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BIOCHEMICAL COMPOUNDS IN THE PELAGIC AND SEDIMENTARY ENVIRONMENT OF ANTARCTIC WATERS

by

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A B S T R A C T

— During two cruises of FS "Meteor" in the Atlantic sector of the Antarctic, Nov. 1980 - Feb. 1981, a range of organic compounds was determined in seawater, particulates and deep-sea sediment pore waters and compared with biological parameters describing phytoplankton and microbiological activities.

Amino acids were determined by HPLC techniques with fluorescence detection of the compounds at their natural levels. Combined amino acids both in solution and from particulate matter as well as mono- and polysaccharides were determined over a wide station grid. DOC, fluorimetric chlorophyll and urea measurements were routinely performed. A distnction was made between water extractable reserve substances in the particulate matter and structural protein and polysaccharide components. —

The changes in the amino acid spectrum of closely spaced sediment samples together with the variations in the sugar : protein ratios from that of the source material (phytoplankton and sediment trap samples) is explained in terms of secondary benthic microorganism activity.

The spectrum of amino acids from water extracts of plankton samples was found to show marked differences from the composition of free amino acids in seawater, with an abundance of acids centered around free glutamine and related products.

Investigations of samples of ice over a range of salinities reflected the pattern of amino acids in plankton cell extracts.

R E S U M E

—Au cours de deux missions du N/O "Meteor" dans la région Antarctique de l'Atlantique, Novembre 1980-Février 1981, une série de composés organiques ont été déterminés dans l'eau de mer, dans le matériel particulaire et dans l'eau interstitielle du sédiment en milieu profond et comparés avec les paramètres biologiques descriptifs du phytoplankton et de l'activité microbiologique.

Les acides aminés ont été déterminés en HPLC avec une détection par fluorescence des composés à leurs concentrations naturelles. Les acides aminés liés, en solution ou associés à la matière particulaire ainsi que les mono et polysaccharides ont été déterminés sur un grand nombre de stations. Le carbone organique dissous (C.O.D.), la chlorophylle (fluorométrie) et l'urée, ont été mesurées en routine. Une distinction a été faite entre les substances de réserve solubles dans l'eau de la matière particulaire et les protéines ou les polysaccharides de structure.

Les variations conconmittantes du spectre des acides aminés d'échantillons proches les uns des autres avec le rapport sucres/protéines du matériel considere (phytoplancton et échantillons des trappes à sédiment) sont expliquées en terme d'activité secondaire des microorganismes benthiques.

Le spectre des acides amines, d'extraits aqueux de plancton montre des différences marquées par rapport à la composition en acides aminés libre dans l'eau de mer, avec une quantité importante de la glutamine et de ses dérivés.

Les analyses de glaces de diverses salinités reflètent le spectre en acides aminés des extraits aqueux de phytoplancton.

K E Y W O R D S

Amino acids, total sugars, water extracts of particulate matter, sugar : protein ratios

M O T S - C L E S

Acides aminés, carbohydrates totaux extraits aqueux de la matière particulaire, rapports sucres/protéines

INTRODUCTION

In a recent publication (Bölter and Dawson, 1982) several aspects of the production and heterotrophic utilisation of dissolved organic compounds in the water columns of the Bransfield Strait and the Scotia Sea have been discussed. The same authors further demonstrated that several metabolites found in the dissolved fraction of seawater could have been derived from the intercellular pools of phytoplankton and that these metabolites were available to heterotrophs whose activity, in spite of the near zero temperature, was comparable to other marine areas. The excess of organic material, both particulate and dissolved, produced during the early spring bloom which is dominated by a limited number of large phytoplankters (M. Elbrächter, pers. comm., 1981) would be broken down relatively slowly at the in situ rates measured.

It is not the intention of the present communication to quantify these rates of production and decomposition but rather to describe the variations in the biochemical composition of particulate and dissolved matter in the water co-

lumn during the spring bloom and to estimate how these changes effect the material sedimenting out to the sea floor and subsequently determine the composition of the surface sediments and interstitial waters.

We have therefore chosen the approach of examining the changes in the amino acid and carbohydrate fractions since the monomeric and polymeric forms of these make up the largest identifiable portion of particulate and dissolved primary organic matter.

MATERIAL AND METHODS

The investigations took place during two cruises of the FS "Meteor" in the Scotia Sea and the Bransfield Strait. The first of these cruises, November - December 1980, dealt with the characterisation of the biochemical compounds in the water column in comparison to the biological activity, the second leg, January - February 1981, was devoted to an investigation of the same region and the characterisation of the sediment interstitial waters. Fig. 1 depicts the station grid covered.

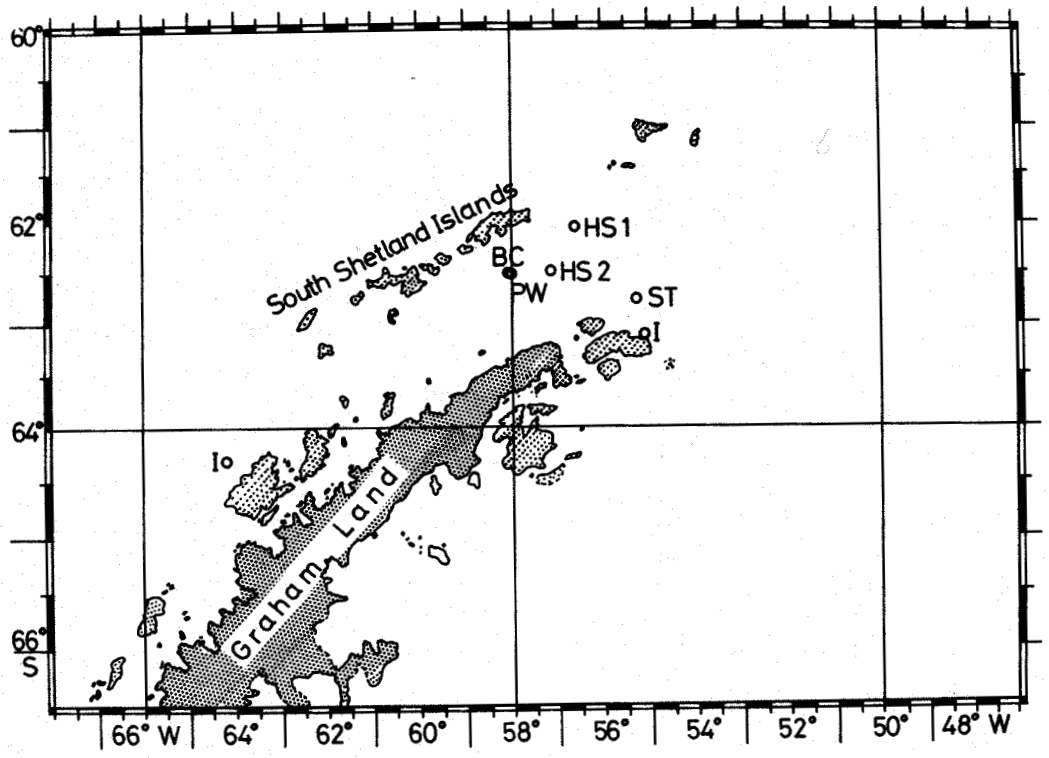

Fig. 1 Stations covered in the Bransfield Strait and Scotia Sea. HS = hydrostation, ST = sediment trap, I = ice sample, BC = box corer, PW = pore water sample.

1. Dissolved compounds

All seawater samples were drawn from 10 dm^3 General Oceanics water samplers in hydrocasts down to 500 m. The sampling stations were chosen on the basis of *in situ* chlorophyll registrations (Impuls Physic sensor). An example of the biological stratification is presented in the computer plot from Hydrosta-

tion 2 ("Meteor" station 73/Fig. 2) together with temperature and salinity profiles.

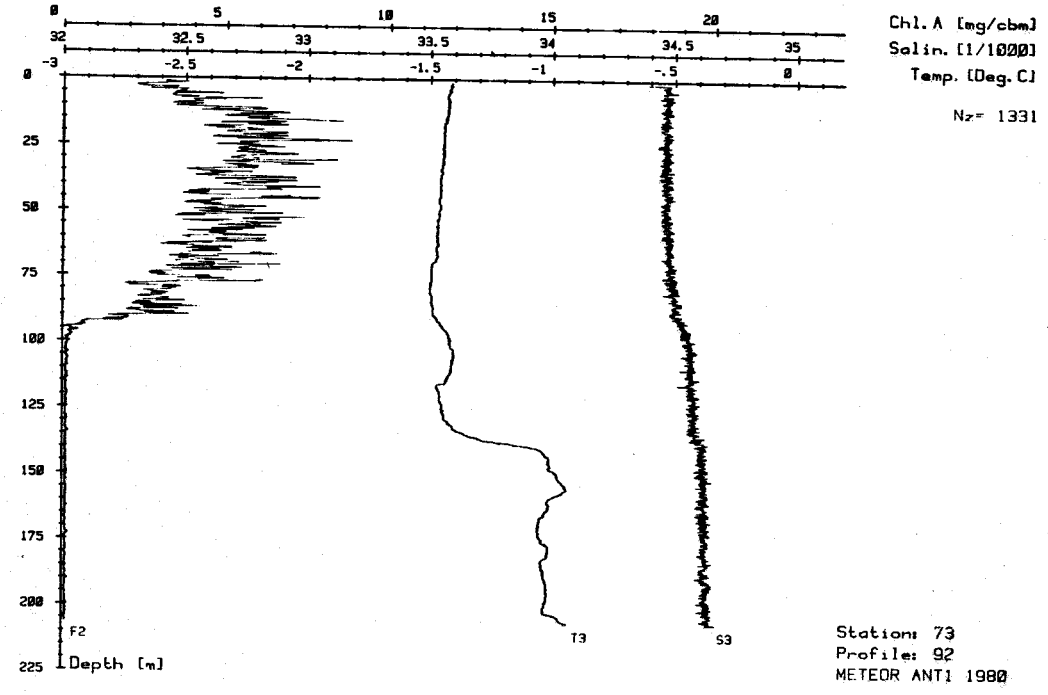

Fig. 2 Biological stratification at Hydrostation 2. Computer plot of chlorophyll (left), temperature (middle) and salinity (right) versus depth. Courtesy H. Haardt and R. Maaßen.

Dissolved organic compounds were determined after filtration under hydrostatic pressure through precombusted GF/C filters. All samples were processed and analysed within a few hours of collection. Samples awaiting analysis were stored at - 20 °C after filtration.

Dissolved free amino acids (DFAA) were determined on 1 cm^3 of filtrate according to the procedures of Lindroth and Mopper (1979) with modifications of Liebezeit and Dawson (1981) and Dawson and Liebezeit (1982). The amino acids were separated as their isoindole derivatives by high performance liquid chromatography with fluorescence detection. An isocratic elution system used for the majority of the analyses detects only a limited number of amino acids; these, however, have been shown to be the dominant free amino acids in seawater samples (Dawson and Liebezeit, 1981; Bölter and Dawson, 1982).

Dissolved combined amino acids were determined as monomeric acids by HPLC after hydrolysis of the seawater sample (4M HCl, 100 °C, 20 h).

Dissolved free monosaccharides (DMCHO) were determined on 1 cm^3 of filtrate according to the class reaction method of Johnson and Sieburth (1977). Dissolved polysaccharides (DPCHO) were determined after subtraction of the value for DMCHO from the total sugar content (DTCHO) obtained after hydrolysis of the seawater sample (0.1M HCl, 100 °C, 20h, Burney and Sieburth, 1977).

Dissolved organic carbon (DOC) was determined by the method of Schreurs (1978) after acidification and sterilisation of the seawater samples upon return to the laboratory in Kiel.

Urea determinations were performed on seawater and thawed-out ice samples by the method described by Koroleff (1976).

2. Particulate samples

Samples for the analysis of particulate compounds were filtered immediately after retrieval of the water samplers. The volume of the water filtered through precombusted GF/C filters depended upon the seston load and varied between 250 cm^3 and 2 dm^3. The filters were stored deep-frozen prior to the analysis on board.

Five filters were collected at each depth sampled for the determination of chlorophyll a, seston and particulate organic carbon and nitrogen, aqueous extractable sugars and amino acids, total amino acids and carbohydrates.

Aqueous extracts of the particulate matter recovered were prepared by heating the filters with 5 cm^3 20% aqueous ethanol for 4 h at 80 °C. The extracts were analysed for extractable free amino acids (EFAA) and extractable monosaccharides (EMCHO) by the methods described above.

Filters for the determination of particulate combined amino acids (PCAA) were hydrolysed for 20 h at 100 °C with 6M HCl. After neutralisation of the hydrolysates with 6M NaOH the constituent amino acids were separated and quantified by HPLC as described for DFAA.

Filters for the determination of the total polysaccharide content of particulate matter (PTCHO) were hydrolysed with 0.2M HCl for 20 h at 100 °C. The resulting monosaccharides were analysed by the class reaction of Johnson and Sieburth (1977) after neutralisation with 0.2M NaOH.

Chlorophyll a was determined on 90% acetone extracts of the filters by a fluorimetric procedure (c.f. Holm-Hansen et al., 1965). The identity of the individual plant pigments was confirmed by HPLC according to Liebezeit (1980), a discussion of the occurrence of chlorophyll b and thus the overestimation of of chl a by spectrophotometric procedures has been given by Bölter and Dawson (1982).

Samples for the estimation of seston weight, POC and PON were returned frozen to Kiel for analysis.

3. Sediment samples

Sediment samples were taken with a 30 x 30 cm box corer. The 40 cm deep cores retrieved were subsampled with disposable syringes (top cut off) with a core diameter of 2.5 cm. Sediment samples at 1 cm intervals were air dried at 60 °C and ground in a pestel and mortar. 100 mg portions were extracted with 2 cm^3 of distilled water for 4 h at 80 °C and the aqueous extracts centrifuged for 5 min at 5000 rpm and analysed for free amino acids and monosaccharides as above.

100 mg portions of the sediments were hydrolysed with 0.2M HCl and the hydrolysate analysed for monosaccharides. Further hydrolysis with 6M HCl allowed the determination of total amino acids by HPLC after neutralisation.

Samples for the analysis of interstitial waters of the sediment layers were recovered by filtration through 0.45 µm membrane filters under pressure

(nitrogen, 10 bar). The porewater samples retrieved were processed as described above.

RESULTS AND DISCUSSIONS

Fig. 2 depicts the chlorophyll a regime at Hydrostation 2 and shows a biolodical stratified water mass with no pronounced hydrographical features and a primary production reaching down to 100 m. Our sampling depths for particulate and dissolved components were chosen to cover the zone of production. Free drifting sediment traps were operated at a depth of 100 m (courtesy B. Zeitzschel and co-workers) i.e. chosen to operate directly below the euphotic zone for a collection period of 12 hours.

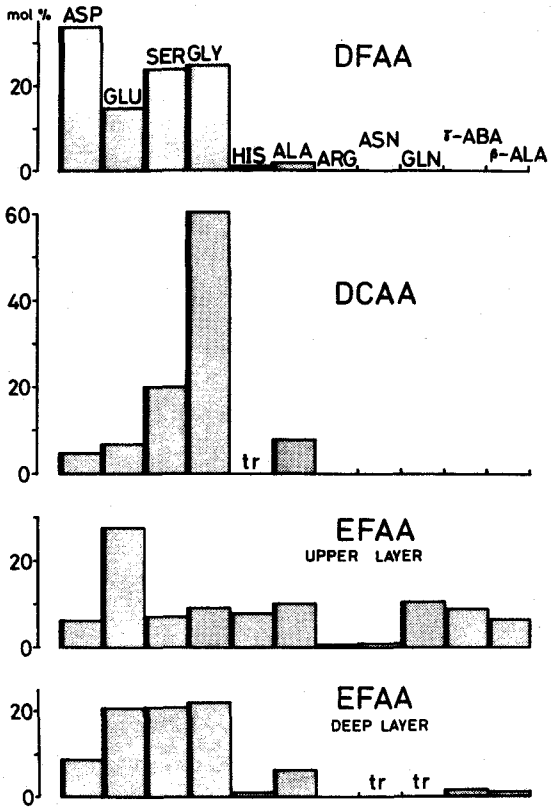

Fig. 3 Mean relative molar composition of free and combined amino acids in the dissolved fraction and extractable amino acids from particulate matter. ASP = aspartic acid, GLU = glutamic acid, SER = serine, GLY = glycine, HIS - histidine, ALA = alanine, ARG = arginine, ASN = asparagine, GLN = glutamine, γ-ABA = γ-amino butyric acid, ß-ALA = ß-alanine.

1. Water column

For simplicity we distinguish between several pools of organic compounds in the water column by considering the following fractions: the dissolved monomeric fraction i.e. free amino acids (DFAA) and total dissolved monosaccharides (DNCHO); the combined or polymeric dissolved fraction i.e. dissolved combined amino acids (DCAA) and dissolved total polysaccharides (DPCHO); the polymeric fraction of particulate matter i.e. that part released after acid hydrolysis including particulate proteins (PTAA) and particulate polysaccharides (PTCHO); the "extractable" fraction of particulate matter i.e. that part released by hot aqueous extraction including amino acids (EFAA) and monosaccharides (EMCHO).

1.1 Amino acid spectra

Fig. 3 depicts examples of the mol% distribution of amino acids in the dissolved monomeric and polymeric fractions and the water extract of particulate matter.

The average free amino acid spectrum of the water column is dominated by the acids aspartic and glutamic acids, serine and glycine with only traces of other metabolites. The extractable acids (EFAA) of the upper water column are rich in histidine, alanine, glutamine and the decarboxylation products γ-amino butyric acid and ß-alanine.

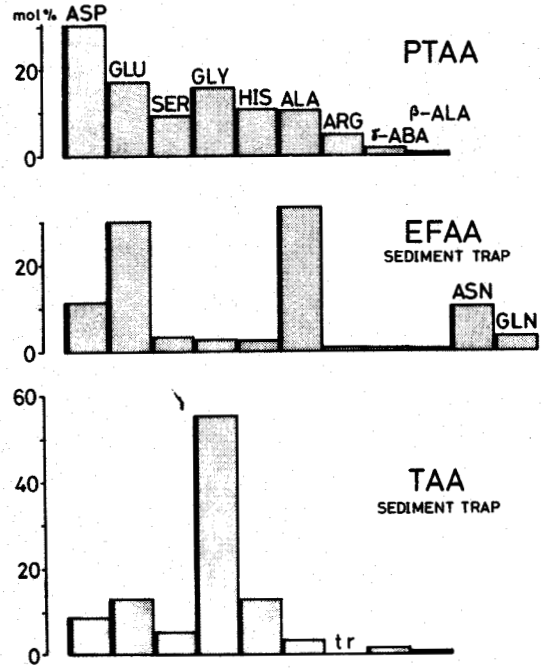

Fig. 4 Average mol% composition of particulate matter hydrolysate (PTAA), extractable amino acids from sediment trap material (EFAA) and total amino acids in sediment trap material (TAA). Abbreviations as in Fig.3.

If these two pools of amino acids were in exchange with each other then the spectrum of DFAA has been modified subsequent to release of cell metabolites to the seawater. The spectrum of amino acids in the dissolved free form may be "diluted" with amino acids released by other processes e.g. the slow hydrolysis of the dissolved and particulate polymeric fractions. The spectrum of amino acids in the DCAA does not suggest that the DFAA is derived from this pool; however, the particulate proteins, or rather the total hydrolysate of particulate matter (PTAA/Fig. 4) show similarities in the spectrum to that of the DFAA.

The spectrum of the amino acids of the particulate proteins shows a pronounced change in concentration of certain amino acids with depth such that at HS 1 the relative content of alanine decreases from ca. 20 to 5 mol%, that of histidine from 10 mol% in the surface layer to 1.4 % at depth and that of γ-amino butyric acid from 2.0 to only trace amounts. The depletion of these amino acids is accompanied by a relative increase in glycine, serine, aspartic and glutamic acids.

Particulate matter from deep layers is shown to be depleted in extractable amino acids both from the spectrum and in the absolute concentrations (mg g^{-1}/ Table 1). This depletion of cell amino acids follows the reduction in chlorophyll even though the seston load remained relatively constant over the depth sampled.

Table 1 Components of particulate matter

depth	EMCHO	PTCHO	EFAA	SESTON	CHL a
m	mg g^{-1}	mg g^{-1}	mg g^{-1}	mg dry weight dm^{-3}	/ug dm^{-3}
0	50.7	72.5	37.7	0.69	9.0
5	35.9	58.5	29.2	1.06	8.9
14	44.3	79.4	23.7	0.97	8.2
26	61.5	81.5	50.8	0.65	7.2
40	28.7	47.8	9.6	1.15	7.0
90	27.2	48.1	9.9	0.81	0.9
100	17.6	36.8	4.4	0.68	1.1
sediment trap 100 m	8.66	28.6	0.71		
sediment cm					
0 - 0.5	0.36	0.63	0.18		
0.5 - 1	0.29	1.22	0.18		
1 - 2	0.26	0.93	0.06		
2 - 3	0.24	1.27	0.09		
3 - 4	0.24	-	0.07		

It would therefore appear reasonable that in the case of this Phaeocystis dominated bloom (M. Elbrächter, pers. comm., 1981) the dissolved free amino acids found in the seawater originated from the cell contents and hydrolysis products of the structural proteins and that these amino acids are subjected to heterotrophic and abiotic modifications. If the amino acids released by the cells could be "frozen" in the water sample, with exclusion of bacterial activity, then the original composition should be maintained (see 2.1 and Fig. 8).

From the differences in the spectra of Figs. 3 and 4 the amino acids alanine, histidine, glutamine, asparagine, γ-amino butyric acid and ß-alanine may be considered to be representative biochemicals from phytoplankton cells. A similar conclusion was reached by Bölter and Dawson (1982). Lee and Cronin (1981) remind us of the role of amino acids in cellular processes i.e. deamination and decarboxylation reactions and thus the finding of such products as γ-amino butyric acid and ß-alanine in samples of particulate matter and dissolved samples may not be too surprising.

1.2 Sugars and the sugar:protein ratio

The free monosaccharide spectrum of natural waters has been shown to be based on relatively few sugars and to comprise mainly of glucose and fructose (Mopper et al., 1980, Liebezeit, 1981). The extractable sugar spectrum from phytoplankton has also been shown to be dominated by one sugar namely glucose (Handa and Yanagi, 1969; Dawson and Liebezeit, unpublished results). The structural sugars found both in the cell wall material of phytoplankton and dissolved as polymeric compounds in seawater on the other hand comprises of a spectrum of pentoses, hexoses and uronic acid residues. Most studies of bacterial utilisation of organic compounds are based on the uptake of radioactive glucose, which in view of the abundance of this sugar in the marine environment and the preference of bacteria for this substrate (Bölter, 1981) appears warranted.

The methods adopted in this study do not differentiate between different monosaccharides either before or after hydrolysis but rely on a class reaction calibrated in terms of glucose. A differentiation is, however, made between monosaccharides, total sugars and the sugars released from particulate matter upon hot aqueous extraction. From Table 1 it may be seen that the absolute concentrations of extractable monosaccharides in particulate matter decrease more rapidly than the polysaccharide fraction and that this decrease is to a large extent independent of the seston load.

The extractable sugars are, however, lost less rapidly than the cellular amino acids as seen from Table 1 and depicted in the form of the sugar:protein ratio of the ex-ractable components EMCHO:EFAA in Fig. 5. Whereas the particulate matter in the upper water column has a ratio of 1 or less, the material at or around 100 m has a ratio approaching 4. The similarity of the sugar:protein curve with that of the ratio of free dissolved sugars and amino acids further suggests that these two pools are indeed in exchange i.e. the cell metabolites contribute to the monomeric fraction of seawater.

Fig. 6 depicts the sugar:protein ratio based on the total sugars and amino acids of particulate matter from HS 1 and shows ratios of less than 1 decreasing down the water column. This hydrostation was also dominated by blooms of Phaeocystis sp. with high chlorophyll contents in the upper 100 m together with high DOC content of the water.

The ratio of sugars to proteins of the dissolved combined fraction of seawater shows an erratic pattern but is in general positive i.e. an excess of polysaccharides compared to proteins. The decrease of polysaccharides relative

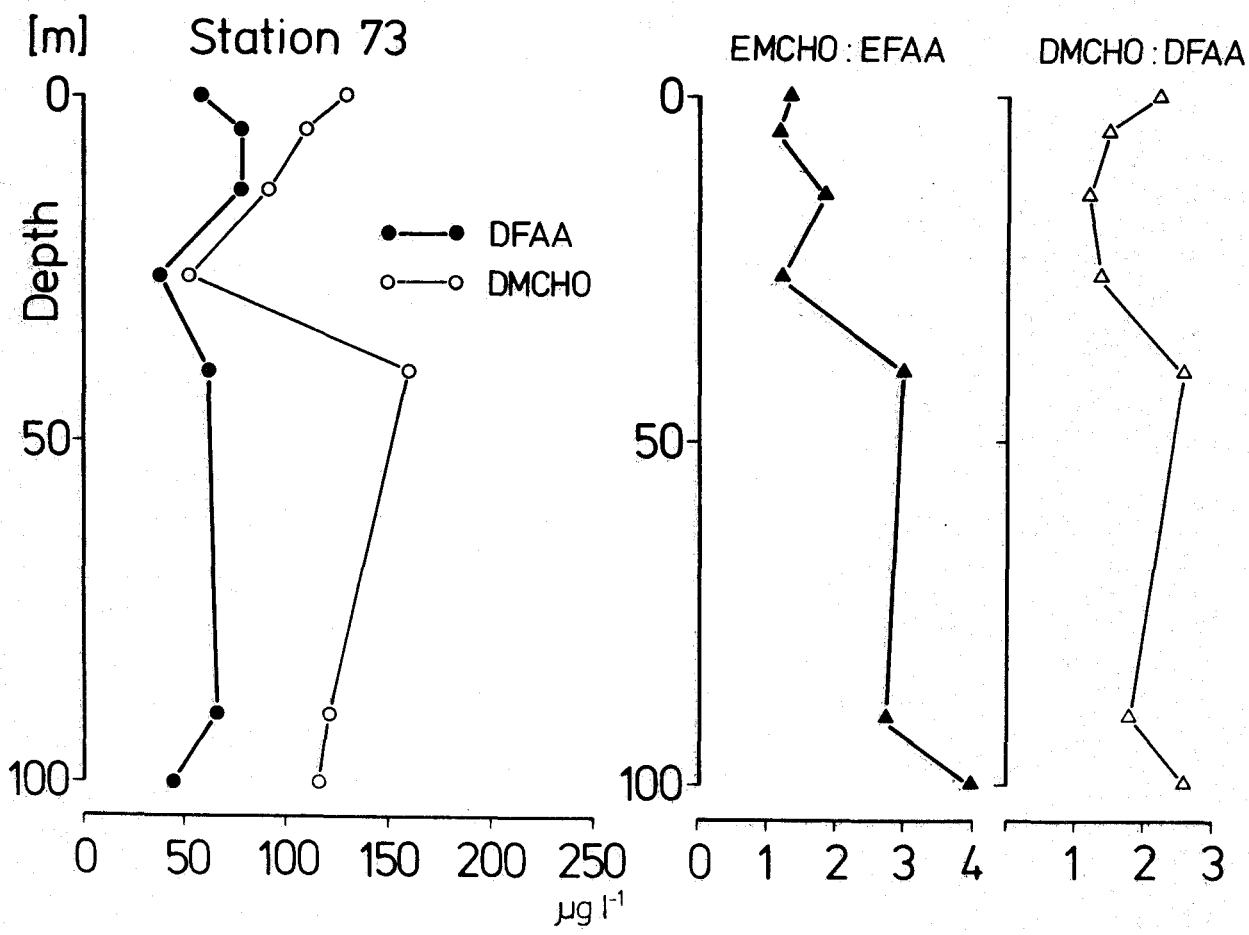

Fig. 5 Profiles of the concentrations of dissolved sugars and amino acids together with the sugar:protein ratios of the seawater and the extractable compounds from particulate matter (DMCHO:DFAA and EMCHO:EFAA resp.) at HS 2.

to proteins in the particulate material suggests that proteins are more stable structural polymers than the polysaccharides of plankton. In the case of Phaeocystis sp. the associated polysacharide material may be in the form of sugar-rich slimes more susceptible to decomposition or in situ hydrolysis.

Although the sugar:protein ratio of the free dissolved fraction is a product of the release of both cell metabolites and decomposition of polymeric material, the similarities of the ratios with those of the extractable cell contents suggest that this is controlled by heterotrophic activity adapted to a supply of both components in the given proportions. This is in many ways supported by the activity measurements of Bölter and Dawson (1982) who showed a higher bacterial turn-over rate for the preferred substrate, glucose, than for amino acid mixtures.

If we view the primary material of photosynthesis as the original source of both monomeric and polymeric sugars then the proportion of water extractable sugars expressed as a percentage of the total should be a characteristic of the source material. From the representation in Fig. 7 it can be seen that 60 % of the sugars of the particulate fraction (in the upper water column, Phaeosystis sp. bloom) may be extracted by a hot water treatment. The proportion of monosaccharides found dissolved in seawater represents, however, less than one half of the original amount (ca. 25 %) in the upper water column, suggesting a selective depletion via biotic or abiotic processes, of the monomeric forms. If the cell metabolites of phytoplankton were "frozen" upon release then the proportion

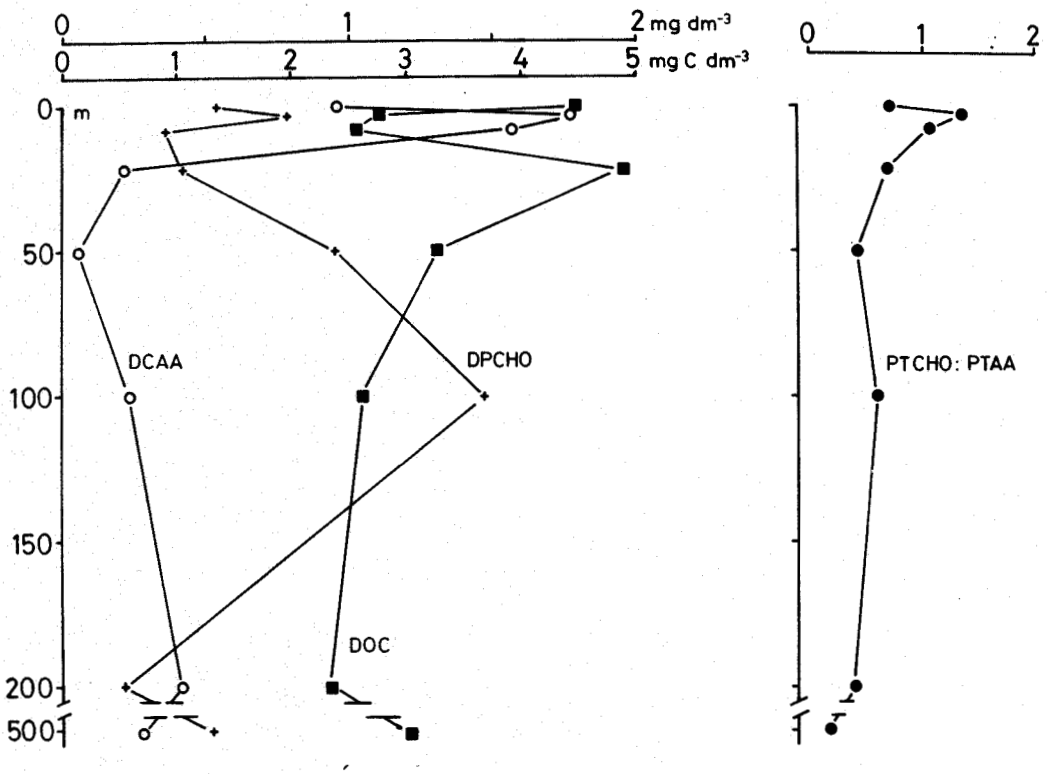

Fig. 6 Dissolved combined amino acids (DCAA), polysaccharides (DPCHO) and dissolved organic carbon (DOC) at Hydrostation 1. Sugar:protein ratio of particulate matter (PTCHO:PTAA).

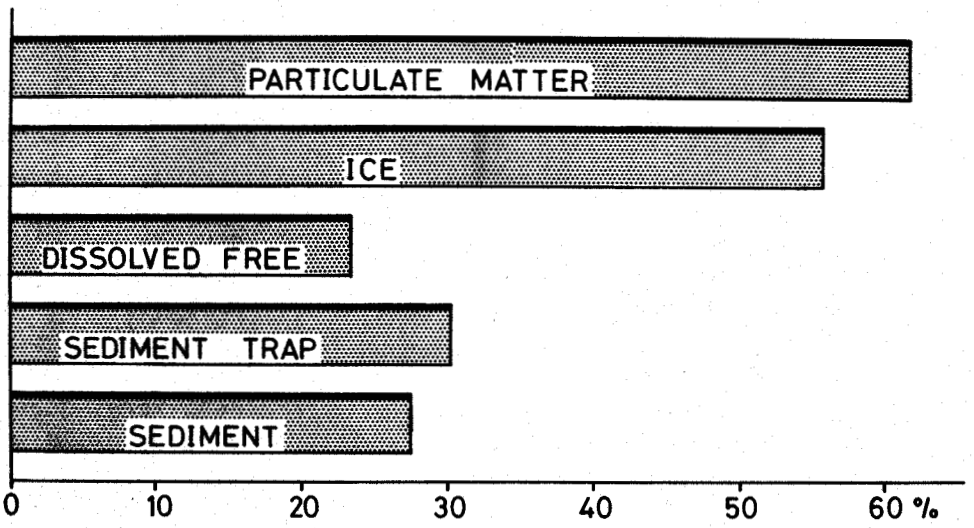

Fig. 7 Proportion of extractable monosaccharides as percentage of total sugars in different phases.

of monomers would be similar in the seawater to that of the source material. This is in fact the case for the plankton found in the brash waters of drift ice and in the ice water upon analysis (see 2).

2. Ice

It is unusual to include drift ice samples in any treatment of the biochemical composition of marine waters. The ice samples analysed were originally of glacial origin and the salinity of the samples depended on the exposure of the ice-floe to brash waters and in one sample over the range of 1 m varied from 1.02 - 11.9 ‰. Common to all ice-floes encountered was the staining of the ice with colours reflecting the species of phytoplankton embedded in the ice. The samples analysed during the "Meteor" ANT I cruise consisted to over 90 % of pennate diatoms (M. Elbrächter, pers. comm., 1981) and although these forms were not found in any significant numbers in the water column samples, the examples presented i.e. the composition of the plankton cells in comparison with their milieu (ice-water filtered through 0.45 µm filters) lends some support to the suppositions made earlier in this paper.

The high dissolved phosphate content of the ice (mean 46 µmol dm^{-3}), low nitrate (around 1 µmol dm^{-3}), high ammonia content (ca. 5 µmol dm^{-3}) and urea values exceeding 10 µmol dm^{-3} points to the fertilisation of the waters of such ice-floes by marine mammals and seabirds, either prior to or subsequent to detachment from the continental glaciers.

2.1 Amino acid spectra

The dissolved and combined amino acids of the ice water were analysed after allowing the ice to thaw-out over a GF/C filter thus ensuring that the water collected was filtered at or around 0 °C under mild filtration conditions (no vacuum applied). The algae filtered was extracted as given before.

The histograms of Fig. 8 cannot be compared with the dissolved or particulate fractions of the water column owing to the different nature of the sample and the species composition. It is, however, apparent that the spectrum of amino acids dissolved in the ice and those found in the intracellular pools of the plankton (PFAA) are remarkably similar. This suggests that the amino acids have undergone no significant alteration subsequent to release. The absolute amounts of DFAA were also astonishingly high (up to 800 µg dm^{-3}). The dissolved combined amino acid level was around 3.6 mg dm^{-3}. The bacterial activity of the ice was measurable but low (M. Bölter, pers. comm., 1981).

Glutamine and related metabolites dominate the spectrum of amino acids and together with alanine, histidine and asparagine are easily recognisable above a protein amino acid dominated spectrum as cell metabolites.

2.2 Sugars and sugar:protein ratio

The fraction of monosaccharides in comparison to the total sugars (i.e. 55 %/Fig. 7) reflects closely the composition of phytoplankton cells extracted under the analytical conditions presented above. The actual levels of mono- and total polysaccharides in the ice samples were high with mean values of 1.36 and 2.66 mg dm^{-3} respectively. It is interesting to note that the sugar:protein ratio for the dissolved monomers was 2.5 (mean) and 0.74 for the polymeric fraction. These values lie in the range reported for the monomeric and polymeric constituents of seawater at Hydrostation 1.

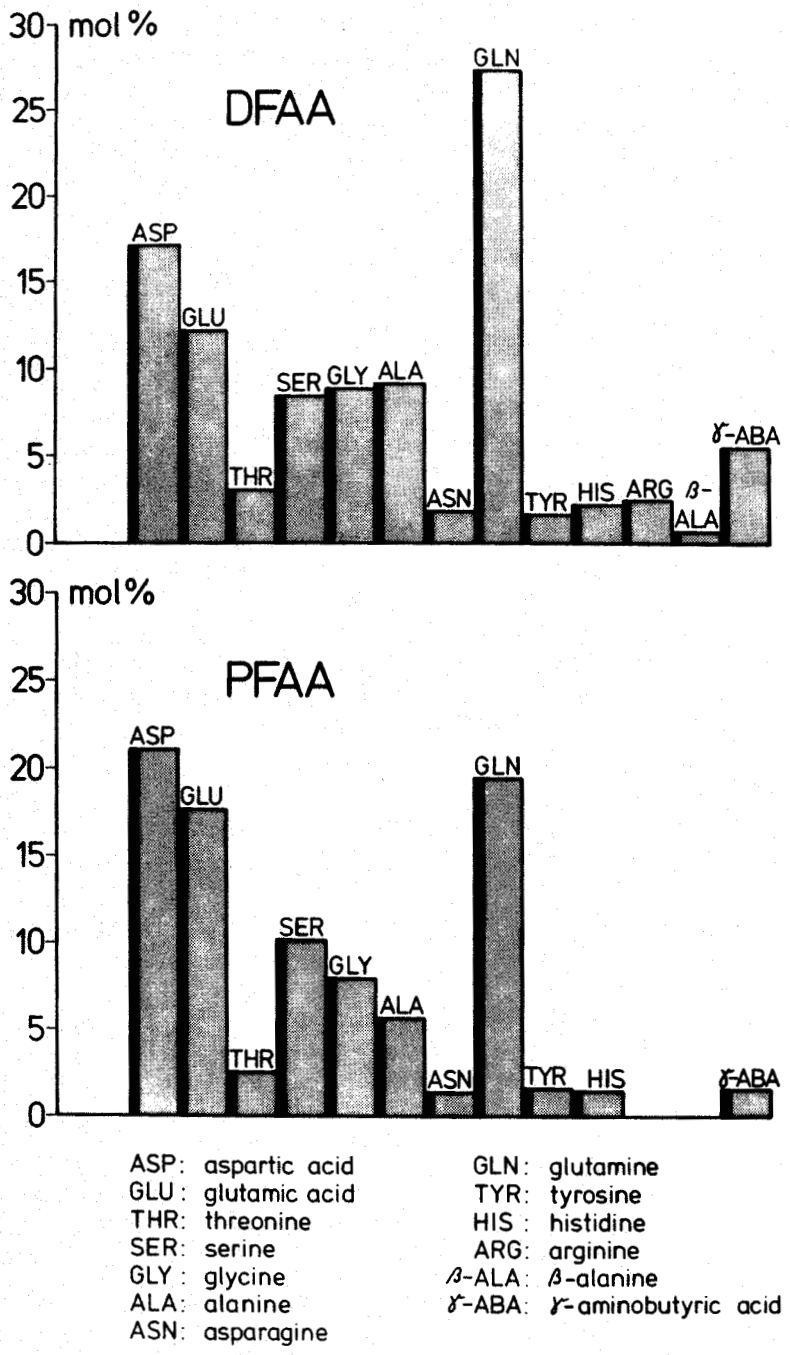

Fig. 8 Average mol% composition of the dissolved free amino acids (DFAA) in ice and free amino acids from ice-plankton water extract (PFAA).

3. Sediment trap material

The sediment trap deployed at 100 m for a period of 12 hours collected material which ressembled the material filtered in the upper water column but nonetheless contained components such as sand grains and larger fecal material which went undetected on the filters. Sediments traps have been shown to be effective in collecting fast sinking particles and may therefore be considered to be

the preferred method for determining the composition of sedimenting particles. The transport or organic material on large particles may be more rapid than previously thought (Lee and Cronin, 1981). These faster sinking particles would include intact phytoplankton cells and secondary produced fecal matter and thus the composition of the material may represent a more integrated sample of the material leaving the upper water column.

3.1 Amino acid spectra

The extractable amino acid spectra (Fig. 4) shows few similarities to that of DFAA. The high amounts of alanine, asparagine and glutamine in the sample deviate from the spectrum obtained upon extraction of the filtered particulates at 100 m. The presence of traces of γ-amino butyric acid and ß-alanine according to Lee and Cronin (1981) suggests that the material has undergone bacterially mediated decarboxylation either in the particles themselves or in the gut of filter feeders before discharge as fecal material. Owing to the composite nature of the sediment trap sample it is difficult ot pinpoint the source of the extractable alanine and dibasic amino acids. In particular from the analysis of the surface sediments it appears that a source material rich in alanine is indeed reaching the seafloor.

It is interesting to note that the absolute amount of EFAA is significantly reduced compared with the particulate matter collected by filter at 100 m (Table 1) and lends support to the argument that the material in the sediment trap is different, older or significantly modified.

3.2 Sugars and sugar:protein ratio

It can be seen that the proportion of extractable monosaccharides is significantly reduced in the sediment trap material compared with the material in the upper water column (Fig. 7) or even the material collected at 100 m (Table 1). This again points to a difference in composition of the collected material.

The sugar:protein ratio of the extractable portion is high (Table 1), around 12:1 compared with the filter material at 100 m (ca. 4:1).

4. Sedimentary environment

Sedimentation rates of 100 cm per 1,000 years have been determined in the Bransfield Strait at 2,000 m water depth (P. Müller, pers. comm., 1981). The cores taken in this study originated from 957 m water depth near the Hydrostations and it is conceivable that sedimentation rates are lower on the flanks of the basin than in the middle. The minimum age of the sedimented material would thus be 10 years cm^{-1}.

Bacterial cell numbers in the sediment (ca. 10 - 20 x 10^8 cells g dry weight) are comparable with sediments from other regions of the world. The bacterial biomass appears to be slightly lower than for instance in the Baltic (L.-A. Meyer-Reil, pers. comm., 1981). Chitinolytic bacterial stains isolated were considerably less active than those forms found in North Sea sediments (D. Thormann, pers. comm., 1981).

All cores investigated were oxic with the exception of one anoxic shallow-water core with high organic input.

4.1 Porewaters

The profiles of DOC and dissolved monomeric sugars for the porewater samples collected show maximum values in the 3 - 4 m layer, below which a marked

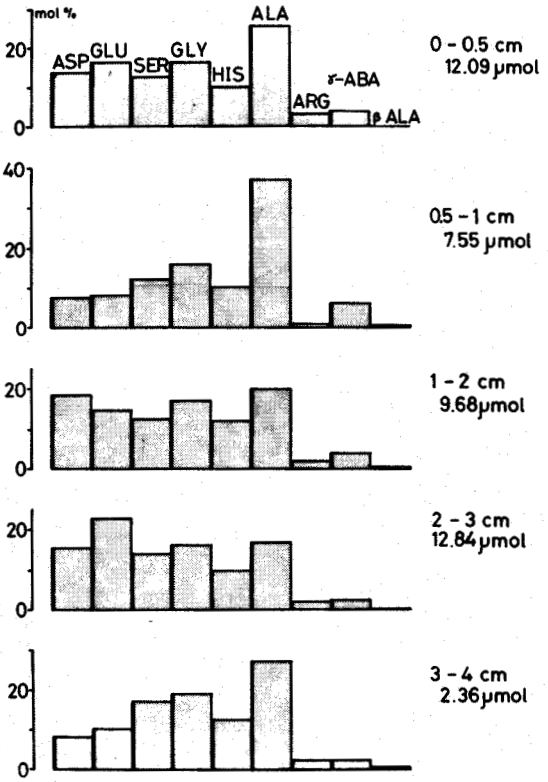

Fig. 10 Relative molar composition of total amino acids in the box core sample. Concentrations given refer to a gram dry weight basis. Abbreviations as in Fig. 3.

The TAA content decreases from the surface to the 0.5 - 1 cm layer and is followed by a marked increase in lower layers. The EFAA concentration remain constant over the first centimeter and shows a minimum in the 1 - 2 cm layer (Fig. 9). If the percentage of EFAA is taken as a measure of heterotophic activity, as evidenced by the presence of cell metabolites such as glutamine and asparagine in this fraction, then the reduction in the levels of these components (5.8 % in the 1 - 3 cm layers compared with a mean of 15 % EFAA above and below) reflects the depletion of utilisable proteins and suggests that the remainder is less attractive or more refractory.

The spectrum of EFAA is clearly dominated by glutamine and alanine with mean values of 21.2 and 27.1 % respectively (Table 2) whereas the spectrum of amino acids in the TAA pool shows a dominance of alanine only in the uppermost layers (Fig. 10). The spectrum of EFAA resembles that of the sediment trap material collected at a similar location.

The role of alanine in the extractable pool is at present unclear but it may be concluded from the relative decrease in this amino acid below the layer of higher microorganism activity (i.e. below 1 cm) that this amino acid is involved in cell metabolism and may be extracted from the intercellular pools.

decrease is discernable reaching more stable values below 8 cm (Fig. 9). Free monosaccharides make up 34.9 ± 9.5 % of the total DOC pool.

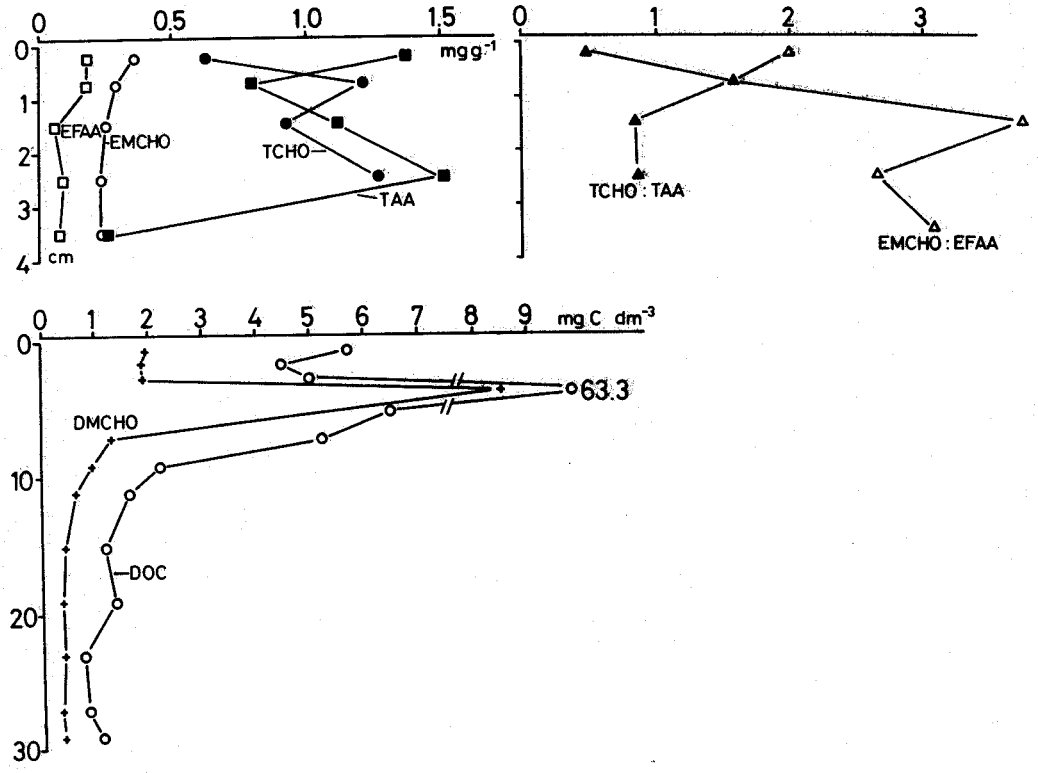

Fig. 9 Concentrations of extractable amino acids (EFAA) and monosaccharides (EMCHO) and total amino acids (TAA) and sugars (TCHO) in the upper sediment layers (upper left). Ratios of sugars to protein (total: TCHO:TAA, extractable: EMCHO:EFAA) (upper right). Profiles of dissolved monosaccharides and dissolved organic carbon in the interstitial waters (lower).

The maximum in DOC concentrations may be related to heterotrophic activity and indeed (G. Graf, pers. comm., 1981) the highest heat production and ATP values below the sediment surface in the same layers.

The unusually high levels of dissolved organic arbon in the porewater suggest a high input of organic matter to these sediments. The decrease in these levels with depth indicates a relatively constant rate of removal of this material.

4.2 Sediment

4.2.1 Amino acid spectra

The results of total amino acid content (TAA) of the sediments sampled in this study (Fig. 10) fall within the range of mean values for surface sediment samples from the Atlantic (0.25 to 17.03 mg g^{-1} d.w.; Degens and Mopper, 1976) and the East China Sea (1.3 to 2.8 mg g^{-1} d.w.; Terashima and Tanaka, 1979). The

Table 2 Relative molar composition of the EFAA pool

depth	0 - 0.5	0.5 - 1	1 - 2	2 - 3	3 - 4 cm
ASP	4.0	4.2	6.9	6.4	6.4
GLU	1.9	1.8	5.0	4.5	5.2
ASN	3.2	2.3	2.7	1.5	1.7
GLN	28.8	28.7	3.6	26.4	18.3
SER	4.0	4.6	8.3	6.1	6.7
HIS	13.6	13.5	17.4	8.5	8.2
ALA	29.1	30.5	28.3	23.0	24.5
GLY	6.4	5.8	14.2	9.3	11.3
ARG	3.9	3.2	8.4	7.0	9.1
-ABA	5.1	5.4	5.2	3.5	4.1
ß-ALA	-	-	-	3.8	4.5
mg g^{-1} d.w.	0.18	0.18	0.06	0.09	0.07

The absolute amounts of alanine in the EFAA fraction has little effect in determining the composition of the TAA or the protein fraction in particular, since only a small percent of amino acids are extracted by the hot water technique (Fig. 9). It is clear from Fig. 10 that alanine must be a major component of structural proteins. The organic matter of the sediments is primarily diatomaceous in nature and the structural polymers should be similar in the sediment and diatom cultures. Hecky et al. (1973) report asparatic acid, serine, glycine and alanine to be the main constituents of the cell walls of cultured diatoms. The uniform spectrum of amino acids in the 1 - 3 cm layers suggest that diatom cell wall material contributes a significant amount of refractory proteins to the sediments.

Nissenbaum et al. (1972) concluded from their investigations in the Dead Sea that acidic amino acids are degraded more rapidly relative to other residues in oxidising environments and may account for the relative depletion of aspartic and glutamic acids in the upper layers. The relative changes in amino acid composition is influenced by a number of biotic and abiotic factors. Monomeric amino acids may undergo condensation reactions subsequent to their release from particulate proteins to reform as high molecular weight aggregates (Brown et al., 1972; Nissenbaum and Kaplan, 1972) and thus be removed from the amino acid pool. Mopper and Degens (1972) reported alanine together with aspartic and glutamic acids and glycine to be the major amino acids of humic material from nearshore sediments.

The observed spectrum of amino acids will be a composite of both organic matter input (with similarities to the source material) and degradation/condensation products formed in the sediments.

4.2.2 Sugars and sugar:protein ratio

The proportion of sugars released upon aqueous extraction as a percentage of the total saccharides for the upper sediment layers shows similarities with sediment trap material and particulate matter filtered at depth (Fig. 7/Table 1).

The ratio TCHO:TAA at the sediment surface (Fig. 9) is almost identical to the ratio for particulate matter filtered below the euphotic zone (Fig. 4) and thus suggests that the material reaching the sediment loses polysaccharides

and proteins at an equal rate during passage through the water column.

The increase of the ratio in the 0.5 - 1 cm layer further supports the finding that heterotrophic activity is higher below the surface than directly at the surface of the sediments and points to a higher remineralisation of nitrogen forms rather than polysaccharides.

The extractable sugar:protein ratio (Fig. 9) shows its minimum at the zone of highest metabolic activity and suggests a preferential removal of sugars from the free pool. The ratio is similar to that found for particulate matter in the water column and increases to higher values with depth in the sediment in a parallel fashion to the transformation of cellular material down the water column.

The organic fraction of the upper sediment layers is augmented with cell metabolites generated in the sediments themselves and the process of resynthesis "refreshes" the originally degraded material with labile metabolites.

5. Summary

To summarise the findings describing the particulate matter leaving the euphotic zone based on filtered samples, the material should have the following qualities if this were the only organic matter reaching the sediment:

1. It has already been modified by secondary biotic and abiotic processes (Fig. 3).
2. It has lost free amino acids relative to sugars (Fig. 5/Table 1).
3. It has lost polysaccharides relative to structural proteins (Fig. 6).
4. It is depleted in water extractable sugars relative to the total (Table 1/ Fig. 7).
5. It is depleted in extractable amino acids (Table 1).
6. It is depleted in cell metabolites such as alanine, histidine, glutamine and decarboxylation products (Fig. 3).
7. It takes on a more protein like structure for the extractable fraction (Fig. 3).
8. It contains a lower proportion of degradable organic matter e.g. pigments are already degraded.

The material probably contains a high proportion of sinking particles which escape collection by filtration techniques. This material may not be phytoplankton and its composition may differ significantly from the particles in suspension above c.f. sediment trap material.

The material recovered in surface sediments shows many similarities with the organic matter recovered in the lower water column particulates e.g. the sugar:protein ratio and the amino acid spectra of the polymeric fraction. Due to secondary processes in the sediments after deposition, the character of the extractable matter changes to reflect the new producers of cell metabolites.

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