Vol. 170: 67–84, 1998 | MARINE ECOLOGY PROGRESS SERIES
Mar Ecol Prog Ser | Published September 3

Seasonal variation of dissolved and adsorbed amino acids and ammonium in a near-shore marine sediment

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ABSTRACT: Dissolved free amino acids (DFAA) and ammonium in the pore water of a coastal sediment at a water depth of 40 m were investigated monthly for more than a year, to improve knowledge on how the concentrations and distributions of these dissolved compounds varied during an annual cycle. Seasonal changes in adsorbed amino acids and ammonium were also studied and adsorption coefficients were calculated. Ammonium distribution in the pore water showed clear seasonal trends. In the warmer period (August and September) there were high concentrations in the pore water, and in winter the lowest concentrations were measured. Pore water concentrations of DFAA were in general low, but showed seasonal trends during the year. At the end of summer when the bottom water temperature reached its maximum (about 14°C), the concentrations of DFAA were also at their maxima. However, a response to the input of organic matter to the sediment was also observed as increased pore water DFAA concentrations. The seasonal response was not strong, which probably was due to several processes (e.g. adsorption, degradation and bacterial assimilation) removing DFAA and thereby preventing large pools of DFAA from being built up in the pore water. Adsorption of ammonium followed the concentration of dissolved ammonium in the pore water and there was neither a relation with input of organic matter nor with temperature in the bottom water. The adsorption coefficient (the dimensionless K) for ammonium was 1.07 ± 0.11 and did not vary during the year The adsorption coefficients for amino acids, which were all higher than K for ammonium, did show seasonal trends and the periods with high concentrations of adsorbed amino acids were related not only to high concentrations of DFAA, but also to recent input of organic matter and probably also to the stimulation of bioturbation as a result of high temperature in the bottom water at the end of summer. The results demonstrated a seasonal variation in K of amino acids, but not ammonium, indicating that the processes controlling dissolved concentrations were substantially different for these compounds.

KEY WORDS: Seasonality · Amino acids · Ammonium · Pore water · Coastal sediment · Adsorption · Adsorption coefficients

INTRODUCTION

Many coastal benthic environments exhibit pronounced seasonality in cycles of nutrient regeneration and sediment-water chemical exchange (e.g. Klump & Martens 1989, Jørgensen 1996). Pore water profiles, benthic fluxes, and transport processes are all strongly influenced by seasonal temperature variations (Blackburn 1980, Klump & Martens 1981). Seasonality is also reflected in benthic systems via fluctuations in the supply of detritus driven by annual cycles in benthic, pelagic and terrestrial primary productivity. Even the deep sea, traditionally thought to be one of the least variable environments on earth, has been shown to be subject to seasonal fluctuations in particle deposition (Rice et al. 1994). These relatively short term oscillations in input will not necessarily alter the steady-state appearance of pore water profiles, yet they may have a significant effect on the rate and timing of nutrient regeneration by benthos.

Previous studies of amino acids in different kinds of marine sediments have examined both the distribution of individual amino acids (mostly in the form of total

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hydrolyzable amino acids) in pore water and sediments as well as the relationship between changes in amino acid concentration and changes in total organic carbon and nitrogen (Whelan 1977, Rosenfeld 1979b, Henrichs et al. 1984, Henrichs & Farrington 1987, Burdige & Martens 1988). These studies have qualitatively demonstrated the importance of amino acids in the remineralization of organic matter. However, except for the studies by Henrichs & Farrington (1987) and Burdige & Martens (1990), there have been few seasonal studies of amino acids and their cycling in sediments. Blackburn (1980) made a seasonal study of ammonium, in an anoxic marine sediment, which showed that ammonium production was closely related to the temperature cycle. Laima (1992) also found in his study of Danish coastal sediments that temperature variations had a pronounced effect on the production rate of ammonium. Otherwise, there seems to be a lack of studies of seasonality in marine sediments and how mineralization rates, adsorption processes and transport processes of amino acids and ammonium are affected by seasonal changes of e.g. temperature, oxygen concentration, organic matter deposition or other parameters which may exhibit sesonal patterns.

Both the composition and the amount of the organic matter have in recent studies been shown to have a strong influence on organic material remineralization in sediments (e.g. Henrichs & Doyle 1986, Sloth et al. 1995, Jørgensen 1996). Diagenesis and adsorption of amino acids seem to depend both on the input rate and the quality of organic material (Rosenfeld 1979b, Wang & Lee 1993). Adsorption to organic material has been shown to be important for amino acids compared to adsorption to clay minerals, and, but to a smaller extent, also for ammonium (Rosenfeld 1979a, b). Therefore it is likely that there is a relation between adsorption and input of organic material, which vary seasonally as a function of variations of primary production. One of the larger sinks for amino acids is probably adsorption. When amino acids have become adsorbed to a sediment particle they can survive degradation and be preserved for a long time in the sediment (Gordon & Millero 1985). How important this process is and how much the adsorption of amino acids affects the distribution in the sediment is not well understood. Laboratory experiments for determining adsorption coefficients of some amino acids using homogenized sediment and addition of labeled amino acids have been made (Henrichs & Sugai 1993, Wang & Lee 1993), but how adsorbed amino acids are distributed in natural sediments in relation to sediment depth and to variation of organic matter input is not well known.

The present seasonal study was performed during a 15 mo period. The objectives were to study how the distributions of dissolved free amino acids and ammonium in the pore water of a near-shore marine sediment vary during an annual cycle and also if variations in the adsorbed (exchangeable) pool of ammonium and amino acids were to be found. Adsorption coefficients for ammonium and amino acids were calculated and we also investigated how the adsorption changed with depth in the sediment. While the composition and content of the organic matter changes with depth it is not unreasonable to suspect that the adsorption of amino acids varies in relation to the organic matter composition. Seasonal variation of adsorption coefficients for both amino acids and ammonium was also measured.

METHODS

Study site. The seasonal study was performed in a coastal sediment of the Gullmar Fjord, western Sweden (Fig. 1). The Gullmar Fjord is 29 km long and the width varies between 1 and 4 km. It is a typical fjord with a sill at 40 m depth and a greatest depth of 120 m in the central part (Fonselius 1990). The total water volume is 2.05 km^3, of which water below the sill constitutes approximately 30% (Svansson 1984).

Two major current systems affect the Swedish west coast: the low saline current flowing northwards along the coast made up by a mixture of Baltic and Kattegat/Skagerrak water, and the flow of water originating from the North Sea/Atlantic bringing more saline water towards the coast from the west (Lindahl 1995). Normally, the water body in the Gullmar Fjord is stratified and the water column is made up of 3 layers: surface water originating from a mixture of Baltic Sea and Skagerrak water (salinity <30), former surface water from the Skagerrak (salinity 30 to 33), and below the sill depth high saline water from the Skagerrak/North Sea area (salinity >33). The Gullmar Fjord has 2 side fjords further up the fjord, Saltkälle Fjord and Färlev Fjord. The only large supply of fresh water to the Gullmar Fjord comes from the river Örekilsälven, which joins the Saltkälle Fjord in its inner part.

The upper pycnocline is between 2 and 20 m depending on season. In winter the upper, less salty water constitutes just a thin layer (about 2 m) and the pycnocline is not as well stabilized as in summer. The second halocline, which constitutes the boundary between the water body in the middle and the deep and almost stagnant water, is more stable and is to be found at 50 to 60 m.

Sandy silt with a rich macrofauna is characteristic for the sediment at the sampling site, which was at the mouth of the fjord, close to the sill, at 40 m depth (Fig. 1). In the well-bioturbated sediment brittle stars dominated the macrofauna (Sköld et al. 1994). There

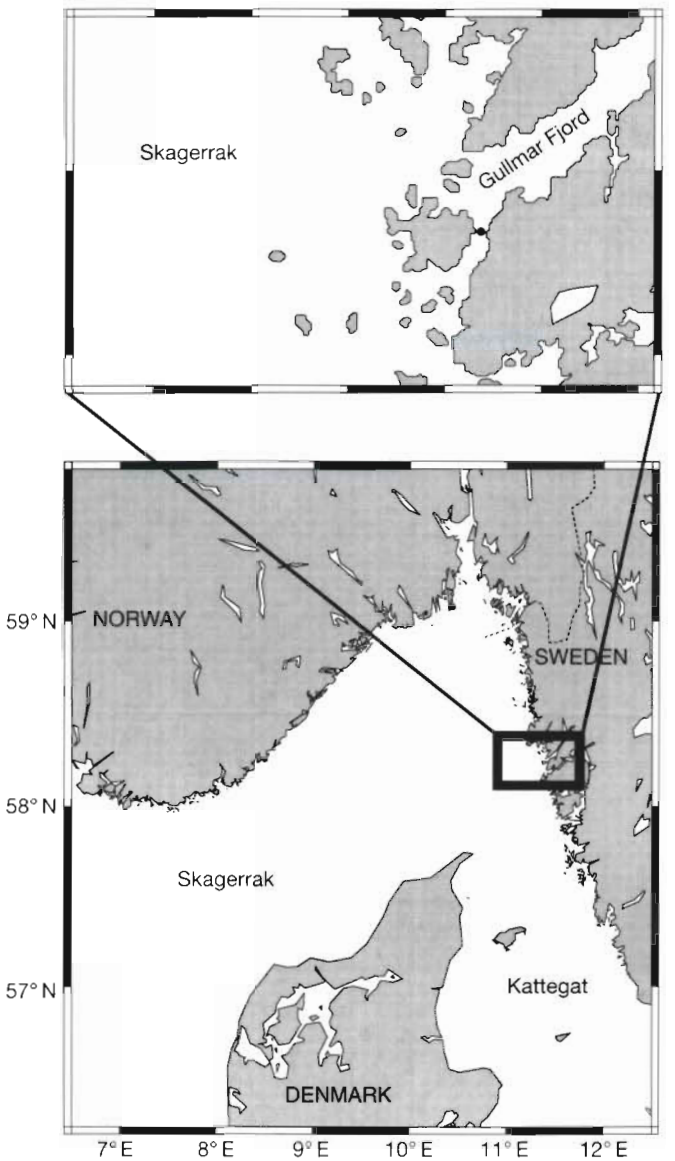

Fig. 1 The Gullmar Fjord and the sampling site (•)

were also polychaetes, urchins (*Brissopsis* spp.) and other echinoderms. Organic carbon content in the uppermost 2 cm of the sediment was between 2.2 and 3.1 (weight % of dried sediment) and decreased to about 2.0 at 10–12 cm depth (Table 1).

The primary production is approximately 200 to 250 g C m^{-2} yr^{-1} in the Gullmar Fjord (Lindahl 1995). At the same time as this study was performed primary production was measured, very close to the sampling site, by Odd Lindahl (unpubl. data) *in situ* from 10 to 20 m depth using a ^{14}C technique, according to Baltic Marine Biologists (1976) (in Lindahl 1988). Oxygen supply is fairly constant at the sampling site during the year, but in the deep basin (120 m) there are normally shorter periods of oxygen depletion in autumn and early winter (Svansson 1984, Fonselius 1990). A more detailed description of the hydrography of the Gullmar Fjord is given by Svansson (1984) and Lindahl (1987).

Sampling procedures. Sediment samples were collected with an improved version of the multiple corer (MUC) described by Barnett et al. (1984) and a box corer (Olausson type, 0.30 m × 0.30 m). The MUC was loaded with 8 plexiglass core tubes with a diameter of 10 cm and length of 60 cm, in which the sediment and about 15 cm of the ambient overlying bottom water was collected. When the box corer was used subsamples were taken with the same plexiglass core tubes from the box immediately after the box corer had been brought aboard. Only cores with undisturbed sediment surface were used. After the overlying water had carefully been siphoned off, the sediment cores were sectioned into depth intervals within 1 h of collection. Pore water was extracted from the sediment by centrifugation [2000 rpm (590 × *g*), 30 min] at *in situ* temperature and the obtained water was subsequently filtered through cellulose acetate filters (0.45 µm pore size), which were precleaned with clean water from a Milli-Q system. Bottom water temperature was measured for each core at every sampling occasion with a thermometer immediately after the cores were brought aboard. Temperature and salinity were also measured with a CTD several times, and temperature obtained with the CTD was compared with the measurements made with the thermometer. Uncentrifuged sediment samples from the various depth intervals were used for determination of carbon and nitrogen as well as for quantification of porosity, which was calculated from the weight of water loss after drying 5 ml of sediment at 70°C for at least 24 h (until constant weight).

Samples for exchangeable amino acids and ammonium were taken simultaneously and from the same core as the pore water samples and were extracted

Table 1. Carbon and nitrogen content in the sediment from the Gullmar Fjord. Range of values represent minimum and maximum values during the year. C_{org}: organic carbon; C_{tot}: total carbon; N_{tot}: total nitrogen. dw: dry weight

Depth (cm)	C_{org} (% of dw)	C_{tot} (% of dw)	N_{tot} (% of dw)	C_{org}/N (molar)
0–1	2.23–2.53	3.62–3.95	0.25–0.34	8.68–10.41
1–2	2.34–3.10	3.61–5.02	0.31–0.36	8.81–10.05
2–4	2.15–3.04	3.24–4.21	0.28–0.35	8.96–10.13
4–6	1.95–2.36	3.32–3.97	0.27–0.33	8.34–8.43
6–8	2.10–2.44	3.19–3.60	0.27–0.30	9.07–9.49
8–10	1.94–2.11	2.91–3.47	0.25–0.26	9.05–9.47
10–12	1.83–2.08	2.80–3.38	0.25–0.26	8.54–9.33

dw = dry weight

with 2 M KCl (Rosenfeld 1979a, Mackin & Aller 1984, Wang & Lee 1990). To 5 ml wet sediment, 5 ml 2 M KCl was added. The mixture was shaken vigorously for 10 min and then centrifuged (590 × *g*, 15 min). This centrifugation-extraction method was not further optimized for this study. The obtained water (supernatant) was then subsequently filtered through precleaned cellulose acetate filters (0.45 µm). All samples were then stored in glass test tubes at –22°C. All glass tubes were thoroughly cleaned, soaked in HCl solution and silanized (coated with dimethyldichlorosilane inside) in order to create a hydrophobic surface and thereby preventing loss of analytes to the glass tube walls due to adsorption. The tubes were then rinsed with toluene, methanol and several times with Milli-Q water. Plastic gloves were worn at all times to avoid contamination.

Analytical procedures. Dissolved free amino acids (DFAA) and ammonium in the pore water and KCl-extracted samples were determined with reversed phase HPLC using a Jasco 800 instrument. The procedure was similar to the method described by Lindroth & Mopper (1979). The HPLC system was fully automatic and placed in a room with constant temperature, 20°C. While ammonium and beta-amino glutaric acid (β-glu) are not normally included in the commercial amino acid standards, they were added in suitable concentrations to a Pierce standard. As derivatization reagent, *o*-phthaldialdehyde-2-mercaptoethanol (OPA) was used. The fluorescence of the OPA-derivatives was measured using a Jasco fluorometer (excitation = 330 nm, emission = 455 nm). Peak areas were integrated and converted to concentrations by their respective fluorescence factors, which were generated for the pure OPA-derivative of each amino acid in the standard solution.

All amino acids in the standard (17 individual amino acids) were separated with good resolution on a HICHROM C18 15 × 0.46 cm column with a flow rate of 1.5 ml min^{-1}. The solvent gradient was formed using HPLC-grade methanol and phosphate buffer, pH 7.0 with 1% tetrahydrofuran (THF). We used a 34 min gradient elution program beginning at 25% methanol and 75% phosphate buffer and ending with 70% methanol, with a number of isocratic steps in the program. Amino acid standards were analyzed both in pure lab water (Milli-Q water) and in artificial seawater in order to check if the ionic strength would affect the elution of amino acids. Since the elution order and retention time were exactly the same in the 2 solutions, all subsequent analyses of the amino acid standard used pure lab water.

The detection limit of this method is approximately 2×10^{-13} mol per injected amino acid (except for lysine where the detection limit is 4×10^{-13} mol) and 5×10^{-13} mol for ammonium. The fluorescence intensity for the OPA-ammonium derivative is lower than for the OPA-amino acids, so the concentration of ammonium in the standard was 10 times higher than for the amino acids. Analytical precision (several repeated injections with a 20 nM amino acid standard solution) was for most of the amino acids less than 7% RSD (relative standard deviation).

Total carbon, organic carbon and total nitrogen in the solid phase of the sediment were determined in dried samples by thermal combustion using a Carlo Erba CHN elemental analyzer.

Calculation of adsorption coefficients. After the sediment had been shaken with 2 M KCl, centrifuged, and the supernatant filtered, the individual amino acids and ammonium in the extracted solution were separated and quantified with HPLC as described above. To calculate the exact amount of exchangeable amino acids or ammonium, the contribution from pore water has to be subtracted:

$$C_{ads} = [(C_{tot} \times V_{tot}) - (C_{pw} \times V_{pw})] / [(5 - \Phi \times 5) \times \rho]$$
(nmol g^{-1} dried sediment)

where C_{ads} = carbon adsorbed, C_{tot} = total carbon, C_{pw} amount of carbon in the pore water, ρ = dry sediment density (assumed to be 2.65 g ml^{-1}), Φ = porosity of the sediment, and V_{pw} = volume of pore water = Φ × 5 (5 ml of wet sediment used).

After correction for concentration in the pore water, adsorption coefficients, K_{ads}, were calculated from the regression line of the exchangeable amino acid or ammonium plotted as a function of the corresponding dissolved free substance in the pore water [K_{ads} = (nmol adsorbed g^{-1} solid)/(µmol dissolved l^{-1} solution)]. K, the dimensionless equivalent of K_{ads}, was calculated using the expression from Berner (1980):

$$K = \frac{1-\Phi}{\Phi} \times \rho \times K_{ads}$$

Estimation of sedimentation. An estimation of sedimentation rate could be made with knowledge of total primary production. Primary production was measured biweekly very close to the sampling site (see above) and a mean value of the primary production per month was used in the calculation of sedimentation rates. Sedimentation rates were calculated using the model presented by Wassmann (1990a):

$$P_E = 0.049 \times P_T^{1.41}$$

where P_E is the export production of particulate organic carbon (POC) out of the photic zone and P_T is the total primary production.

This equation was found by Wassmann (1990a, b) to be valid for the boreal coastal zone of the North Atlantic, but only when total primary production ranges from 60 to 250 g C m^{-2} $period^{-1}$. The ratio P_E:P_T

has an upper limit in the boreal coastal environments of about 0.5, but over shorter intervals higher $P_E:P_T$ ratios (up to 0.8) can be measured. In our case, the $P_E:P_T$ ratio was mostly around 0.5, and we used this model to estimate the sedimentation rate for each month throughout the 15 mo study period. While P_E is the export production out of the photic zone, some assumptions have to be made before we can take it that the export production is close to the sedimentation to the seafloor. The photic zone in the Gullmar Fjord is about 15 to 20 m deep and there is no pycnocline between the bottom of the photic zone and the sediment of the sampling site at 40 m depth. There is a small outflow of the surface water and a small inflow of the Skagerrak water, but horizontal transport is not strong at this site because of the topography (several small islands around and outside the sampling site). The important water exchange in the Gullmar Fjord takes place north of the sampling site over the central part of the sill into the fjord. Because of the short distance between the bottom of the photic zone and the seafloor, the degradation of POC in the water column from the photic zone down to the bottom should be very small. For these reasons we assume that the export production is close to the primary sedimentation flux to the sediment, and we use the estimate of export production as a measure of the net POC input to the seafloor.

This method gave us an estimate of sedimentation over the year and fitted our needs for this study.

Statistics. A paired *t*-test (95% significant level) was used to compare the 2 sediment sampling methods, the MUC and the box corer. Monthly differences were tested using analysis of variance (ANOVA) after Cochran's test for homogeneity of variances. If the ANOVA showed significant differences between months a Student-Newman-Keuls test (SNK test) was used to analyze which month differed. While replicates were not taken each month, some of the variances used in the ANOVA model are 'borrowed', which means that a mean value of all other variances (for each analyte, respectively) was used for those cases.

RESULTS

Bottom water temperature and sedimentation to the seafloor

Bottom water temperature was measured every month during the study period and the lowest bottom water temperature (2.5°C) was found in March and the warmest (15.0°C) in September (Fig. 2). This is a normal temperature cycle in the Gullmar Fjord at the depth of 40 m (Fonselius 1990) and agrees well with other temperature measurements in the fjord. Primary production was about 230 g C m^{-2} yr^{-1} and the estimated sedimentation 105 g C m^{-2} yr^{-1}. Monthly sedimentation rates were estimated according to the model of Wassmann (1990a, b) and are shown together with primary production in Fig. 3.

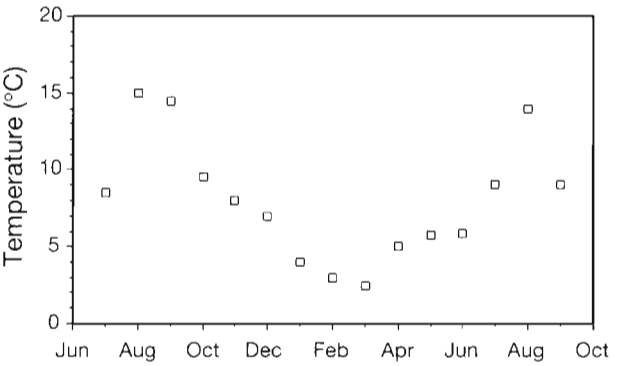

Fig. 2. Temperature in the bottom water during the year

Distribution of amino acids and ammonium in pore water

DFAA in the pore water were mainly protein amino acids. Taurine, ornitine and other amino acids not included in the standard solution were rare in the samples. Chromatograms showing a pore water sample (0 to 1 cm) and a KCl extract (0 to 1 cm) are presented in Fig. 4. The concentration of total DFAA (the sum of 16 individual amino acids) did not exceed 4 µM in any month during the year. The highest value (3.8 µM) was measured in August 1992, and the lowest (0.238 µM) in February 1993. All amino acids were in low concentrations, compared to other similar studies, but the concentrations of DFAA tended to increase at the end of summer. The largest concentrations of amino acids were found in the uppermost centimeter of

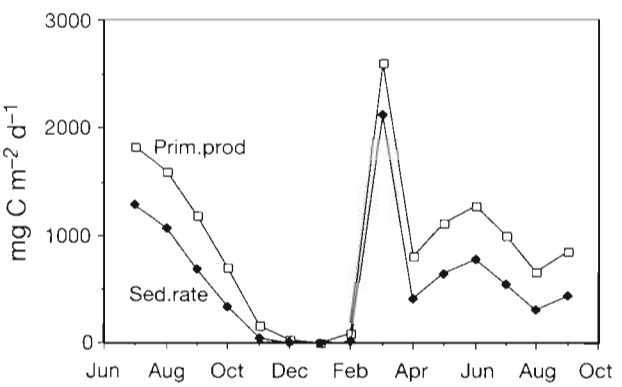

Fig. 3. Primary production and estimated sedimentation during the year

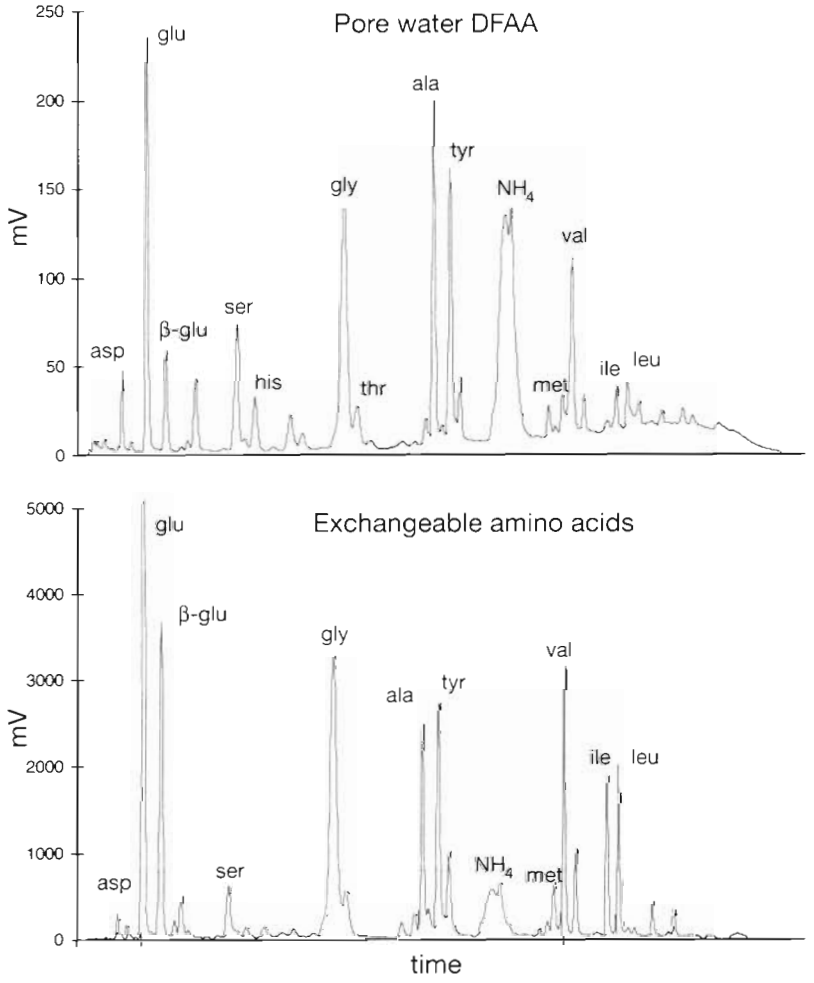

Fig. 4. Typical chromatograms from a pore water sample and a KCl extract. Upper: a pore water sample from 0–1 cm. Concentration range in this sample was between 13 nM [methionine (met)] and 780 nM (ammonium). Lower: a KCl extract from 0–1 cm. Concentration range in the KCl extract was between 0.117 µM (Met) and 7.07 µM glutamic acid (glu)]. Elution order: asp, aspartic acid; glu, glutamic acid; β-glu, β-aminoglutaric acid; ser, serine; his, histidine; gly, glycine; thr, threonine; ala, alanine; tyr, tyrosine; val, valine; ile, isoleucine; leu, leucine

the sediment. The concentration of DFAA decreased slightly with depth, with the exception of leucine. For leucine the concentration increased slightly with depth. Glycine showed a submaximum between 1 and 2 cm depth in late summer, which none of the other amino acids did. Pore water profiles of the most abundant amino acids, which were aspartic acid, glutamic acid, serine, glycine and sometimes alanine and leucine, are shown in Fig. 5. Ammonium increased with depth during all months but with different slopes of the pore water gradient (Fig. 5).

One way to visualize the seasonal variation of the DFAA in the pore water is to draw isopleths. Pore water ammonium showed clear seasonal trends during the year. In the uppermost surface sediment the concentration varied from 10 to 25 µM in winter and from 40 to 60 µM in late summer (Fig. 6). Looking at the isopleths of amino acids, a rather complex pattern at first emerged. All of the amino acids showed a small increase in concentration in the uppermost sediment in late summer. This increase could also be seen a few cm down in the sediment. In the period January to April, most of the amino acids showed high concentrations at 5 to 9 cm depth. Variations in concentration over the year for serine, one of the most common amino acids in this sediment, was between 0.05 and 0.6 µM in the uppermost cm, with the highest value in August. Other amino acids like aspartic acid, glutamic acid, glycine and alanine showed a concentration range, in the uppermost part of the sediment during the year, of 0.02–0.25, 0.02–0.3, 0.05–0.8 and 0.01–0.5 µM, respectively.

Differences between months or seasons?

The paired *t*-test (95% confidence intervals) showed no significant difference between cores taken at the same time with the MUC and the box corer, with respect to each substance (ammonium, aspartic acid, glutamic acid, serine and alanine) which was measured in the pore water of all cores. For pore water sampling in this sediment, these 2 sampling methods were therefore considered to be equal.

A 2-factor ANOVA model (with SNK test) was used to see if there were significant differences between months and/or seasons. The first factor was months divided into 15 levels (15 months) and the second factor was depths divided into 2 levels (2 depths, 0–1 and 1–2 cm). All amino acids, except for glycine, showed higher concentrations in the uppermost surface sediment, the first level (0–1 cm), and ammonium had higher concentrations in the second level. In the case of ammonium, the SNK test showed that August and September were significantly different compared to the rest of the year. October, November, May, June and July formed another group which also differed significantly from the last group, December to April. Three groups were identified, of which 1 group could be

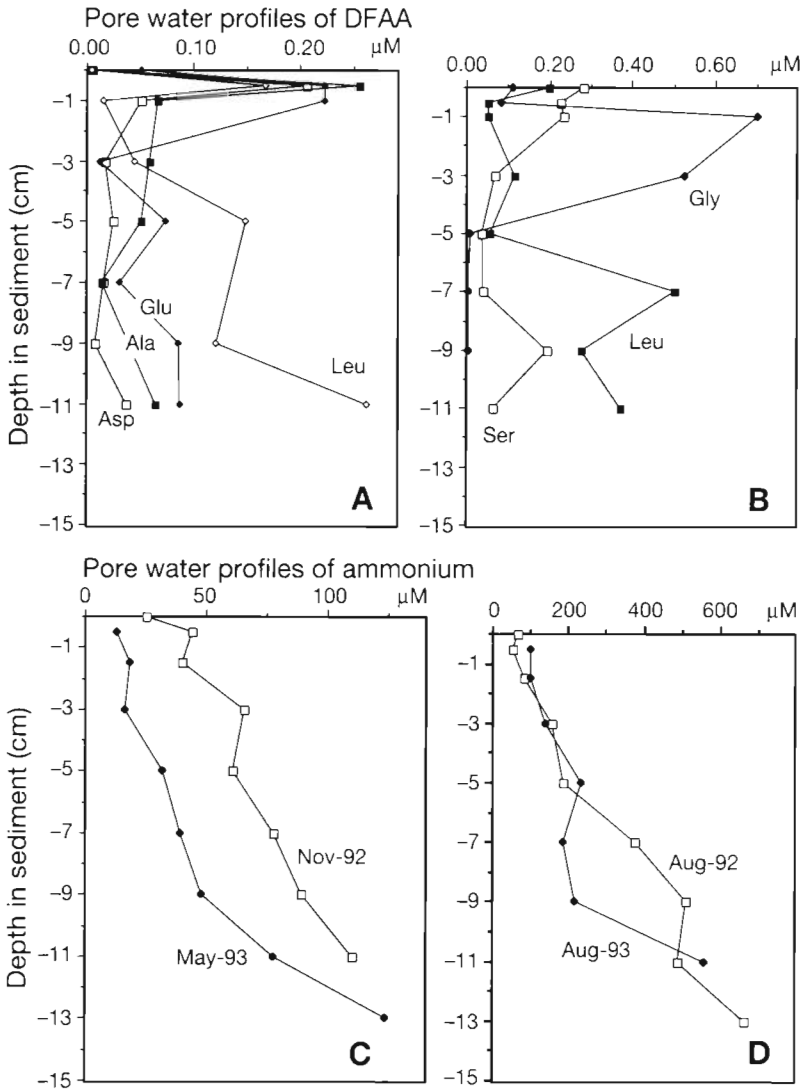

Fig. 5. Typical pore water profiles of amino acids and ammonium. Concentrations at depth zero are bottom water concentrations. (A) Aspartic acid, glutamic acid, alanine and leucine from August 1993. Leucine showed a small increase with depth, which not was observed for the other amino acids. (B) Serine, glycine and leucine from September 1993. (C) Ammonium from November 1992 and May 1993. (D) Ammonium from August 1992 and 1993

divided into 2 (Table 2). In other words 4 seasons could be defined for ammonium: (1) the long winter, consisting of December to April, (2) spring and early summer, consisting of May, June and July, (3) late summer, consisting of August and September, and (4) autumn, formed by October and November.

The same model was used for the amino acids and a similar, but not quite as regular, pattern emerged. The 4 seasons could also be defined for the amino acids. All amino acids showed a significant difference between late summer and the rest of the year, but in the other seasons the amino acids showed rather individual trends. Aspartic acid and glutamic acid both showed a small increase in concentration in April after the winter with low and almost uniform concentrations. There were no significant differences between months from November to June, except for the small increase in April. In July and October the concentration was slightly higher compared to the winter months. Serine showed, except for August and September (late summer), a small increase in April, otherwise there were no significant differences between months from February to July. In October and November the concentrations were almost as low as in the winter months. Glycine also showed high values in late summer and a small increase in April and July. In general glycine showed higher concentration in depth 2 (1 to 2 cm); all the other amino acids were for most of the time higher in the surface sediment and decreased further down.

Table 2. Differentiation of the months into different groups by ANOVA. '1' represents periods with the highest concentrations and '3' represents the lowest concentrations. For amino acid definitions, see Fig. 4 legend

	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
NH_4^+	2	1	1	2	2	3	3	3	3	3	2	2	2	1	1
Asp	2	1	1	2	3	3	3	3	3	2	3	3	2	1	1
Glu	2	1	1	2	3	3	3	3	3	2	3	3	2	1	1
Ser	3	1	1	3	3	3	3	3	3	2	3	3	3	1	1
Gly	2	1	1	3	3	3	3	3	3	2	3	3	2	1	1
Ala	2	2	2	3	3	3	3	3	3	3	3	3	2	2	2

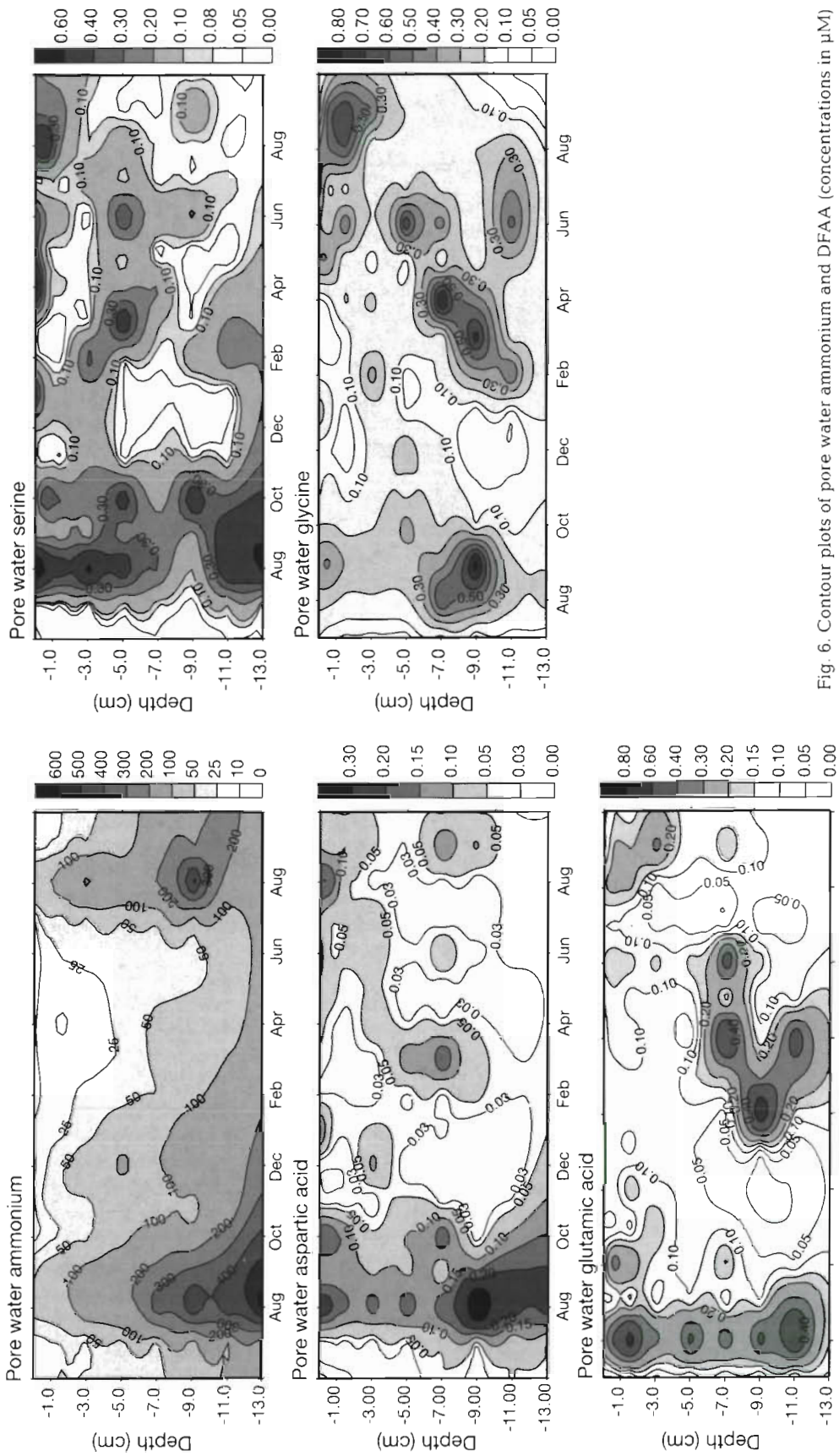

Fig. 6. Contour plots of pore water ammonium and DFAA (concentrations in µM)

Alanine was in relatively high concentration in July to September; all other months of the year the concentration was lower and quite uniform (Table 2).

Adsorption of amino acids and ammonium

To illustrate how the adsorbed (exchangeable) amino acids and ammonium varied with depth in the sediment and with season, contour plots (isopleths) were drawn (Fig. 7). Adsorption of ammonium was higher in late summer compared to the rest of the year, and in general the amount of adsorbed ammonium increased with depth. The behaviour of the amino acids was different from ammonium in that adsorbed amino acids normally were in high concentrations at the sediment surface and decreased with depth. All adsorbed amino acids showed similar patterns. The amount of adsorbed ammonium was related to the amount of dissolved free ammonium in the pore water, while the amount of adsorbed amino acids were just partly related to the DFAA in the pore water.

Adsorption coefficients were calculated plotting concentrations of DFAA or ammonium in the pore water as a function of adsorbed concentrations, and the slope of the regression line was taken as the adsorption coefficient (K_{ads}). In the regression analysis 5 to 9 data points were used for each plot (15 plots for 15 months) and the regression coefficients, r^2, were 0.50 to 0.95. To see if K_{ads} changed with depth, values for every month and each depth (15 values for each depth in the sediment = 1 mean value for each depth) were used to calculate depth specific mean values of K_{ads} in the sediment. Regression analysis was made and the linearity was accepted as significant when $p < 0.05$. For each plot (7 plots for 7 depths) 10 to 15 data points (for each compound) were used and the r^2 were 0.50 to 0.90. K_{ads} for amino acids were all higher in the uppermost layer of the sediment (Table 3). For aspartic acid and glutamic acid, K_{ads} (mean K_{ads} for the year) were very high in the first 4 to 6 cm, and deeper K_{ads} were much lower and nearly constant. The other amino acids showed similar trends but it was just the first 1 or 2 cm which were higher. In general, for all amino acids, the uppermost part of the sediment showed the highest K_{ads} and this was clearest in late summer. K_{ads} (mean K_{ads} for the year) for ammonium did not vary with depth, and had a mean value of 1.27 ± 0.14 (if 0.61 is treated as an outlier).

K_{ads} for each month were then used to calculate the dimensionless K per month, using a mean porosity for the 0 to 12 cm depth of the sediment. Annual mean values of K could be calculated for each species in 2 different ways: the sum of K for all the individual depths in Table 3 divided by the number of depths, or K_{ads} for each month transformed to K with the mean porosity for the top 12 cm of the sediment, divided by the number of months (Fig. 8). These 2 mean K for the year should be equal and the difference between them was very small (Table 4).

Adsorption coefficients

Adsorption of ammonium varied seasonally, but K did not show any significant variation with season. K (valid for 0 to 12 cm in the sediment) had a mean value over the year of 1.07 ± 0.11 and this small variation could not be related to any seasonal variation of bottom water temperature or input of organic matter (Fig. 8).

There were large variations of K for the amino acids during the year, but the pattern in which K varied was similar for all amino acids. K was low in winter and increased after the spring bloom; later in autumn K decreased again. The seasonal variations of K for the amino acids in the sediment appeared to be more obvious in the uppermost zone whereas the variations were smoothened out further down in the sediment.

Table 3. Adsorption coefficients (K_{ads}) and dimensionless adsorption coefficients (K) for the most common amino acids and ammonium. K_{ads} and K are mean values for the 15 mo study period. *$r^2 < 0.5$, $p > 0.05$. dm = data missing. Φ = porosity of the sediment

Depth	Φ	Asp		Glu		Ser		Gly		Ala		NH_4^+	
		K_{ads}	K	K_{ads}	K	K_{ads}	K	K_{ads}	K	K_{ads}	K	K_{ads}	K
0–1	0.88	20.1	7.3	71.5*	25.8	15.1	5.5	12.9	4.7	35.1*	12.7	1.44	0.52
1–2	0.80	6.94	4.6	35.0	23.2	7.57	5.0	5.69	3.77	19.2	6.9	1.14	0.75
2–4	0.79	19.9	14.0	22.4	15.8	7.65	5.4	4.26	3.00	16.4	10.8	1.19	0.84
4–6	0.76	11.7	9.79	13.2	11.0	3.58	3.0	2.58	2.08	13.9	9.81	0.61	0.51
6–8	0.74	1.26	1.14	14.4	13.1	3.4	3.1	6.82	6.19	8.57	7.17	1.12	1.02
8–10	0.72	1.13	1.2	22.5	20.9	dm	dm	4.05	3.77	5.61	5.09	1.44	1.40
10–12	0.71	1.78	1.96	18.9	20.8	dm	dm	dm	dm	dm	dm	1.29	1.39

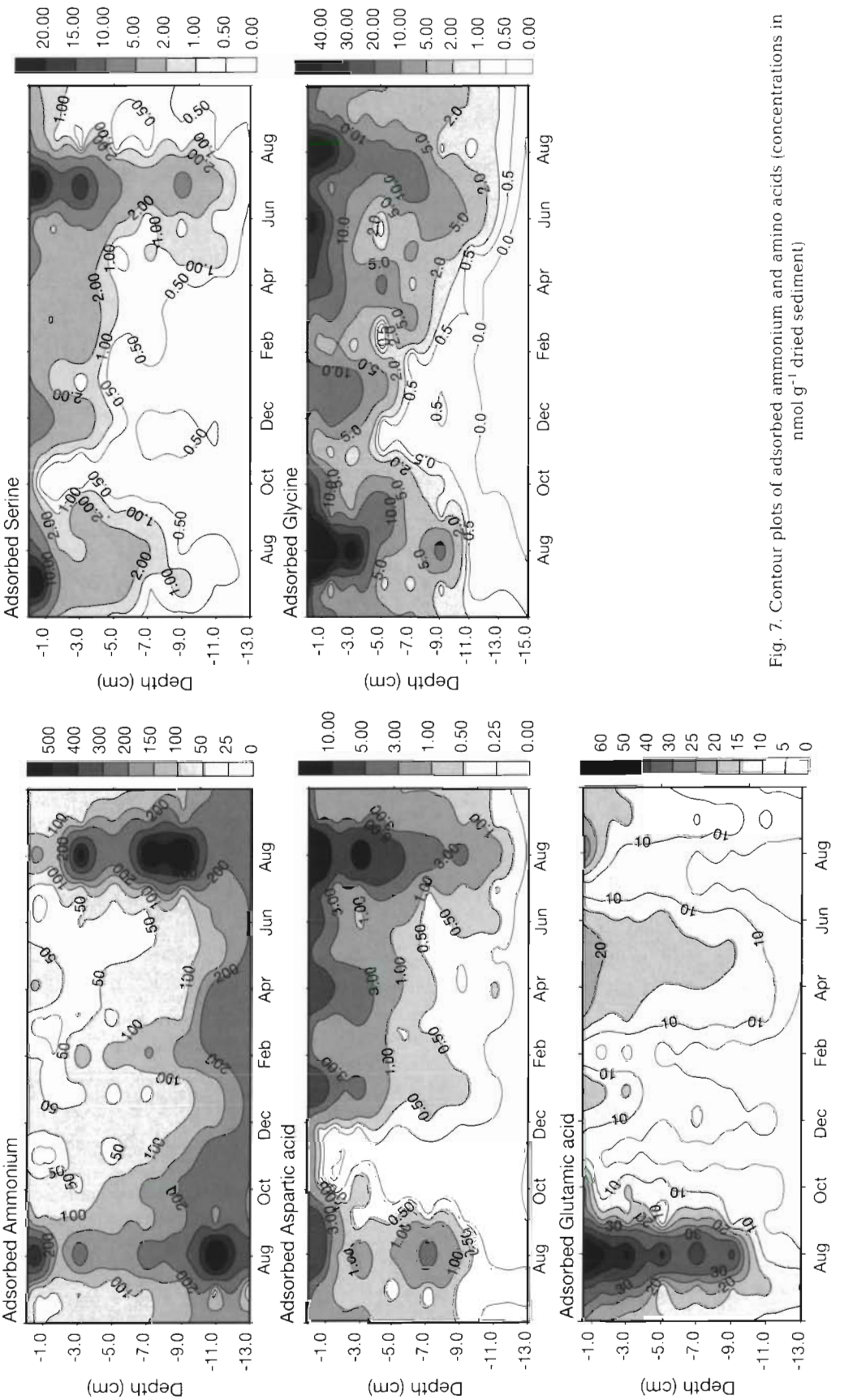

Fig. 7. Contour plots of adsorbed ammonium and amino acids (concentrations in nmol g^{-1} dried sediment)

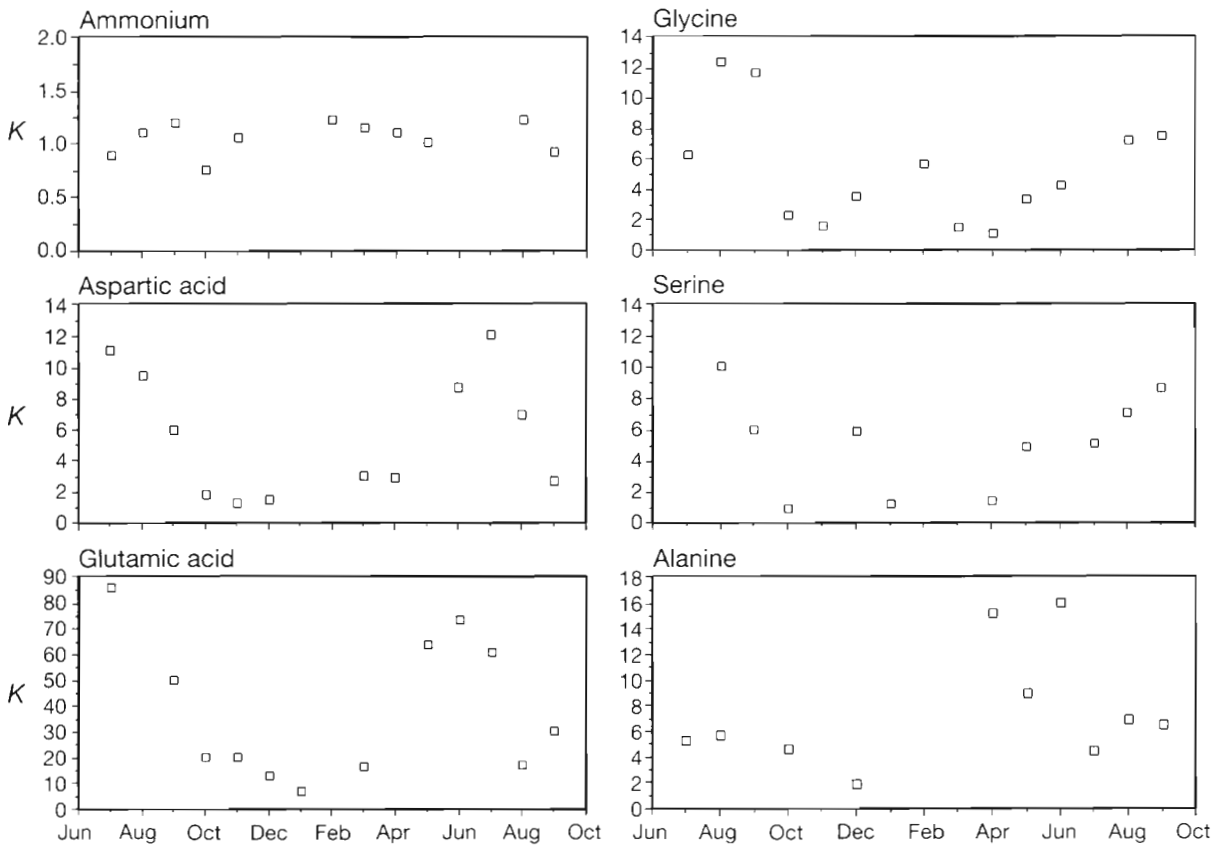

Fig. 8. Seasonal variation of adsorption coefficients (K) for depth 0–12 cm during the year for ammonium, aspartic acid, glutamic acid, glycine, serine and alanine

DISCUSSION

Amino acids and ammonium distribution in pore water

Distribution of DFAA in the sediment from the Gullmar Fjord was similar to the distribution found in other organic rich sediments (e.g. Henrichs et al. 1984, Henrichs & Farrington 1987, Burdige & Martens 1990), but the concentration of DFAA was lower. In the sediment from Buzzards Bay, Massachusetts, Henrichs & Farrington (1987) found concentrations of total DFAA of about 30 µM in the surface sediment from the sampling station at 13 to 16 m depth. In the highly reducing sediment from Cape Lookout Bight, North Carolina, Burdige & Martens (1990) measured total DFAA in a concentration range of 20 to 60 µM in the surficial sediment. Sugai & Henrichs (1992) found concentrations of total DFAA in the sediment from 60 m depth in Thumb Cove, Resurrection Bay, Alaska, in a similar range as in the sediment from the Gullmar Fjord. Different concentrations of amino acids in different sediments can be explained by several factors: differences in the quantity and quality of organic matter input; differences in production, degradation and assimilation rates of amino acids and in the balances between these rates; and differences in adsorptivities. There may also be a relation between high concentrations of DFAA and the sulfide content of sediments (Henrichs et al. 1984, Burdige 1989, Burdige & Martens 1990).

Table 4. Annual mean values of K for the whole core calculated in 2 different ways. Mean K from Table 3 and mean K from Fig. 8

	NH_4	Asp	Glu	Ser	Gly	Ala
Table 3	1.0	5.7	18.6	4.4	5.1	7.5
Fig. 8	1.1	7.0	38.3	5.2	5.3	7.6

The activity of benthos in the sediment (including micro-, meio-, and macrofauna) varies depending on temperature, oxygen concentration and input of organic matter, and this may also alter the rates of mineralization (e.g. Blackburn & Henriksen 1983, Klump & Martens 1989, Landén et al. unpubl.) which influence the distribution of dissolved species in the pore water. This sediment, close to the sill in the Gullmar Fjord, is well oxygenated and bioturbated by macrofauna

throughout the year. The overlying bottom water at the sampling site is well oxygenated throughout the year. One explanation for the lower DFAA concentrations found here compared to other sediments may be that adsorption of amino acids was higher in this sediment. K for glutamic acid, aspartic acid (with exception of the depths 6 to 12 cm), alanine, serine and glycine were all higher (see below) than for ammonium and also higher than laboratory determined K for the corresponding amino acids (Henrichs & Sugai 1993, Wang & Lee 1993). In the study of Wang & Lee (1993) glutamic acid and alanine had adsorption coefficients (slopes of regression line, K_{ads}) of 11.0 and 9.1, respectively, which is lower for glutamic acid but in a similar range as in this sediment. In the sediment slurry used by Henrichs & Sugai (1993) the determined K for glutamic acid and alanine was much lower, 0.50 and 0.37, respectively. Organic carbon content in the sediment used by Henrichs & Sugai (1993) was low (0.6 to 0.7%) compared to the sediment used by Wang & Lee (1993) (Flax Pond, Long Island, New York) which had an organic carbon content of 2.8%, similar to the sediment in this study. The content of organic carbon in this sediment was measured 4 times during the year, but there seems to be no seasonal trend for the total organic carbon. The composition, however, of the organic matter may be different during the year due to seasonal variations of degradation rates of the settled organic matter. We suggest that the higher adsorption in the sediment from the Gullmar Fjord may be due to the high organic carbon content, but also to the composition of the organic matter reaching the seafloor and the intensive bioturbation, which may provide attractive sites for adsorption of amino acids by exposing new surfaces in the sediment.

Distributions of amino acids and ammonium have been studied in pore waters at different sites, but there are few reported studies of how the distribution changes during annual cycles. Burdige & Martens (1990) did a 14 mo study of an anoxic sediment and they found no strong seasonal variations in the DFAA profiles. A conclusion made by Henrichs et al. (1984), from their study of Peruvian sediments, was that the major features of DFAA concentrations and compositions in sediment were probably due to production and consumption by bacteria. Microbial activity in coastal marine sediments at most sites in the temperate zone is generally regulated by seasonal changes of input of organic matter, bottom water temperature and oxygen concentration. Laima (1992) did a seasonal study of Danish coastal sediments, which were highly influenced by seasonal changes in temperature and organic matter input, and found that even the tightly bound pool of ammonium in the sediment (shaken several times with potassium chloride) varied seasonally. Therefore, another factor which may have a great influence on the seasonal distribution of dissolved ammonium, and also of DFAA, in sediments is adsorption.

Comparing sedimentation rates (Fig. 3) and the distribution of ammonium in the pore water (Fig. 6), there were no obvious relations. Variation in the distribution of ammonium in the pore water seemed to be much more related to the seasonal changes in the bottom water temperature (Fig. 2) than to input of organic matter. Ammonification (like other biological processes) is shown to be dependent on temperature (Blackburn 1980, Kemp et al. 1990), and the production of ammonium most probably increased when the temperature in the bottom water increased at the end of summer. This is also what other investigations have shown (Blackburn & Henriksen 1983, Klump & Martens 1989). Temperature seemed to be the paramount seasonal factor affecting ammonium occurrence in this pore water.

The seasonal variation of the amino acid distributions in the pore water did not appear to be mostly dependent on bottom water temperature as did ammonium. The contour plots of DFAA were compared to the sedimentation rates (Fig. 3) to see if high concentrations of DFAA could be related to recent input of organic matter to the sediment. In late autumn and most of the winter there were low concentrations of DFAA in the uppermost pore water, and sedimentation rates were also low or zero. Primary production started in March and after input of fresh organic matter there was a response in the sediment observed as increased concentrations of DFAA. In the uppermost pore water the concentrations of DFAA increased in spring and reached maxima in the warmest period (August and September) in most cases. Samples were taken monthly in this study and the sediment response of organic matter input in March could therefore be seen in April for most of the DFAA. The time-lag in this sediment (the time it takes before a response to the sedimentation event can be observed in the sediment) appeared to be a few weeks. After the big algal bloom in March the primary production continued, but at lower rates, during spring, summer and early fall, and DFAA concentrations increased due to both delivery of fresh organic matter and increasing temperature in the bottom water.

There was no large pool of DFAA in any season during the year. Amino acids are intermediates in degradation reactions and the fate of amino acids is not always easy to predict. When bottom water temperature increased or input of fresh organic matter increased, followed by increased mineralization rates (Landén et al. unpubl.), no obvious pool of amino acids was built up. Most probably there was an increased production of DFAA, but higher benthic activity will

also increase the assimilation and degradation rates, and amino acids are commonly used by benthic microorganisms as a nitrogen source. However, bacterial assimilation and degradation is not the only sink for amino acids; there are other additional sinks, of which adsorption is one of the larger. All this makes the interpretation of the seasonal distribution pattern complicated. One explanation as to why we did not observe a more obvious seasonal variation of DFAA distributions may be that the rate of consumption of amino acids increased with higher benthic activity: greater assimilation, greater degradation, and higher adsorption (K for amino acids did vary during the year). This means that we probably did not see the whole picture; the enhanced production rates of DFAA during parts of the year were smoothened out by higher rates of consumption and adsorption.

Adsorption of amino acids and ammonium

One of the possible sinks for DFAA in sediments is adsorption, which may be an important way to preserve amino acids from further degradation. Amino acids and ammonium can be adsorbed to surfaces of sediment particles, including organic material, or be incorporated into humic substances. Several studies of amino acid adsorption (Rosenfeld 1979b, Henrichs & Sugai 1993, Wang & Lee 1993) and ammonium adsorption (Rosenfeld 1979a, Boatman & Murray 1982, Mackin & Aller 1984, Laima 1992) have been made and adsorption coefficients for ammonium and some of the amino acids have been calculated.

When calculating adsorption coefficients for ammonium and amino acids it is in most cases assumed that there is a linear relationship between dissolved free substances and the corresponding adsorbed substances (Berner 1980). Physiochemical processes are assumed to be of major importance in the adsorption/desorption processes of DFAA and ammonium in this sediment. Neutral and acidic amino acids are suggested to undergo reversible adsorption, while basic amino acids adsorption are probably irreversible and may preferentially undergo condensation reactions (Jørgensen et al. 1981). DFAA and ammonium were plotted against the adsorbed (exchangeable) concentrations for each depth and all months. Compared to ammonium there were sometimes bad regression lines in the plots of DFAA versus adsorbed amino acids, mostly because of one point which seemed to be very much off the line. This point was in all cases the sample from the uppermost part of the sediment, 0 to 1 cm. This made us believe that there was not a simple linear adsorption throughout the sediment core. In the uppermost centimeter the amino acids adsorbed to the sediment to a much higher extent than further down in the sediment, probably due both to the high content of fresh organic matter and its specific composition. This indicated that amino acids compared to ammonium adsorbed to a much greater extent to organic matter than to clay minerals in the sediment. This is also what has been found in other studies (Rosenfeld 1979b, Henrichs & Farrington 1987, Wang & Lee 1993). Also K for amino acids varied during the year and appeared to vary with input of organic matter, which can be explained with the same theory. Fresh organic matter might provide more attractive sites for amino acid adsorption than do older and more refractory material and mineral particles. Since the data from the uppermost surface sediment (0 to 1 cm) was removed from the plot the assumption of a linear relationship fitted well for the rest of the sediment cores (Fig. 9, for serine). Another potential explanation for this pattern could be that the KCl treatment damages invertebrate cells and higher amino acid concentrations in the KCl extract may therefore be due to release of intracellular free amino acids. Invertebrates, e.g. molluscs and polychaetes, contain taurine as a major amino acid, together with alanine and glycine (Jørgensen et al. 1981). In pore water samples or the KCl extract from this site neither taurine nor particularly high concentrations of alanine or glycine were found. This made us believe that contributions of intracellular free amino acids from damaged infauna was a minor source of amino acids in the samples.

In the contour plots of adsorbed amino acids (Fig. 7) it can be seen that the highest concentrations of adsorbed amino acids were found in the surface sediment, and the amount of adsorbed amino acids in-

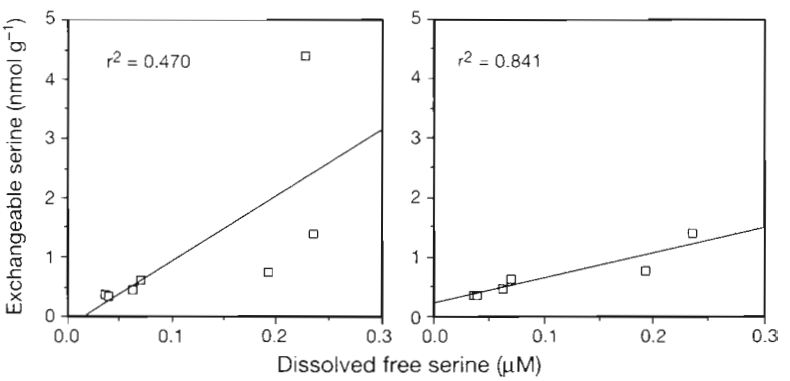

Fig. 9. Adsorbed serine plotted as a function of dissolved free in the pore water. (A) All data included, (B) all data except the value from the uppermost (0–1 cm) part of the sediment included

creased at the end of summer when the bottom water temperature was higher. One suggestion as to why the adsorption was higher in summer may be a combination of the higher benthic activity (more amino acids were hydrolyzed from peptides and proteins when degradation rates increased) and more intensive bioturbation, which changed the composition of the organic matter in the sediment making new sites for amino acid adsorption available. This means that adsorption of amino acids did not necessarily depend directly on bottom water temperature, but some other processes which in turn were related to the bottom water temperature.

The uppermost part of the sediment involves a very dynamic system. Amino acids are intermediates in the degradation processes which always occur both in the oxygenated part of the sediment and in the anoxic layers. One way to preserve amino acids in sediments is adsorption, and to what extent this will occur depends on several factors, e.g. content and composition of organic matter, available sites in clay minerals, and bioturbation. The adsorbed amino acids and ammonium may then act as a buffer and desorb from the sediment solid phase when the concentration of pore water DFAA and ammonium decrease. Generally the content of fresh organic material is much higher in the uppermost surface layer of the sediment and the composition of the organic matter is also different compared to the composition further down, because of degradation and burial of more or less degraded material (Burdige & Martens 1988, Henrichs 1992). The very high adsorption coefficient in the first centimeter of the sediment supported the theory that amino acids preferably adsorbed to organic material compared to mineral surfaces.

Concentrations of adsorbed amino acids were lowest in winter (November to February) when there was no or very low sedimentation and probably also low activity of bioturbating fauna. After the high sedimentation rates in March there was an effect on adsorption for most of the amino acids in April, and the concentration slowly increased further during summer and early fall. This newly deposited material seemed to constitute some very attractive surfaces for adsorption of amino acids. Therefore, there were also higher K for those months for some of the amino acids (Fig. 8).

Other investigations (Henrichs & Sugai 1993, Wang & Lee 1993) have shown that adsorption behaviour can be related to functional groups. According to these studies basic amino acids often have a greater adsorption capability to sediment surfaces than neutral or acidic amino acids. In this study it was also found that lysine, a basic amino acid with a net positive charge, adsorbed to the sediment, but dissolved free lysine was at such low a concentration in the pore water it was not possible to calculate the adsorption coefficient for lysine. Basic amino acids are also suggested to undergo irreversible adsorption to a large extent, and so lysine is not an easily extractable amino acid like the neutral and acidic amino acids are. In recent studies (Rosenfeld 1979b, Hedges & Hare 1987, Henrichs & Sugai 1993, Wang & Lee 1993) in which K have been determined for amino acids, it has also been noticed that K for glutamic acid is higher compared to other acidic or neutral amino acids. This is also what we found in this study. Glutamic acid had a much higher K compared to aspartic acid, serine, glycine and alanine, but these K reported here are still comparable with K determined earlier (Rosenfeldt 1979b, Wang & Lee 1993). Annual mean K for the whole core (0 to 12 cm) is shown in Table 4. Why glutamic acid adsorbed to a much greater extent than aspartic acid (which also is an acidic amino acid) could be due to functional group effect, steric advantages or other chemical interactions. The difference in the functional group of the 2 amino acids is one more $-CH_2$ in glutamic acid (R = CH_2–CH_2–COO^-) and whether the difference in functional groups is the reason for the better adsorption capacity is hard to say. The potential problem with leakage of glutamic acid from eukaryotic cells, which would overestimate K, was assumed to be of minor importance and has already been discussed above. With the present knowledge we are not able to explain the higher K for glutamic acid in marine sediments.

Seasonal variation of adsorption coefficients

When the adsorption coefficients from this study are compared to other adsorption studies it should be noted that most other studies were conducted on sieved and/or homogenized sediment. In this study the sediment was as natural as possible. K values for ammonium determined by Boatman & Murray (1982) in the sediment from Saanich Inlet, British Columbia, which was not homogenized, were 0.55 to 2.5 and Rosenfeld (1979a) obtained values of 0.8 to 1.6 in homogenized sediment from Long Island Sound, Florida Bay and Pettaquamscutt River, Rhode Island. Mackin & Aller (1984) studied different sediments in order to see if the adsorption coefficient for ammonium varies from one site to another and they found that K was almost uniform (1.0 to 1.7) in the various types of sediments investigated. In this study K for ammonium was 1.07 ± 0.11 (annual mean value for the whole core down to 12 cm), and the seasonal variation of K was very small. This study supports earlier determinations of K for ammonium, and results from this study also showed that no seasonal variation in K for ammonium was to be found.

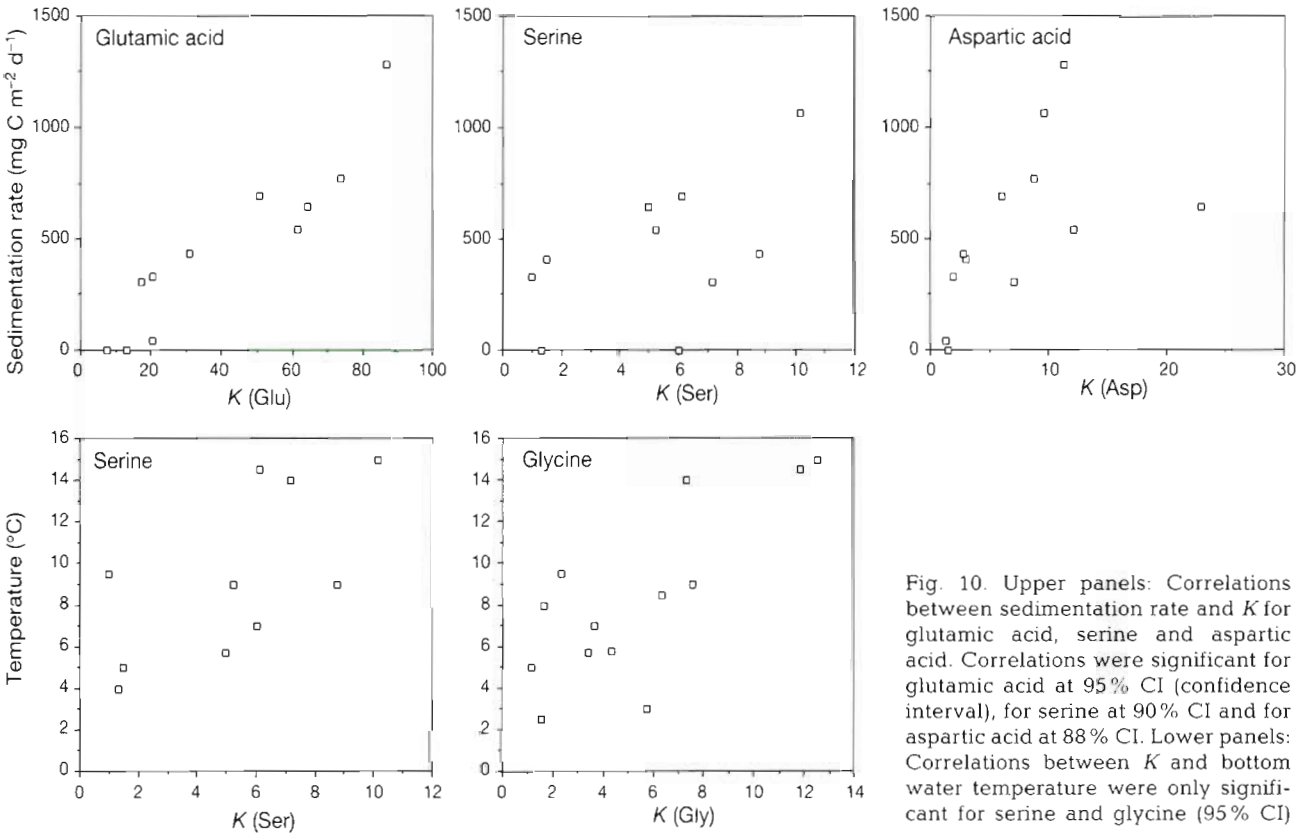

Fig. 10. Upper panels: Correlations between sedimentation rate and K for glutamic acid, serine and aspartic acid. Correlations were significant for glutamic acid at 95% CI (confidence interval), for serine at 90% CI and for aspartic acid at 88% CI. Lower panels: Correlations between K and bottom water temperature were only significant for serine and glycine (95% CI)

Correlations were calculated between K and sedimentation rates and K and bottom water temperature (Fig. 10). For some of the K there were significant correlations with sedimentation rates; glutamic acid had a significant correlation coefficient, r, of 0.927 (95% CI), serine had a r of 0.609 (90% CI) and aspartic acid had a r of 0.543 (88% CI) (Pearsons correlation coefficients). The other amino acids showed a similar pattern but correlations were not significant in these confidence intervals. Correlations between K and temperature were just significant for glycine (r = 0.760) and serine (r = 0.658). K for ammonium showed no correlation with sedimentation rates or with temperature (r = 0.007 in both cases).

The adsorption coefficients for amino acids varied during the year and the trend appeared to be an effect of both input of organic matter and bottom water temperature, mainly as a consequence of other microbially mediated reactions which have a temperature dependence. Correlation with sedimentation rate could be seen in spring due to input of fresh organic material from the algal blooms and K increased before there was any significant change in the bottom water temperature (Fig. 7). The adsorption coefficients increased after the primary production had started to be deposited on the seafloor later in March and hydrolyzation of POM had started. This new fresh organic matter on the sediment surface probably offered more available sites for adsorption as discussed above. During late autumn and winter the adsorption coefficient decreased until the next period of input of fresh organic material. K was higher in the warmer periods and appeared to correlate with temperature, but there are probably some other effects that are temperature dependent (e.g. activity of dwelling fauna) which may enhance K.

When K for every depth were compared it was noticed that there was an increasing trend because of decreasing porosity in the sediment cores. K for amino acids decreased with depth, because of rapidly decreasing K_{ads} as discussed earlier. Such effects will never be noticed if the experiment is performed on sieved or homogenized sediment, or sliced into too large parts.

What controls adsorption?

Adsorption is extremely important because it may dramatically affect the fate and impact of chemicals in the environment. It can also be a complex process and it is not always easy to understand what controls it.

Wang & Lee (1990, 1993) did laboratory experiments to study adsorption coefficients for methylated amines and found that the K was inversely related to sediment grain size. Wang & Lee (1990) also found that adsorption of amines appears to be even more dependent on porosity than is the case for ammonium. Clay mineral and organic matter content is also known to influence adsorption of amino acids and ammonium (Rosenfeld 1979a, b, Henrichs & Sugai 1993). Adsorption to clay minerals is much better understood than adsorption to organic matter. Natural sedimentary organic matter is composed of a mixture of various compounds, providing a variety of adsorption sites on the organic coating at the sediment surfaces. It seems to be reasonable that K for amino acids are higher in the uppermost part of the sediment, where the porosity is high and the composition of organic matter is different, compared to deeper in the sediment.

The temperature dependence of adsorption of amino acids and ammonium is not well defined, but Mackin & Aller (1984) found in laboratory experiments that the temperature had no or only a small effect on ammonium adsorption. To the best of our knowledge there have been no studies of the temperature dependence of amino acid adsorption. We therefore assumed that temperature had a similar effect on amino acid adsorption as it has for ammonium as described by Mackin & Aller (1984). There were no indications of a dependence of temperature alone in this sediment. The temperature may on the other hand have an indirect effect on adsorption, because bioturbation was probably stimulated by increased temperature and the dwelling fauna enhanced the reworking of the sediment, which should provide new sites for adsorption.

What controls the adsorption of amino acids in this sediment needs to be further examined, but it seemed to be at least partly controlled by the content and composition of organic matter and by porosity. Adsorption, in turn, affected the distribution of DFAA in the pore water. Differences in content and composition of organic matter between different sediments may contribute to K for amino acids being different from one sediment to another.

For an improved knowledge of what controls adsorption of amino acids in marine sediments, other investigations of amino acid adsorption behaviour are needed. These include: the temperature dependence of amino acid adsorption in marine sediments; the influence of bioturbation on adsorption in different types of sediments; what kind of organic matter provides the most attractive adsorption sites; how long do adsorbed amino acids escape degradation in oxic and anoxic sediments; and how great the role of amino acid adsorption is in the benthic nitrogen cycle. As a result of the dependence of amino acid adsorption on organic matter (quantity, composition), seasonal variation in input of organic matter has in this study also been shown to affect adsorption and adsorption coefficients of amino acids in coastal sediment. The lowest concentrations of adsorbed amino acids were found in winter (November to February) when primary production and sedimentation to the seafloor was infinitesimal.

CONCLUSIONS

(1) Seasonal variations in the pore water distributions of both dissolved free amino acids and ammonium were observed in a near-shore marine sediment. The variation of ammonium during the year followed the annual temperature cycle, probably due to increased production driven by increased mineralization of ammonium as a result of increased temperature in bottom water. DFAA did not show the same dependence of temperature as did ammonium. The variation of DFAA during the year seemed to follow both temperature and input of organic matter. All DFAA had pore water concentration minima in winter when the sedimentation rate to the seafloor was lowest. DFAA concentrations in the pore water started to increase after deposition of the spring bloom and before any increase of bottom water temperature. The seasonal signal of pore water DFAA was suppressed probably due to removal processes (e.g. adsorption, degradation, assimilation) occurring simultaneously with DFAA production, induced by organic matter input and increase of temperature.

(2) Seasonal variations were also observed in adsorption of both amino acids and ammonium. Ammonium adsorption followed the concentration of dissolved ammonium in the pore water, which was higher at the end of summer. Amino acid adsorption also followed the DFAA concentration in the pore water, but there was also a relation to input of organic matter This indicated that amino acids adsorbed to organic matter compared to mineral surfaces to a much greater extent than did ammonium.

(3) K (the dimensionless adsorption coefficient) for ammonium was measured throughout the year and it did not exhibit any seasonal variation. Annual mean K was 1.07 ± 0.11, and K was not related to temperature or input of organic matter. K for the amino acids varied seasonally in response to input of organic matter and probably also indirectly with temperature, due to exposure of new surfaces by stimulation of bioturbation in late summer. All amino acids varied in a similar pattern, with minimum K in winter and high values during spring and summer. K for the amino acids were all higher than K for ammonium.

Acknowledgements. Special thanks to Stefan Hulth for help during sediment sampling, and to the skilful and helpful crew on board RV 'Arne Tiselius' and RV 'Oscar von Sydow' at Kristineberg Marine Research Station. We also thank Odd Lindahl for access to data and for valuable discussions, and Mona Petersson for determinations of particulate carbon and nitrogen in sediment. This project was supported financially by the Swedish Natural Science Research Council (NFR) and the Swedish Environmental Protection Agency (NV).

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Editorial responsibility: Otto Kinne (Editor), Oldendorf/Luhe, Germany

Submitted: December 11, 1997; Accepted: May 29, 1998
Proofs received from author(s): August 10, 1998