water	Bottom	90		0.87	34.42			
3	23.11.98	Water	Bottom	90	413.09	0.8	29.49		2.75	
3	25.11.98	Water	Bottom	90	396.90	0.8	39.62		2.77	
3	26.11.98	Ice		0-10	34.49	0.04	4.02		0.35	2.23E+06
3	26.11.98	Ice		10-15	28.44	0.01	3.72		0.16	1.80E+06
3	26.11.98	Ice		15-20	21.38	0.01	3.01		0.09	1.28E+05
3	26.11.98	Ice		20-25	17.50	0.03	2.99		0.31	2.13E+06
3	26.11.98	Brine		0-10	725.93		87.31		13.84	2.70E+06
3	26.11.98	Brine		10-15	568.60		74.38		6.5	2.51E+06
3	26.11.98	Brine		15-20	360.76		52.53		5.11	2.21E+06

4	17.11.98	Water	Surface		315.88	1.88	32.68				1.23E+06
4	20.11.98	Water	Surface	>11.1	312.06	2.035	34.985	564	494.4		
4	23.11.98	Water	Surface	>17.5	297.50	2.115	39.455	661	650.5		1.12E+06
4	25.11.98	Water	Surface	>20.2	347.35	1.81	37.015	609	612.4		4.10E+06
4	20.11.98	Water	Middle	50	310.85	2.045	35.095	610	490.0		1.23E+06
4	20.11.98	Water	Bottom	90	314.12	1.995	32.585	562	465.6		
4	23.11.98	Water	Bottom	90	306.40	1.99	36.38	602	468.9		1.48E+06
4	27.11.98	Ice		0-5	36.31	0.125	7.42	54	3.3		
4	27.11.98	Ice		5-10	28.15	0.055	4.61	41	10.9		5.53E+05
4	27.11.98	Ice		10-15	21.59	0.04	4.42	65	10.5		
4	27.11.98	Ice		15-20	26.76	0.04	3.19	19	8.7		
4	27.11.98	Brine		0-10	712.84		107.73	967	987.9		1.14E+07
4	27.11.98	Brine		10-15	538.89	1.88	85.81	720	704.8		1.24E+07
4	27.11.98	Brine		15-20	354.29	1.63	55.085	427	529.3		1.83E+07
5	17.11.98	Water	Surface		276.47	2.08	31.92				4.68E+05
5	20.11.98	Water	Surface	>11.1	326.56	2.345	34.9	175			
5	27.11.98	Water	Surface	>23	388.59	2.405	37.12	286		3.51	
5	30.11.98	Water	Surface	>27.2	468.00	2.54	37.435	199			
5	1.12.98	Water	Surface	>32.8	441.26	2.535		251		3.12	
5	18.11.98	Water	middle	50	331.34	2.235	31.945			3.78	
5	20.11.98	Water	middle	50	351.32	2.22	34.36	186			0.00E+00
5	23.11.98	Water	middle	50	376.00	2.46	37.255	293		3.24	
5	27.11.98	Water	middle	50	387.60	2.47	37.61	304		2.98	
5	18.11.98	Water	bottom	90				252			0.00E+00
5	20.11.98	Water	bottom	90	351.91	2.25	34.38	173			
5	30.11.98	Water	bottom	90	472.00	2.4		299		2.61	
5	1.12.98	Water	bottom	90	441.26	2.705	42.665	325			
5	1.12.98	Ice		0-5	31.36	0.195	5.263	79		0.87	5.45E+06
5	1.12.98	Ice		5-10	35.46	0.12	4.84	74		0.74	9.66E+06
5	1.12.98	Ice		10-15	27.77	0.115	3.64	73		0.62	1.06E+07
5	1.12.98	Ice		15-20	19.19	0.0625	3.103	98		0.33	5.43E+06
5	1.12.98	Ice		20-25	17.36	0.07	2.9	66		0.39	3.76E+07

5	1.12.98	Ice	25-30				85	0.53	9.79E+06
5	1.12.98	Brine	0-5	521.87	2.54	77.96	2106	11.89	1.29E+07
5	1.12.98	Brine	5-10	491.60	2.17	67.43	1623	8.69	1.34E+07
5	1.12.98	Brine	10-15	528.81	2	61.35	1692	4.34	1.24E+07
5	1.12.98	Brine	15-20	683.95	2.96		1108	3.22	7.02E+06
5	1.12.98	Brine	20-25	680.00	2.72	38.41	1558	2.45	8.89E+06