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Concentration, Molecular Weight Distribution and Neutral Sugar Composition of DOC in Maritime Antarctic Lakes of Differing Trophic Status

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Abstract. The molecular weight distributions and hydrolysable neutral sugar composition of dissolved organic carbon (DOC) was investigated in four maritime Antarctic lakes on Signy Island of different trophic status; Heywood Lake (eutrophic), Light Lake (oligo-mesotrophic), Sombre Lake and Moss Lake (both oligotrophic). Tangential flow ultra-filtration (TFU) was used to separate DOC into high molecular weight (HMW; >1000 Da) and low molecular weight (LMW; <1000 Da) size fractions. Pulsed amperometric detection-high performance liquid chromatography (PAD-HPLC) was used to determine the hydrolysable neutral sugar molecular composition of each size fraction. Total DOC concentrations defined the trophic trend in the four lakes and ranged from 8 to 303 μM. The <1000 Da fraction of all the lakes dominated the DOC distribution, comprising 76% in Light Lake which also had the highest chl-*a* concentrations. Heywood Lake was relatively enriched in >1000 Da total organic carbon and had extremely high concentrations of total hydrolysable neutral sugars (11 μM) corresponding to 43% of total DOC. However, no clear pattern was apparent with regard to lake trophic status and potential sources of DOC, and the measured variations in individual aldose concentration, composition and their various molecular weight fractions.

Key words: dissolved neutral sugar, carbohydrates, dissolved organic carbon, Signy Island, eutrophic, mesotrophic, oligotrophic, lakes

1. Introduction

As in other aquatic environments, variations in the molecular weight of dissolved organic carbon (DOC) in maritime Antarctic lakes are likely to be a function of dissolved organic matter (DOM) source and microbiological transformations (Allen, 1976; Goldman et al., 1987; Tranvik, 1990; Tulonen et al., 1992; Skoog and Benner, 1997). Carbohydrates have been identified as

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[★] Author for correspondence. E-mail: p.convey@bas.ac.uk one of the largest chemically recognisable components of DOM, estimated to make up from <1 to about 30% of the total DOC pool in freshwaters (Satoh et al., 1987; Münster, 1993); this range is likely to be artificially wide, and partly accounted for by the analytical methods employed to measure carbohydrate composition, which vary among studies and address different pools (Pakulski and Benner, 1994; Skoog and Benner, 1997).

Questions remain on the metabolism of DOM by bacterioplankton, which are responsible for funnelling carbon from the microbial food web to higher organisms (Azam et al., 1983). Traditionally, small, simple molecules (<1000 Da) have been considered to be the most available to microorganisms (Saunders, 1976). In contrast, the size-reactivity continuum hypothesis supports the view that oceanic high molecular weight material (>1000 Da) can be very bioreactive and may support even more bacterial production than the <1000 Da fraction (Amon and Benner, 1996). In humic lacustrine environments the highest bacterial growth efficiencies have been measured in high molecular weight DOM fractions relative to those obtained with <1000 Da fractions (Tranvik, 1990; Tulonen et al., 1992). Conversely, enrichment experiments on blackwater rivers have consistently indicated that low molecular weight DOC was most available to bacteria compared with intermediate and high molecular weight material (Münster, 1985; Meyer et al., 1987). While the <1000 Da size fraction dominates the molecular weight distribution of DOM in marine environments (Benner et al., 1997), in other aquatic environments larger, >1000 Da, material is as, if not more, prevalent (Benner, 2003).

The maritime Antarctic lakes on Signy Island offer limnic environments where catchment vegetation is sparse and limited to mosses and lichens (Heywood et al., 1980). A highly seasonal light regime and low temperatures at high latitudes result in lake food chains that are truncated and dominated by microbes. However, a range of trophic status is represented by several lakes on the island, through enrichment by sea mammals and birds. We consider these lakes significant in that they provide molecular weight distributions and characteristics of DOC typical of microbially dominated freshwater systems, allowing comparisons to be made with information known about DOC in humic lakes and in other aquatic environments.

While data on the concentration and molecular composition of carbohydrates in seawater are available (Rich et al., 1996; Borch and Kirchman, 1997; Skoog and Benner, 1997), few comparable investigations have been carried out in freshwater lake environments (Wicks et al., 1991; Tranvik and Jørgensen, 1995) and no such studies have been conducted on Antarctic lakes. Molecular level data of the carbohydrate composition of the <1000 Da size fraction are rarely available.

The development of tangential flow ultra-filtration (TFU) allows a relatively rapid method for the separation and concentration of different size fractions of DOM (Benner et al., 1997). TFU was used in this study because of its ability to concentrate as well as separate different size fractions of DOM without chemical modification of the sample. Generally, Antarctic lakes are oligotrophic and depauperate in DOC. The concentration factor obtained during filtration with this technique allowed trace levels of neutral sugar compositions of dissolved polysaccharides to be measured accurately.

In this paper we present the first detailed study of the molecular weight distribution of DOM in Antarctic lakes exhibiting a range of trophic status, and describe the molecular composition of hydrolysable neutral sugars as a proportion of total DOC concentrations in a >1000 Da fraction and <1000 Da fraction. A further focus of the study is to link variations in the molecular size distribution and carbohydrate yield of the DOC fractions to both autochthonous and allochthonous characteristics of the lakes, including chemical and physical variables, bacterial numbers and productivity, trophic status, catchment vegetation and the presence of seal and bird populations that may cause lake enrichment.

2. Description of the Lakes

The four contrasting lakes chosen for this study, Heywood Lake, Sombre Lake, Light Lake and Moss Lake are situated on Signy Island, (60°43′ S, 45°38′ W), South Orkney Islands (Figure 1). Physical and chemical characteristics of these lakes, and influences on their organic geochemistry, are given in Table I. These lakes were initially described by Heywood (1967), and subsequently have been the subject of further description and a range of biological studies including those of Light et al. (1981), Hawes (1990), Ellis-Evans (1990) and Butler (1999a, b).

3. Materials and Methods

3.1. SAMPLING

Studies were carried out on Signy Island during the austral summer of 1996/1997, with samples being collected during the lake open water period in January and February 1997. Samples of c.10–12 L of water were collected from an inflatable dinghy over the deepest point of each lake from a depth of 3–4 m. A Cole Parmer Masterflex® 12 V DC powered drive pump fitted with a pump head (Model No. 7016-19, and Masterflex silicone tubing (Model No. 96410-15; all supplied by Cole Parmer, USA) were used. Teflon tubing was used to connect in-line filters, which were supported by teflon filter holders. Supor® membrane filters (0.8 μM and 0.2 μM) were used sequentially for initial water filtration. The in-line filter arrangement allowed the

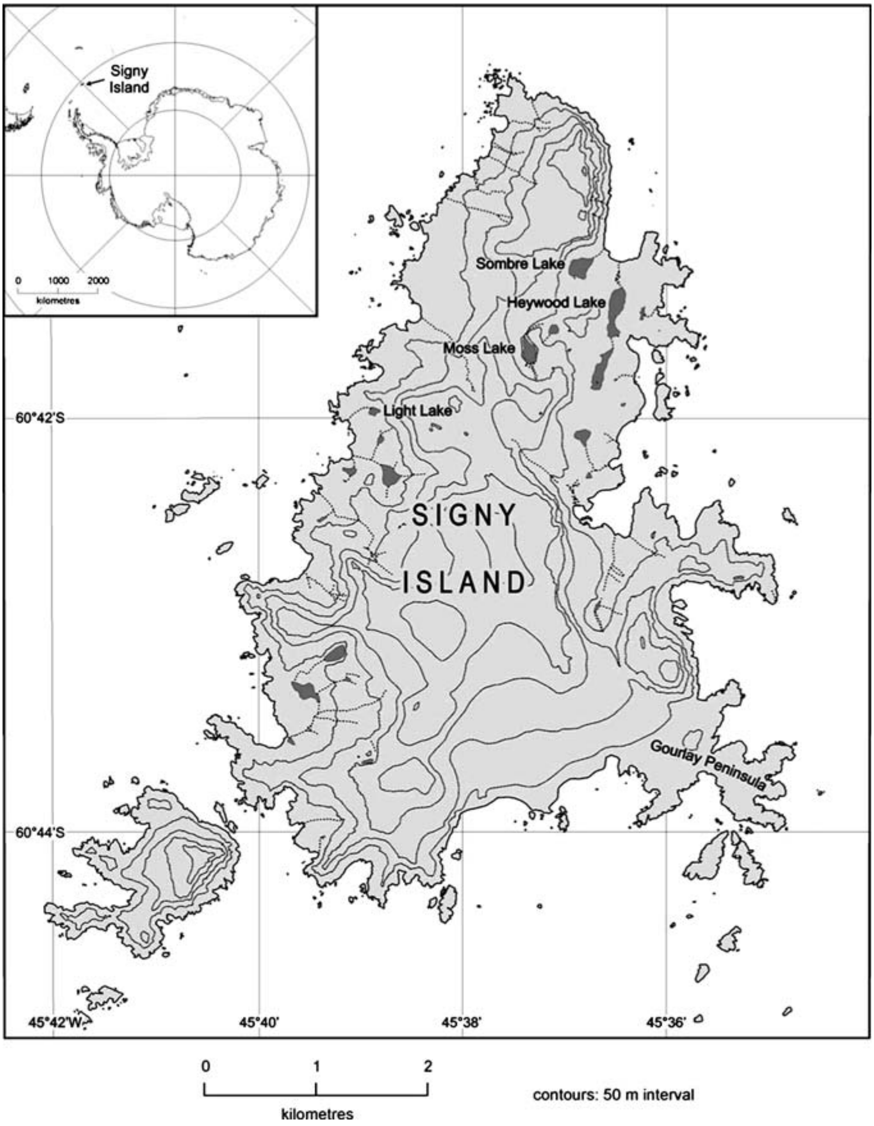

Figure 1. Map of Signy Island showing the locations of the four study lakes. The regional location of Signy Island is shown in inset.

removal of particulate matter during sampling, preventing the formation of dissolved artefacts that may occur in the period immediately after collection.

The samples were collected in high density polyethylene carboys which had been soaked overnight and rinsed six times with 20% hydrochloric acid and deionised water (Millipore 'Purite M50' system). To remove any residues, several litres of water were pumped from the lake through the tubing before a sample was collected and the acid-washed sample containers were

Table I. Summary of physical and chemical features of the four study lakes on Signy Island, drawing on data from the Signy Island lakes monitoring programme and Ellis-Evans (1991)

	Heywood lake	Sombre lake	Light lake	Moss lake
Area (ha)	4.22	2.43	0.49	1.32
Mean depth (m)	2.0	5.0	1.7	3.4
Max depth (m)	6.0	11.4	4.4	10.2
Volume (m^3)	96,200	132,600	9090	52,440
Open days/annum	99	88	60	56
Max temp (°C)	5.3	4.5	3.7	nd
Catchment area (ha)	53.7	86.6	0.6	22.01
Dates sampled	24/01/97–27/01/97	1/02/97–10/02/97	20/01/97	18/02/97–19/02/97
Total DOC (μM)	248	86	184	81
HMW DOC (μM)	172	46	71	42
LMW DOC (μM)	94	49	141	29
Chl-*a* ($mg\ m^{-3}$)	16.3	6.5	16.9	1.4
NH_4–N (μM)	16.7	2.1	4.8	0.4
PO_4–P (μM)	2	0.4	0.4	0.1
Bacterial numbers ($\times 10^9\ L^{-1}$)	10	2–3	nd	0.1–0.2
Bacteria productivity ($\mu g\ C\ L^{-1}\ h^{-1}$)	0.25–1.0	0.15–1.06	nd	0.42
Biomass ($\mu g\ C\ L^{-1}$)	10	4.2–75.7	nd	
Organic geochemical influence	Heavy fur seal impact Prasiola crispa extensive in catchment	Some fur seal impact Lichen and mosses in catchment Bottom water column anoxia in winter	Small giant petrel colony in catchment Strong phytoplankton development Benthic filamentous algae and cyanobacterial mats	Extensive benthic moss, cyanophytes and algae Minimal phytoplankton development

rinsed three times with lake water before they were filled. The samples were returned to the laboratory at the British Antarctic Survey's Signy research Station within two hours of completion of collection, where fractionation of DOM into four separate size fractions by TFU commenced immediately.

A 125 mL water sample for total DOC analysis was collected separately. The DOC sample bottle was rigorously rinsed with lake water and, upon return to the laboratory, the sample was immediately stored at −20 °C.

3.2. INORGANIC NUTRIENTS AND DOC ANALYSIS

Data for mean concentrations of NH_4–N, PO_4–P and chlorophyll-*a* (chl-*a*) were obtained from the BAS lake-monitoring programme that, between 1973 and 1996, monitored a number of chemical and physical variables of the 16 lakes on Signy Island year round. After 1996, the research station on Signy Island has been operated only during the austral summer and sampling was, therefore, carried out each year during November and February. Nutrient analyses followed the methods of Mackereth et al. (1989). For measurements of chl-*a* concentrations, 1 L aliquots of water were filtered onto Whatman GF/C filters, which were then extracted with cold 95% methanol for 24 h. Chl-*a* was measured spectrophotometrically (Cecil Instruments), correcting for turbidity by taking readings at 665 and 750 nm. The equations provided by Marker et al. (1980a, b) were used to calculate chl-*a* concentrations. DOC was measured using a Shimadzu TOC-5000A Total Organic Carbon Analyser equipped with a platinised quartz catalyst.

3.3. SAMPLE PREPARATION

In the laboratory, DOM in each 10 L water sample, was separated using a Millipore Minitan II TFU unit (Millipore, USA) into four different nominal molecular weight limit (NMWL) size fractions >300,000 NMWL (UF1), < 300,000– > 30,000 NMWL (UF2), <30,000– >1000 NMWL (UF3), and < 1000 NMWL (UF4). TFU works by continuously pumping water from a sample reservoir across a membrane of defined pore size and back to the sample reservoir (Buffle et al., 1992). TFU was carried out in concentration mode whereby, material larger than NMWL of the membrane is in the sample reservoir forming the retentate. Material smaller than the NMWL of the membrane passes through to form the permeate. The separation of DOM into the four size classes was achieved by processing the sample sequentially through polysulphone membranes of firstly 300,000 NMWL followed by a 30,000 NMWL membrane followed by a 1000 NMWL membrane. Four membrane cassettes were used for the larger NMWL separations within the acrylic housing giving a total surface area of 0.240 m^2 and eight membranes were used for the 1000 NMWL separations giving a total surface area of 0.384 m^2. During the TFU procedure the UF1, UF2 and UF3 fractions (retentates) were concentrated between 10 and 20 times to a volume of 0.5–1 L each and stored at −20 °C in acid washed HDPE bottles prior to analysis (Benner, 1991). The total volume of permeate from the final filtration step (UF4) was collected and 2 L were kept frozen (−20 °C) for analysis. The standard operating conditions for the 300,000 NMWL membrane and the 30,000 NMWL membranes consisted of an inlet pressure of 10 psi and an output pressure of 8 psi. The 1000 NMWL membranes were run with a inlet pressure of 20 psi and a outlet pressure of 18 psi. TFU of a 10 L sample to 1 L using the 300,000 NMWL and 30,000 NMWL membranes took approximately 30 min for each fractionation. TFU of the 30,000 NMWL membrane permeate, approximately 8–1 L took about 10 h.

It was found that most of the differences in molecular weight distribution of DOC, neutral sugar yields (as % DOC) and compositions between size classes of dissolved organic matter (DOM) occurred between high molecular weight (HMW) DOM and low molecular weight (LMW) DOM. Therefore, the UF1, UF2 and UF3 fractions were grouped together as a weighted average and presented as high HMW DOM. The UF4 fraction was presented as LMW DOM. This put the data in a context most commonly used to discuss size classes of DOM (e.g. Benner, 2003).

3.4. HYDROLYSIS, SEPARATION AND DETECTION OF DISSOLVED NEUTRAL SUGARS

The sample work-up procedure included a combination of steps used by previous workers (Wicks et al., 1991; Skoog and Benner, 1997). Samples were dried in a Savante SpeedVac® fitted with a VaporNet® controller. The dried samples were reconstituted in 1 M HCl and hydrolysed (3 h, 100 °C). The hydrolysate was allowed to cool, diluted and deoxyribose (Sigma) was added as an internal standard. The acid hydrolysate was brought to a pH of 5.5–6.0 with $CaCO_3$ (Skoog and Benner, 1997). After sonicating, rinsing and centrifuging the $CaCO_3$ residue several times, the rinsings were filtered and dried in the Savant Evaporator. The residue was resuspended in water and desalted with Bond-Elut cation and anion exchange columns (100 mg). External composite standards and a Milli-Q water blank were run in a batch with four samples to quantify losses during hydrolysis. Final quantification of individual sugars was calculated using the external standard recovery data and the internal standard. Neutral sugars (fucose, rhamnose, arabinose, galactose, glucose, xylose, mannose and ribose) were separated with an isocratic 18 mM NaOH elution (1 mL min^{-1}) using an anion exchange column (Carbopac PA-1, Dionex) fitted with a Carbopac PA guard column. The columns were mounted in a high performance liquid chromatography

(HPLC) system (Kontron). The detection system used was an Antec Decade Electrochemical Detector operated in a pulse mode fitted with a gold working electrode and an Ag/AgCl reference electrode. The data were acquired, integrated and manipulated using KromaSystem 2000 software.

Samples and standards were injected using the partial-fill sample loop method (Wicks et al., 1991). Four standard sugar solutions in the range 2.7–27 μM were injected at the beginning and end of each batch of samples (mean CV of peak area, 10.5, $n = 16$). Xylose and mannose co-eluted and since the response factor for these two sugars were equal when injected separately, both were determined together using one peak.

4. Results

4.1. CHL-A AND INORGANIC NUTRIENTS

Mean chl-*a* concentrations across the four lakes ranged from 2 to 17 mg m^{-3} (Table I) with Light Lake and Heywood Lake having similar mean chl-*a* concentrations followed by Sombre Lake and Moss Lake having the lowest values. Mean NH_4–N values decreased in the order Heywood > Light > Moss ~ Sombre. Mean NH_4–N was approximately 1–3 μM in Moss Lake and Sombre Lake, 5 μM in Light Lake and 17 μM in Heywood Lake. PO_4–P concentrations in the three clear water lakes (Sombre, Light and Moss) were <0.5 μM while those in Heywood Lake reached mean concentrations of >2 μM.

4.2. MOLECULAR WEIGHT DISTRIBUTION OF DOC

Total DOC concentrations define a clear metabolic trend in the four lakes and range from 81 to 303 μM. Heywood Lake contained the greatest concentrations of DOC in both fractions compared with the other lakes, with the exception of the LMW fraction of Light Lake (Table I). This fraction comprised 39–76% of total DOC, with Light Lake containing the highest proportion and Heywood Lake the lowest (Figure 2). The distribution of DOC concentration across the two fractions presented as absolute concentration (Table I) or as a % of DOC (Figure 2) showed no apparent relationship with trophic status.

4.3. ABUNDANCE AND HYDROLYSABLE NEUTRAL SUGAR YIELD

Total concentration of hydrolysable neutral sugars in Heywood Lake was 11 μM, approximately one order of magnitude greater than those measured in the other three lakes (1014–1427 nM). Total hydrolysable neutral sugar-C across all the lakes accounted for 7–65% of total DOC in the order Heywood

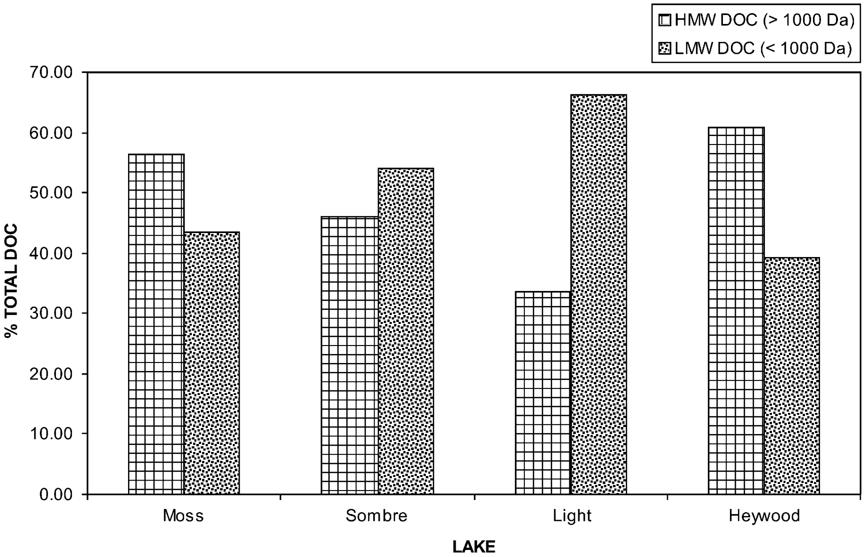

Figure 2. Molecular weight distribution of DOC between HMW and LMW DOC in the four study lakes. Data are mean values of the two samples taken from each of Heywood, Sombre, and Moss Lakes normalised to the total amount of DOC measured. Only one sample was taken from Light Lake.

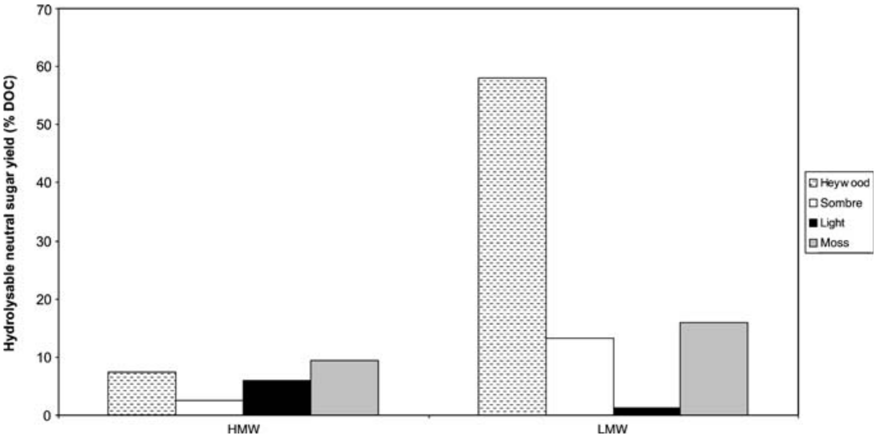

Figure 3. Carbon normalised hydrolysable neutral sugar yields in HMW and LMW DOM in the four study lakes.

Lake > Moss Lake > Sombre Lake > Light Lake. Heywood Lake had 3–9 times as much DOC accounted for by hydrolysable neutral sugars than the other lakes (Figure 3). In Heywood, Sombre and Moss Lakes the LMW DOM fraction was enriched in hydrolysable neutral sugars compared with the HMW DOM and vice versa in Light Lake.

The LMW DOM fractions for each lake were analysed for both dissolved free neutral sugars and hydrolysable neutral sugars. However, although dissolved free neutral sugars were present and glucose, galactose and fructose were tentatively identified using HPLC, the dissolved free components were not quantified due to being close to the detection limits of the method (20 nM).

4.4. MOLECULAR COMPOSITION OF HYDROLYSABLE NEUTRAL SUGARS

Concentrations of individual sugars (fucose, rhamnose, arabinose, galactose, glucose and xylose/mannose) in the four lakes ranged from 22 nM (fucose) in Sombre Lake to >6000 nM (glucose) in Heywood Lake. The relative contributions of the various individual sugars to total DOM and the LMW fractions tended to be dominated by glucose followed by rhamnose > galactose ≥ arabinose ≥ xylose/mannose > fucose in Heywood, Sombre and Moss Lakes (Figure 4). In the HMW DOM of all the lakes the different neutral sugars contributed 10–30% and this distribution also occurred in the LMW DOM in Light Lake. However, in the other three lakes the LMW fraction was heavily dominated by glucose which ranged between 61 and 80 mol% (Figure 4). Expressing the individual saccharides from each fraction as a weight percentage of total hydrolysable neutral sugar yield on a glucose-free basis (Cowie and Hedges, 1984) gave high variability between the different lakes but showed no patterns consistent with trophic status or

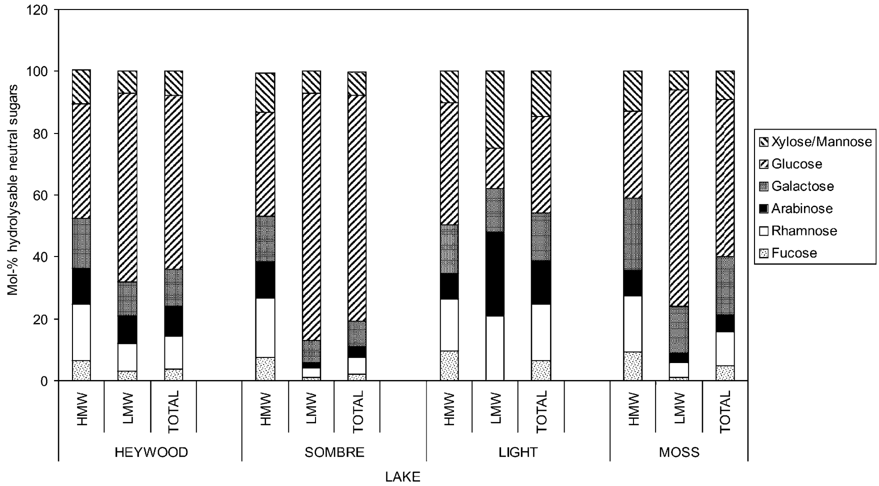

Figure 4. Relative contribution of various individual sugars to HMW DOM, LMW DOM and total DOM in the four study lakes.

animal/bird influence. Application of the weight percent sugar parameters (galactose + arabinose) and (fucose + rhamnose) in each of the four lakes did not differentiate carbohydrate source.

5. Discussion

5.1. MOLECULAR WEIGHT DISTRIBUTIONS OF DOC

Interpretation of patterns of DOC molecular weight distributions is complex. Marine systems, dominated by phytoplankton exudates and other autochthonous carbon dominated systems, are usually enriched in < 1000 Da material (Carlson et al., 1985). In contrast, studies from other lake and marine environments indicate that algal blooms at specific stages of development cause an enrichment in high molecular weight organic matter while bacteria utilise high molecular weight products and release low molecular weight materials (Cole et al., 1984; Meyer et al., 1987; Amon and Benner, 1994, 1996).

The pattern of relative DOC concentrations in the different size fractions was broadly similar across Heywood, Sombre and Moss Lakes ranging between 30 and 60%. For comparison, it has generally been found that in clearwater lakes high molecular weight material comprises 10–20% of total DOC increasing to 50% in humic lakes (Tranvik, 1998). Seawater, in which plankton are the major source of carbon is dominated by LMW DOC (70%; Benner, 2003) while 80% of river water DOC is HMW, originating from soil and vascular plants (Hedges et al., 1994, 2000). The fraction of HMW DOC in other lakes has been found to increase as the concentration of total DOC increases (Middleboe and Søndergaard, 1995). However, there was no clear relationship between the size distribution of DOC and total DOC concentration across the four lakes of this study.

Some difference in the size distribution of DOC, a dominance of LMW DOC was present in Light Lake compared with the other lakes (Figure 2). Light Lake has limited inflows and outflows (Heywood, 1967) and, despite its low inorganic nutrient concentrations, relatively high chl-*a* levels (Table I). A strong phytoplankton development and well developed benthic filamentous algal and cyanobacterial mats are likely related to its proximity to a seabird colony, which has been suggested to supply low but ecologically significant levels of nutrients to the lake (Heywood, 1967). The enrichment of Light Lake, which has minimal allochthonous organic matter input, a stable water column and elevated chl-*a* levels could be responsible for the LMW fraction dominating the DOC size distribution to a greater extent than seen in the other lakes (cf. Carlson et al., 1985). However, Light Lake has received little attention from previous researchers and supporting data on its microbiology and nutrient inflows are unavailable.

Heywood Lake, which is heavily impacted by Antarctic fur seals (*Arctocephalus gazella*), has the highest concentration of DOC with lowest proportion of LMW DOC and the highest proportion of HMW DOC. It also has phytoplankton blooms and bacterial populations that are approximately 1–2 orders of magnitude higher (Butler, 1999a: Table I) than in the other lakes, caused by enrichment by the seals (Table I; Ellis-Evans, 1981, 1990; Butler, 1999a, b, 2000). In this particular environment the higher molecular weight organic matter is probably directly related to seal activity, which can resuspend sediments and entrain moss and lichen derived organic material into the water column from the lakeshore. Such large disturbances may mask microbial DOC characteristics.

The distribution of DOC molecular weight in Moss and Sombre Lakes is considered to represent a typical baseline distribution for pristine oligotrophic lakes, where nutrients are limited and productivity is very low. Light Lake is a system which deviates slightly from the baseline pattern due to slightly greater complexity brought about by its physical character and limited nutrient enrichment. Heywood Lake represents an environment that has been significantly disturbed by seal activity involving several different processes which could potentially affect DOC size distribution. In the absence of specific organic geochemical and microbiological data it is impossible to ascertain how these processes may interact to produce the DOC size distribution pattern observed.

5.2. ABUNDANCE AND YIELD OF HYDROLYSABLE NEUTRAL SUGARS

Globally, concentrations of hydrolysable neutral sugars in aquatic environments are extremely variable ranging from 0.05 to >100 μM (Münster and Chróst, 1990; Wicks et al., 1991; Borch and Kirchman, 1997; Gremm and Kaplan, 1998). Concentrations of total hydrolysable neutral sugars in Light, Moss and Sombre Lakes were comparable to those commonly measured in oligotrophic – mesotrophic freshwaters from other environments (Tranvik and Jørgensen, 1995). Heywood Lake had a similar concentration of total dissolved carbohydrates to that reported in eutrophic Lake Plußsee (Münster, 1985).

Hydrolysable neutral sugars typically contribute 1 to ~30% of DOC in natural waters and while Sombre, Moss and Light Lake fall within that range, Heywood Lake apparently represents an upper end member of the range of hydrolysable neutral sugar yields (43%) in aquatic environments (Figure 5). This characteristic is probably caused by its enrichment through the activities of seabirds and mammals.

Hydrolysable neutral sugar yield has been used to indicate the state of degradation of organic matter with high values indicating undegraded organic material (Cowie and Hedges, 1994). In other environments high neutral

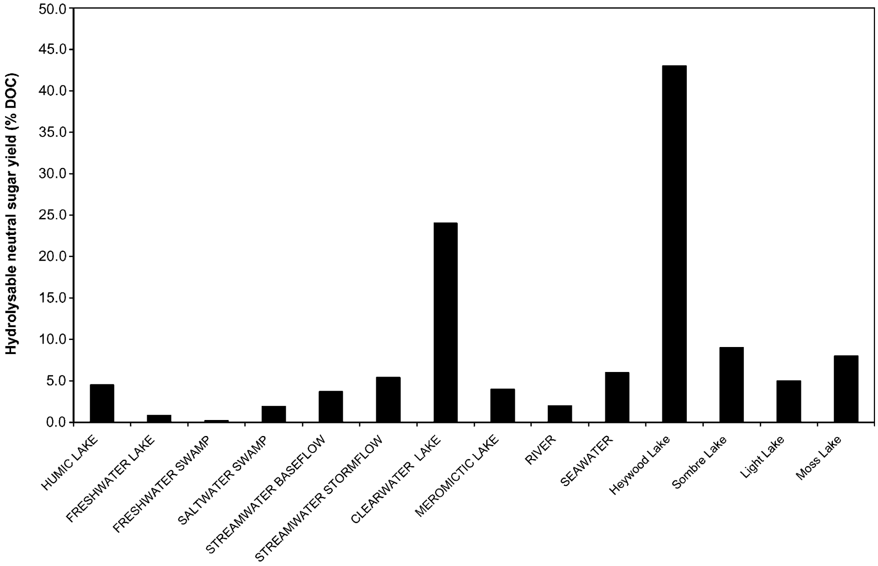

Figure 5. Comparison of the neutral sugar yields of DOC from different aquatic environments compared with the lakes of this study. Humic lake and clearwater lake [data from Tranvik and Jørgensen (1995)]; freshwater lake, freshwater swamp and saltwater swamp [data from Wicks et al. (1991)]; streamwater data (Gremm and Kaplan, 1998), meromictic lake data (Hayakawa, 2004) and river and seawater (Benner, 2003).

sugar yields of UDOM have been used as indicators of the contribution of phytoplankton derived DOM in coastal waters (Benner and Opsahl, 2001; Benner, 2003). Despite minimal allochthonous inputs to Light Lake hydrolysable neutral sugar yields of total DOC were lower than in the other lakes (Figure 5). In contrast, however, the relative hydrolysable neutral sugar yields in different molecular weight fractions for Light Lake are typical of productive waters dominated by autochthonous carbon (McCarthy et al., 1996; Benner and Opsahl, 2001).

Hydrolysable neutral sugar yields as a proportion of total DOC may be lower in Light Lake due to a higher turnover rate through microbial recycling, which may prevent their accumulation. However, we do not have data to support this speculation.

Hydrolysable neutral sugar-C dominated low molecular weight organic matter in Sombre and Heywood Lakes, while in Moss and Light Lakes higher molecular weight organic material was somewhat more enriched in hydrolysable neutral sugar-C (Figure 3).

In Heywood and Sombre Lakes, the dominance of hydrolysable neutral sugar-C in molecular weight organic matter compared with molecular weight materials is different to that observed in other aquatic environments in which organic material of >1000 Da (UDOM) was found to be enriched in polysaccharides (Amon and Benner, 1994; McCarthy et al., 1996).

There was no clear relationship between trophic status and the hydrolysable neutral sugar yield of total DOC (Figure 5) nor of the yields in the organic carbon of LMW or HMW fractions (Figure 3).

5.3. HYDROLYSABLE NEUTRAL SUGAR COMPOSITION

Almost all of the molecular weight fractions were dominated by glucose. In Sombre Lake, Heywood Lake and Moss Lake proportions of glucose in the LMW fraction were higher (80, 61 and 85 mol% respectively) than usually seen in natural waters (Figure 6) although comparable values have been reported from different environments, such as Okefenokee Swamp water, and from low molecular weight material from deep equatorial Pacific samples (Figure 6). Different sugars have been related to catchment characteristics and sources (Cowie and Hedges, 1984; Depetris and Kempe, 1993). Glucose has been associated with the cellular contents of phytoplankton and high molar percentages are produced by diatoms, galactose with diatom cell walls and bacteria and ribose with bacteria. (McCarthy et al., 1996; Skoog and Benner, 1997; Benner and Opsahl, 2001). In other studies rhamnose, fucose, arabinose

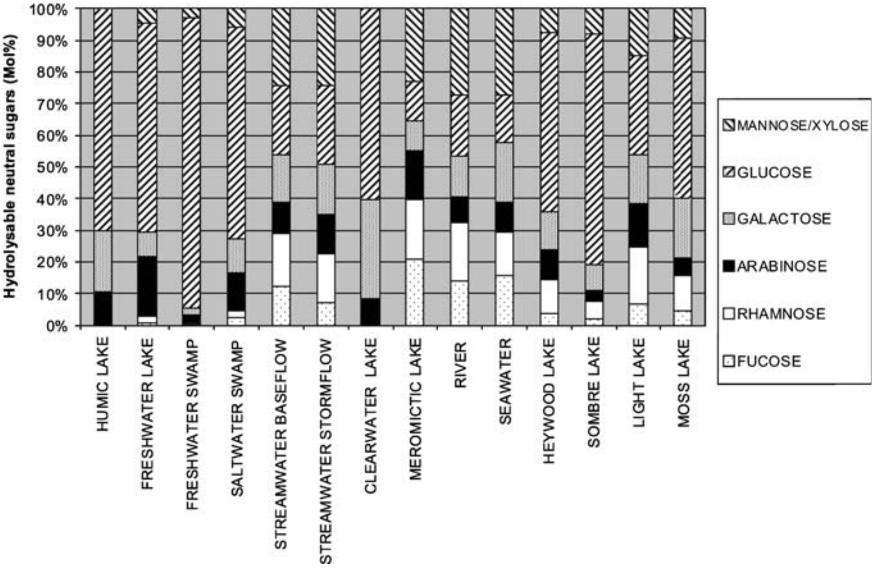

Figure 6. Comparison of hydrolysable neutral sugar composition from different aquatic environments. Humic lake and clearwater lake data from Tranvik and Jørgensen (1995) (Figure 1). Freshwater lake, freshwater swamp and saltwater swamp data taken from Wicks et al. (1991). streamwater data (Gremm and Kaplan, 1998), meromictic lake data (Hayakawa, 2004) and river and seawater (Benner, 2003).

and xylose can be abundant in samples collected after phytoplankton blooms with colony forming bacteria and zooplankton; xylose and arabinose have been found at relatively high levels in soils and fucose tends to indicate a bacterial origin (Gremm and Kaplan, 1998; Hayakawa, 2004). To summarise, there have been several attempts to use carbohydrates as organic matter source indicators but patterns tend to be inconsistent among studies and environments. Compositions were found to be similar in river, phytoplankton bloom and marine UDOM despite a wide range of sources. The similarity of composition maybe a feature attributed to diagenetic modification of original composition to a more uniform 'degraded' composition or to the contribution from heterotrophic microorganisms (Benner and Opsahl, 2001 and references therein).

Although the hydrolysable neutral sugar composition of Moss Lake had relatively high levels of galactose compared to Sombre Lake, total DOC concentrations, the yields of total hydrolysable neutral sugar-C/DOC and the molecular weight distribution of DOM in the two lakes were similar and did not reflect differences in the disturbed Sombre Lake environment compared to non-seal influenced Moss Lake.

6. Conclusions

(1) In Heywood Lake, elevated DOC concentrations, a greater proportion of high molecular weight DOC and high hydrolysable neutral sugar concentrations dominated by glucose compared to the other lakes studied on Signy Island, are due to eutrophication caused by the presence of fur seals in and around the lake and seepage flow through surrounding moss banks and muddy catchment areas.

(2) DOC concentrations, molecular weight distributions and hydrolysable neutral sugar composition did not show evidence that Sombre Lake is starting to suffer organic enrichment from recent increases in the fur seal population in its catchment, in contrast with recent planktonic and nutrient studies (Butler, 1999b). The insensitivity of the characteristics of DOC as an indicator of this perturbation may be due to the substantial flow through of water within this lake during the summer melt, or large seasonal and inter-annual changes in DOC which are known to occur but could not be identified by this short-term study.

(3) Higher DOC concentrations in Light Lake and higher chl *a* and inorganic nutrients compared to Moss and Sombre Lakes support the hypothesis that allochthonous inorganic nutrients leached through seepage water from moss banks and from an adjacent Giant Petrel colony may increase phytoplankton biomass. The molecular weight

distribution of DOC in Moss and Sombre is thought to be typical of Antarctic nutrient limited lakes.

(4) The hydrolysable neutral sugar yields in total DOC, HMW or LMW DOM nor molar compositions of the lake waters showed differences reflecting potential sources of DOC, or patterns which related to their trophic status.

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