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Amino acid biogeochemistry in the Laurentian Trough: vertical fluxes and individual reactivity during early diagenesis

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Abstract—The detailed composition of total hydrolysable (THAA), dissolved free (DFAA) and combined (DCAA) amino acids was studied in settling particles and the solid phase and porewaters of underlying sediments in the Laurentian Trough to evaluate their sources and individual reactivities during early diagenesis. Vertical fluxes of THAA measured at 150 m depth (234–980 μmol/m^2/day) represented 3.8% of the average daily primary production and 8–16% of total organic carbon (TOC) and 24–42% of total nitrogen (TN) fluxes. THAA concentrations decreased from 89 ± 39 to 39 ± 4.4 μmol/g from settling particles to the top 3 cm sediments, with no significant change of the %THAA-C and %THAA-N. However, these parameters decreased with depth in the sediments (10–13 to 7–8% and 30–45 to 22–28%, respectively) indicating a selective THAA removal. THAA composition of settling particles and sediments was relatively uniform and showed a marked enrichment in serine, threonine and glycine relative to fresh plankton which is ascribed to the selective preservation of diatom cell-walls. Serine was the more specific diatom tracer; it covaried with diatom lipid biomarkers, was relatively more abundant at a seaward site and increased downcore reflecting the selective preservation of diatom cell-walls. An increasing trend with sediment depth was also observed for aspartic acid whereas glutamic acid and histidine decreased. Porewater DFAA and DCAA accounted for 3–25% of total DOC and showed low levels in the surface zone of most intense solid phase THAA decay. Both fractions showed clear compositional differences related to the prevailing source material: DCAA, as solid phase THAA, were dominated by serine and threonine + glycine, whereas DFAA were enriched in glutamic (Glu) and β-aminoglutaric acids (βGlu), probably originating from bacteria. These patterns changed with depth in the sediments: the proportion of serine and βGlu increased in DCAA and DFAA, respectively, whereas that of glutamine, alanine and Glu decreased in the DFAA pool. The preferential downcore decay and conversion of Glu into βGlu was reflected by a consistent increase of βGlu/Glu ratios, particularly at a landward station where the higher rates of sedimentation and OM burial favor the continued metabolism of bacteria in deeper sediment layers. © 1998 Elsevier Science Ltd. All rights reserved

Key words—Amino acids, Vertical fluxes, Solid phase, Porewater, Early diagenesis, Reactivity

INTRODUCTION

The conversion of inorganic nitrogen to amino acids, aliphatic amines, polyamines, pyrimidines and purines during photosynthesis is the major source of organic amino compounds in the sea (Lee, 1988). In some environments, the assimilation of inorganic nitrogen by bacteria can be also significant (Kirchman *et al.*, 1991). A portion of these compounds is transported in the form of rapidly sinking particles to bottom sediments. The magnitude of this flux is closely related to primary productivity, increasing about 250-fold for every 10-fold increase in productivity (Lee and Cronin, 1984). Amino acids represent about 10–25% of total organic carbon (TOC) and 30–50% of total nitrogen (TN) in sediments and their degradation usually accounts for about 10–20% of TOC and 80% of TN remineralization (Wefer *et al.*, 1982; Henrichs *et al.*, 1984; Henrichs and Farrington, 1987; Burdige and Martens, 1988; Lee, 1988; Cowie and Hedges, 1992).

Because of their important role in the cycle of organic matter (OM) in the ocean, amino acids were included in our study of the organic composition and relative reactivity of different OM fractions in settling particles and sediments of the Laurentian Trough, a 1200 km long, 300–450 m deep coastal environment. In previous papers the bulk composition (carbon, nitrogen, carbohydrates, proteins, total amino acids, lipids and pigments), specific lipid biomarkers (fatty acids, sterols and hydrocarbons), as well as the flux and early diagenesis of

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OM in sinking particles and sediments were examined (Colombo *et al.*, 1996a,b,c, 1997). Overall, these studies indicated that the vertical flux of OM in the St. Lawrence is dominated by terrigenous and zooplanktonic contributions with a lower incidence of fresh phytoplankton. The characterized fraction of total organic carbon consisted of lipids (17–37%), carbohydrates (7.9–16%), hydrolyzable amino acids (8.4–16%) and labile proteins (0.3–2.6%). A clear land–sea gradient is apparent in terms of sedimentation rates (higher in the landward direction) and relative marine contribution. At a landward site, settling particles and sediments showed higher C/N ratios and a stronger contribution of vascular plant *n*-alkanes and fatty acids and petrogenic hydrocarbons, whereas marine lipids, including specific diatom tracers, were more abundant in the seaward direction. Very labile marine lipids that were enriched in settling particles were rapidly lost near the sediment–water interface. The preferential decay of marine components continued with depth in the cores resulting in similar residual lipid patterns at 35 cm depth. However, landward and seaward sediments could still be discriminated by C/N ratios and their fatty acid and hydrocarbon composition.

In order to evaluate the behavior of amino acids under contrasting conditions of organic inputs and early diagenesis, in the present paper we report the detailed composition of amino acids in settling particles and the solid phase and porewaters of underlying sediments sampled in spring and mid-summer at two sites along the terrestrial–marine gradient.

MATERIALS AND METHODS

Sampling

A detailed description of the study area and sampling methods was presented in earlier papers (Colombo *et al.*, 1996a,b). Briefly, settling particles were intercepted with two unpoisoned, free-drifting sediment traps suspended at 150 m depth, at landward (L) and seaward (S) sites in the Laurentian Trough (Fig. 1) during May and July 1988. After 8–30 h of deployment, the traps were recovered and the samples collected into 2 l glass jars. The water was decanted, swimmers and intact copepods were eliminated and the material was split for micro-

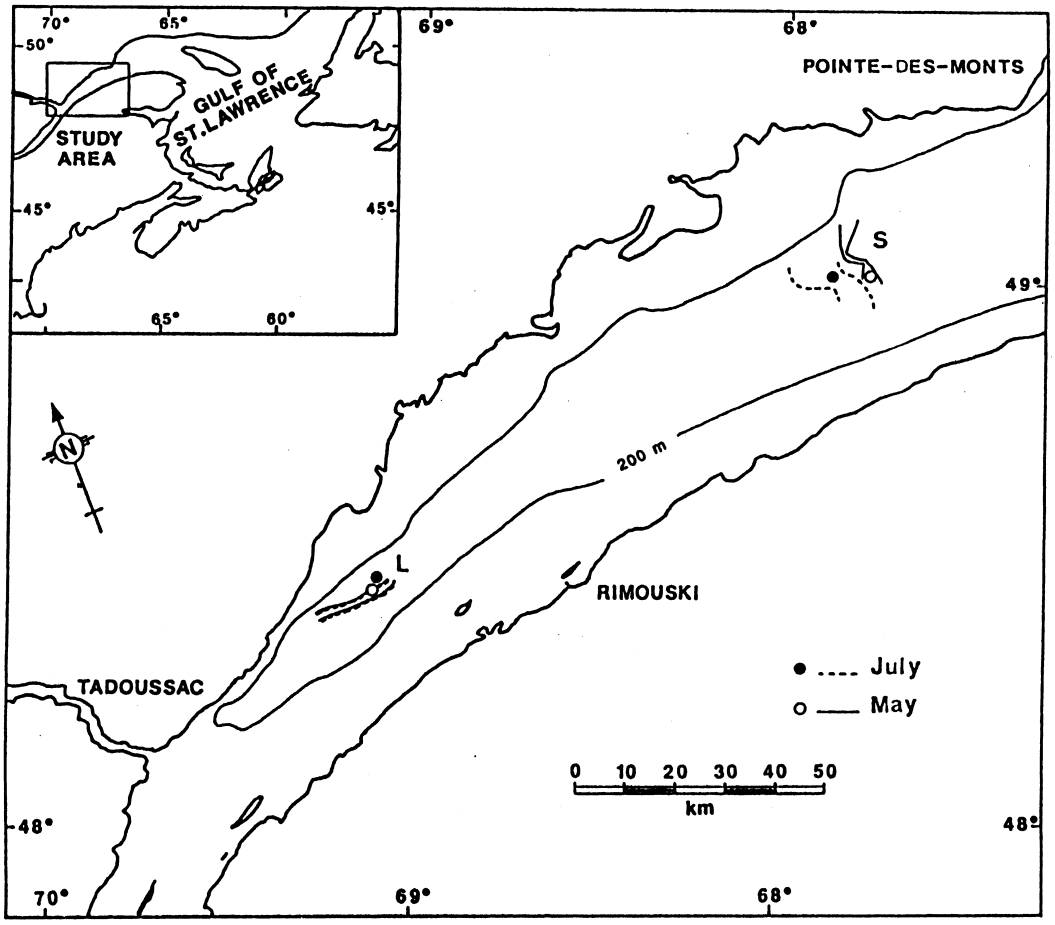

Fig. 1. Drifting sediment trap trajectories and coring sites in the Laurentian Trough.

scopic examination, for the determination of total particle flux and for chemical analysis. Plankton samples were collected in horizontal and vertical tows made at both stations with 75 and 333 μm mesh nets. Undisturbed bottom sediments were recovered during each period of sediment trap deployment using a 0.1 m^2 box corer. The cores were immediately subsampled in a glove box under a forced flow of N_2 by scraping successive ≈2 mm thick layers in the first cm and then taking 1 cm thick slices every 1 to 5 cm depth and at 5 cm intervals down to 35 cm depth. Porewater from each subsample was subsequently extracted and filtered through precombusted Whatman glass fiber filters (1.2 and 0.7 μm) with a Reeburgh-style squeezer and collected in acid-washed, precombusted amber bottles. All samples were stored at −20 or −40°C until analysis.

Amino acid analysis

Amino acid composition was determined by pre-column *o*-phthaldialdehyde (OPT) derivatization and separation of the components by reversed-phase high performance liquid chromatography (HPLC) followed by fluorescence detection (Lindroth and Mopper, 1979; Dawson and Liebezeit, 1983). Dissolved free amino acids (DFAA) were determined by direct injection of porewaters into the HPLC after reaction with the OPT-mercaptoethanol reagent (10 min after mixing with borate buffer at pH = 13.5). For dissolved combined amino acid (DCAA) analyses, porewaters were evaporated at 100–110°C, cooled, acidified with 6 N HCl, flushed with N_2 and hydrolysed for 22–24 h at 110°C. Samples were neutralized with NaOH, reacted with the OPT reagent and injected into the HPLC system. The concentration of DCAA was obtained by substraction of DFAA levels, after correction for the recovery yields. Total hydrolysable amino acids (THAA) were determined in 60–200 mg of dried trap material and about 1 g of wet sediments using the same hydrolysis procedure with the addition of a 30 min-sonication step with 6 N HCl. After hydrolysis, the samples were centrifuged, diluted and reacted with the fluorescent tag in a similar manner.

Analyses were performed on a Waters 600 multi-solvent delivery system equipped with a Waters U6K injector, a 4.6 mm × 15 cm, 3 μm Supelcosil LC-18 column and a Perkin-Elmer LS-5 fluorescence spectrophotometer operated at 340 nm (excitation) and 450 nm (emission). The mobile phase components were aqueous methanol and 34 mM phosphate buffer at pH 6.8. The gradient program varied the methanol concentration from 15 to 47% in 10 min and then increased the concentration to 77% in 20 min. The column equilibration time was 12 min and the flow rate was 1 ml/min. A reference mixture of 23 authentic amino acid standards (Sigma) containing aspartic acid (Asp), glutamic acid (Glu), β-aminoglutaric acid (βGlu), muramic acid (Mur), asparagine (Asn), serine (Ser), glutamine (Gln), histidine (His), glycine (Gly), threonine (Thr), arginine (Arg), tyrosine (Tyr), alanine (Ala), β-aminobutyric acid (βAbu), α-aminobutyric acid (αAbu), tryptophan (Trp), methionine (Met), valine (Val), phenylalanine (Phe), isoleucine (Ile), leucine (Leu), ornithine (Orn) and lysine (Lys), was used to assign the identities. This mixture was resolved into 21 peaks, with an incomplete separation of Gln and His and the co-elution of Thr and Gly (T + G) under the specified analytical conditions. Recovery assays carried out with the standards indicated that during the hydrolysis step, Asn and Gln were almost quantitatively converted to Asp and Glu whose recoveries were 170–180%, while Trp and Met experienced severe losses. Thus, the reported Asp and Glu values for DCAA and THAA include the contribution from Asn and Gln. Amino acid data have been corrected for blank values (negligible for THAA, ≈10% and ≈16% average signal for DFAA and DCAA, respectively) and for the recovery yields (average 79 ± 19). The recovery was optimal for DFAA analyses (mean: 97%). Due to their erratic responses, Orn and Lys were omitted. Mur, βAbu and αAbu were always below the detection limits. The analytical precision of the method averaged ±8.1% (RSD).

RESULTS AND DISCUSSION

Solid phase amino acids: THAA fluxes, concentrations and early diagenesis

The concentration of THAA in settling particles ranged between 40 and 145 μmol/g, with higher values at the seaward site and during the summer at both stations (Table 1). These trends were followed by all organic components and reflect the different contribution of OM-poor terrestrial detritus (highest at L in May), and of organic-rich marine material (highest at S and during July), according to the position of the stations along the land–sea gradient and the seasonal cycle of primary production (Colombo *et al.*, 1996a). The amino acid yields normalized to TOC were relatively low, more constant at S (208–216 μmol THAA/100 mg TOC) and increasing in July at L (168 to 225 μmol THAA/100 mg TOC), reflecting the shift from terrestrial runoff in the spring to more marine primary production in the summer.

The calculated fluxes of THAA varied from 234 to 980 μmol/m^2/day (Table 1) and were higher at station L in July. THAA accounted for an average of 13% of the TOC and 37% of the TN fluxes. The values increased in July at L due to the higher contribution of biogenic material, and remained more or less constant at S (Table 1). The grand mean THAA carbon flux (28 mg/m^2/d) represents 3.8%

Table 1. Total concentration, fluxes and relative composition of total hydrolyzable amino acids measured at 150 m depth at a landward (L) and seaward (S) stations in the Lower St. Lawrence Estuary

					Mole%											
Sample	Total (μmol/g)	THAA-C (%)	THAA-N (%)	Flux (μmol/m^2/d)	Asp	Glu	Ser	His	T + G	Arg	Tyr	Ala	Val	Phe	Ile	Leu
L, May 12	40.3	9.6	34.1	423.0	12.2	11.2	21.8	–	22.4	4.0	1.8	12.7	2.1	2.2	4.2	5.3
L, May 12	57.9	10.3	36.2	666.0	10.0	9.7	18.5	2.3	29.0	2.1	1.5	11.5	3.6	2.9	4.0	5.0
L, May 13	48.5	10.8	37.8	262.0	11.8	12.0	20.0	1.7	17.8	4.9	2.7	12.2	4.3	2.6	5.1	4.9
Mean	48.9	10.2	36.0	450.3	11.3	11.0	20.1	1.3	23.1	3.7	2.0	12.1	3.3	2.6	4.4	5.1
L, July 15	86.7	13.8	39.4	980.0	9.4	9.4	30.5	0.8	23.2	–	1.3	11.4	4.2	3.6	3.2	2.7
S, May 9	93.7	13.8	37.0	646.0	9.9	11.0	29.6	1.9	20.0	2.3	1.4	6.5	4.2	4.2	8.8	–
S, May 10	124.0	15.9	42.0	421.0	8.0	9.2	28.5	4.8	22.1	3.1	1.6	9.0	3.5	3.4	3.1	3.8
S, May 10	66.1	8.4	24.0	245.0	9.3	8.9	29.3	–	20.5	0.9	2.2	10.1	4.7	4.0	4.9	5.4
Mean	94.6	12.7	34.3	437.3	9.0	9.7	29.1	2.7	20.9	2.1	1.7	8.5	4.1	3.9	5.6	3.0
S, July 17	145.0	13.6	37.1	268.0	8.2	8.8	22.9	4.0	22.6	5.5	3.2	11.9	3.8	2.9	2.5	3.8
S, July 18	137.0	12.8	37.5	234.0	10.2	11.1	25.1	–	17.8	2.9	2.8	13.7	4.2	3.2	3.8	5.0
Mean	141.0	13.2	37.3	251.0	9.2	10.0	24.0	2.0	20.2	4.2	3.0	12.8	4.0	3.0	3.1	4.4

–: below detection limits.

of the average daily primary production calculated for a 153-day ice-free period (745 mg C/m^2/d), similar to the values reported for other moderately productive coastal areas (Lee and Cronin, 1982).

The THAA fluxes measured at 150 m depth in the St. Lawrence are similar to those reported for the Bransfield Strait (462 μmol/m^2/d at 323 m depth; Liebezeit and von Bodungen, 1987) and are lower than those published for the Gulf of Trieste (390–1385 μmol/m^2/d at 16 m; Faganeli, 1989); Peru Upwelling (1053 μmol/m^2/d at 52 m; Lee and Cronin, 1982) and Dabob Bay (280–1625 μmol/m^2/d at 60 m; Cowie and Hedges, 1992). In these shallower traps, THAA accounted for a higher fraction of TOC (10–31%) and TN (40–68%) reflecting the greater 'freshness' of this material collected in or close to the euphotic zone. The partial decay of our settling organic material is reflected by the %THAA-N which is considered to be a good qualitative indicator of the degree of OM alteration (Whelan, 1977; Henrichs *et al.*, 1984; Cowie and Hedges, 1994). According to Cowie and Hedges (1992), values of %THAA-N below 38% indicate diagenetic alteration and this parameter averaged $36 \pm 5.3\%$ in our traps. The composition of THAA gives a further indication of partial amino acid alteration (see below).

The THAA levels in the 0–3 cm sediment layer ranged from 31 to 47 μmol/g (Table 2) with higher values at the landward station (42 ± 2.6 versus 35 ± 2.7 μmol/g at S) reflecting the stronger OM fluxes, higher sedimentation rates and deeper bioturbation observed at this site (Colombo *et al.*, 1996b). This difference disappeared at the bottom of the cores where THAA levels declined to 15–18 μmol/g (Fig. 2). The amino acid yield of the sediments in the top 3 cm averaged 177–201 μmol THAA/100 mg TOC, similar to the traps, but only 111–127 μmol THAA/100 mg TOC at 35 cm depth. These changes of the THAA concentrations from settling particles to surface and deeper sediments reflect an intense amino acid removal. In the first stage of diagenetic alteration, from settling particles to the top 0–3 cm sediments, the drop of THAA levels (89 ± 39 to 39 ± 4.4 μmol/g) is proportional to that of TOC and TN as indicated by the similarity of the %THAA-C and THAA-N in trap particles (12 ± 2.6 and $36 \pm 5.3\%$) and sediments (11 ± 1.5 and $39 \pm 5.3\%$, respectively). Deeper in the sediments, the decrease of the %THAA-C (10–13 to 7–8%) and %THAA-N (30–45 to 22–28%) from the top 0–3 to 35 cm depth indicates preferential removal of THAA relative to TOC and TN (Fig. 3).

An important proportion of the total sedimentary decay of THAA occurs in the first 5 cm of the cores (39% at L and 53% at S; Fig. 2). The loss of THAA over the entire length of the cores represents 21% of the decrease of TOC and 67–80% of that of TN, the higher percentage of TN loss corresponding to the seaward site. This greater THAA utilization is probably related to the predominance of marine inputs and lower sedimentation rates at this station (Colombo *et al.*, 1996b). The proportions of TOC and TN remineralized as THAA in the Laurentian Trough are comparable to those reported for Buzzards Bay and Cape Lookout Bight, 11–27% of TOC and 82% of TN (Henrichs and Farrington, 1987; Burdige and Martens, 1988).

Solid phase amino acids: THAA composition, sources and individual reactivity

Figure 4 shows the relative composition of THAA in settling particles and sediments compared to that of fresh plankton samples. The most conspicuous changes of THAA patterns occurs between fresh plankton and settling particles, e.g. reduction of the proportion of Asp and Glu and strong increase of Ser and T + G. Only subtle differences are observed between particles, surface and 30 cm-

Table 2. Total concentrations and major components of total hydrolyzable (THAA), dissolved combined (DCAA) and dissolved free (DFAA) amino acids in sediment cores collected at a landward (L) and seaward (S) stations in the lower St. Lawrence Estuary

		THAA						DCAA						DFAA						
			mole %						mole %						mole %					
Depth (cm)	Sample	total (μmol/g)	Asp	Glu	Ser	T+G	Ala	total (μM)	Asp	Glu	Ser	T+G	Ala	total (μM)	Asp	Glu	βGlu	Ser	T+G	Ala
0–0.6	L, May	43.0	11.2	8.9	23.2	25.1	9.8	2.5	2.8	–	20.2	49.3	–	2.2	4.5	24.5	4.1	7.7	5.9	24.1
	L, July	44.0	12.5	11.8	23.1	24.8	9.5	2.7	–	–	17.8	23.3	4.1	3.1	5.2	41.6	11.9	4.5	2.3	15.6
	S, May	37.2	10.5	9.2	23.0	22.7	11.6	4.4	0.2	–	14.6	85.3	–	5.8	3.3	38.3	2.9	6.4	2.9	34.5
	S, July	30.6	12.3	10.7	25.0	22.7	9.8	2.3	3.0	–	15.7	31.3	6.7	1.8	3.9	45.0	12.8	3.9	4.4	7.2
0.6–1	L, May	38.8	11.4	7.3	21.9	21.6	10.8	0.8	13.8	35.0	22.2	3.4	26.4	2.4	4.2	42.5	12.5	6.7	4.6	10.0
	L, July	43.1	12.2	13.1	24.0	24.1	10.0	4.0	3.3	–	24.4	41.1	11.5	5.2	3.8	41.9	17.1	2.5	2.3	15.6
	S, May	33.4	11.7	9.8	24.7	20.5	11.4	1.1	–	–	31.7	62.7	–	1.6	9.4	45.0	13.1	6.9	3.8	15.0
	S, July	36.2	12.7	10.9	25.3	22.3	9.6	2.0	–	–	22.7	49.9	9.9	4.0	5.0	47.0	18.0	2.5	3.5	6.8
1–2	L, May	39.7	11.7	8.9	23.3	23.4	11.7	3.4	–	–	4.0	87.6	3.6	3.5	4.3	45.7	12.9	4.6	3.1	10.9
	L, July	41.0	10.2	10.9	21.3	28.1	8.5	2.1	4.8	–	26.1	28.1	11.9	8.8	2.1	35.7	13.2	1.6	1.3	35.5
	S, May	33.4	14.4	12.9	28.2	17.3	11.4	3.5	6.3	12.9	23.4	32.3	13.5	4.0	4.2	37.8	10.0	4.5	5.5	23.3
	S, July	36.2	12.1	12.1	25.1	20.4	10.9	5.9	4.2	–	12.9	78.6	0.6	6.6	5.2	34.9	11.7	3.8	8.3	10.8
2–3	L, May	46.9	12.0	10.0	25.3	22.4	11.3	3.5	7.4	25.7	19.7	26.7	9.1	3.0	3.7	43.7	16.0	6.7	4.7	10.0
	L, July	41.7	11.2	12.6	24.9	21.8	10.1	4.8	5.8	–	27.4	39.4	–	12.6	3.3	37.1	16.3	4.1	5.2	9.2
	S, May	35.6	12.9	10.6	25.5	19.9	11.2	–						2.0	4.5	51.5	17.0	6.5	3.5	11.5
	S. July	39.5	10.6	9.6	24.1	26.6	11.1	8.7	6.6	–	17.0	43.9	11.5	4.2	7.1	49.0	19.5	1.7	3.1	6.9
3–4	L, May	33.5	12.8	9.9	27.2	20.0	11.3	2.6	0.4	–	24.1	45.2	6.4	3.2	3.7	52.2	21.9	2.8	1.6	6.3
	L, July	34.1	10.6	9.8	24.3	24.3	10.0	5.9	8.8	–	25.9	32.9	1.8	9.1	2.5	43.2	21.9	2.6	2.9	11.6
	S, May	35.4	13.4	10.8	25.5	20.9	9.8	6.7	4.5	4.6	19.8	34.5	8.6	2.1	4.3	50.0	16.7	6.2	4.3	12.4
	S, July	37.3	11.4	9.9	24.8	22.3	10.2	24.1	1.4	–	4.5	37.6	21.5	9.4	6.4	41.2	15.3	3.7	5.1	7.1
4–5	L, May	34.0	11.6	9.3	26.3	22.3	11.1	2.6	9.2	–	32.6	44.0	–	4.1	2.9	47.9	24.5	2.6	3.1	6.9
	L, July	30.8	11.2	12.8	22.8	23.2	9.6	0.5	–	–	–	100.0	–	11.0	2.8	42.9	28.2	2.9	3.1	4.2
	S, May	22.0	13.4	10.4	25.7	22.4	11.2	4.2	5.7	–	29.1	41.9	9.9	4.0	6.4	46.4	21.0	4.6	2.1	6.9
	S, July	28.3	13.6	12.6	25.7	22.0	9.6	13.1	6.9	–	22.7	47.3	10.8	11.1	5.4	42.4	17.8	3.1	3.7	7.8
9–10	L, May	33.4	12.1	9.6	25.6	21.8	9.9	20.3	6.2	–	13.2	63.0	7.8	10.4	2.9	31.7	21.8	5.5	6.3	7.4
	L, July	28.2	9.7	11.5	21.5	33.9	9.4	25.1	11.9	–	19.2	39.0	12.2	15.9	3.6	31.4	16.7	4.1	7.3	7.5
	S, May	20.0	14.0	9.9	27.2	23.2	10.3	16.2	9.0	5.2	28.9	39.4	9.5	5.3	3.8	28.3	18.5	10.4	6.8	13.4
	S, July	22.2	11.9	10.3	26.7	26.7	9.9	13.4	4.2	–	27.4	49.3	11.4	5.0	3.6	45.2	31.0	1.8	2.4	4.2
14–15	L, May	25.9	13.3	9.8	23.0	22.1	11.6	5.0	17.6	12.2	14.5	15.3	3.6	8.4	4.3	28.0	21.4	13.1	7.7	9.2
	L, July	21.9	11.2	12.0	24.3	26.2	9.4	11.6	5.6	–	28.8	30.7	13.5	5.3	2.4	45.3	39.8	1.7	2.3	2.3
	S, May	18.2	15.0	7.7	28.2	17.6	12.1	17.6	6.9	8.6	31.1	34.6	10.8	6.1	5.6	22.6	17.5	17.5	9.5	8.2
	S, July	24.6	10.9	8.4	23.6	30.5	9.1	32.2	9.2	–	23.9	36.0	12.4	10.1	3.9	28.5	19.7	4.5	7.2	6.1
19–20	L, May	26.1	10.2	7.1	24.6	30.9	10.8	8.5	5.2	1.4	26.1	46.8	12.2	7.2	4.3	23.6	24.4	17.9	7.9	6.7
	L, July	20.7	10.9	12.5	23.9	23.1	10.8	10.5	7.6	1.1	31.9	30.4	7.7	4.2	1.7	41.9	44.3	1.7	2.6	1.9
	S, May	14.4	13.5	8.4	25.9	19.0	7.5	12.6	5.9	3.8	37.8	23.4	6.3	3.4	5.0	28.5	23.5	10.9	14.1	7.1
	S, July	18.1	14.5	10.1	28.0	25.3	8.0	9.8	5.1	–	42.4	32.4	8.3	4.9	4.1	35.3	32.2	1.6	6.9	1.8
24–25	L, May	19.2	12.7	9.3	24.0	22.8	12.7	6.9	5.5	–	21.7	44.4	12.9	2.9	3.1	31.5	35.0	11.9	5.8	5.0
	L, July	20.2	13.1	10.9	27.0	20.7	10.9	15.6	8.3	5.5	20.9	27.6	12.4	2.3	2.7	36.3	36.3	3.0	3.3	6.0
	S, May	23.8	14.4	10.0	26.4	19.3	9.8	15.1	5.3	8.7	41.1	28.6	11.7	2.8	6.9	20.7	16.9	22.0	10.0	10.2
	S, July	18.6	12.9	9.2	27.3	20.7	10.8	16.8	7.1	2.3	28.1	32.4	9.0	3.7	2.7	38.6	34.8	3.4	4.1	3.8
29–30	L, May	21.5	12.1	8.7	25.1	21.3	10.1	8.7	4.5	–	18.7	53.5	7.5	2.9	1.4	35.9	37.2	8.6	3.4	4.1
	L, July	22.9	11.1	10.7	23.5	28.7	8.6	11.2	7.1	2.5	33.9	37.2	6.5	2.3	3.0	38.7	44.3	5.7	4.8	2.6
	S, May	19.1	13.9	9.3	27.9	19.0	11.3	11.4	5.2	2.1	16.4	50.0	17.3	2.8	3.9	30.0	34.6	7.9	5.7	3.6
	S, July	18.0	13.4	8.2	28.7	27.6	13.0	10.1	4.0	–	41.2	33.3	12.4	3.7	9.7	33.8	28.4	3.2	3.2	4.9
34–35	L, May							2.7	4.2	–	23.8	51.0	10.5	2.7	1.5	38.1	46.3	3.7	1.5	2.2
	L, July	16.8	13.2	9.6	27.4	26.6	8.5	2.7	6.7	–	41.3	29.5	6.8	2.7	4.4	42.6	45.6	4.4	–	0.4
	S, May	14.9	14.6	8.1	26.3	23.0	12.7	1.4	4.1	0.5	44.4	31.5	8.4	1.4	2.1	36.4	32.9	9.3	5.0	4.3
	S, July	17.8	14.3	9.1	28.9	25.0	11.9	2.7	4.1	–	32.2	34.3	8.1	2.8	4.6	33.9	26.4	4.6	6.4	5.7

deep sediments, whose amino acid spectra are dominated by Ser and T + G (20–30% THAA each) followed by Asp (10–15%), Ala (≈10%) and Glu (≈10%) whereas in plankton, Ala, Asp and Glu are more abundant. As has been observed by other authors (Bamstedt, 1986; Cowie and Hedges, 1992), the amino acid patterns of phytoplankton and zooplankton are very similar, except perhaps for a significantly higher proportion of Asp in phytoplankton (Fig. 4).

Relatively invariant THAA distributions have often been reported for biotic and abiotic compartments of different environments reflecting the poor performance of these compounds as biomarkers of OM sources (Siezen and Mague, 1978; Rosenfeld, 1979; Lee *et al.*, 1983; Henrichs *et al.*, 1984; Henrichs and Williams, 1985; Montani and Okaichi, 1985; Henrichs and Farrington, 1987; Burdige and Martens, 1988; Cowie and Hedges, 1992). More specific amino acid signatures have been reported for bacteria (Mur, Glu and perhaps βGlu), marine invertebrates (taurine and Gly; Henrichs *et al.*, 1984; Henrichs and Farrington, 1987) and the cell-wall protein of diatoms which is enriched in Gly, Ser and Thr (Hecky *et al.*, 1973). The abundance of these latter amino acids as well as their relative increase in deeper suspended material, sinking particles and sediments have been attributed to the selective preservation of this resistant complex (Siezen and Mague, 1978; Lee and

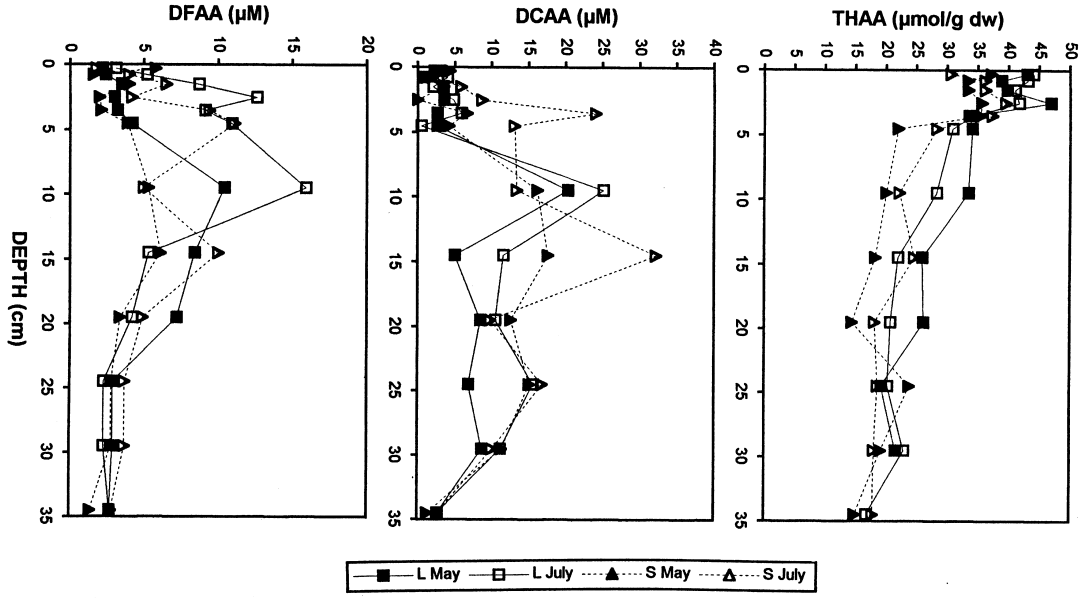

Fig. 2. Sediment porewater (DFAA and DCAA) and solid phase (THAA) profiles of amino acids at both stations and sampling periods.

Cronin, 1984; Müller *et al.*, 1986; Burdige and Martens, 1988; Cowie and Hedges, 1992).

The marked abundance of Ser and T + G in our trap and sediment samples relative to fresh plankton, which is the main amino acid source (see below), would then reflect the selective preservation of the diatom cell-wall complex. This further supports the interpretation of a partial degradation of

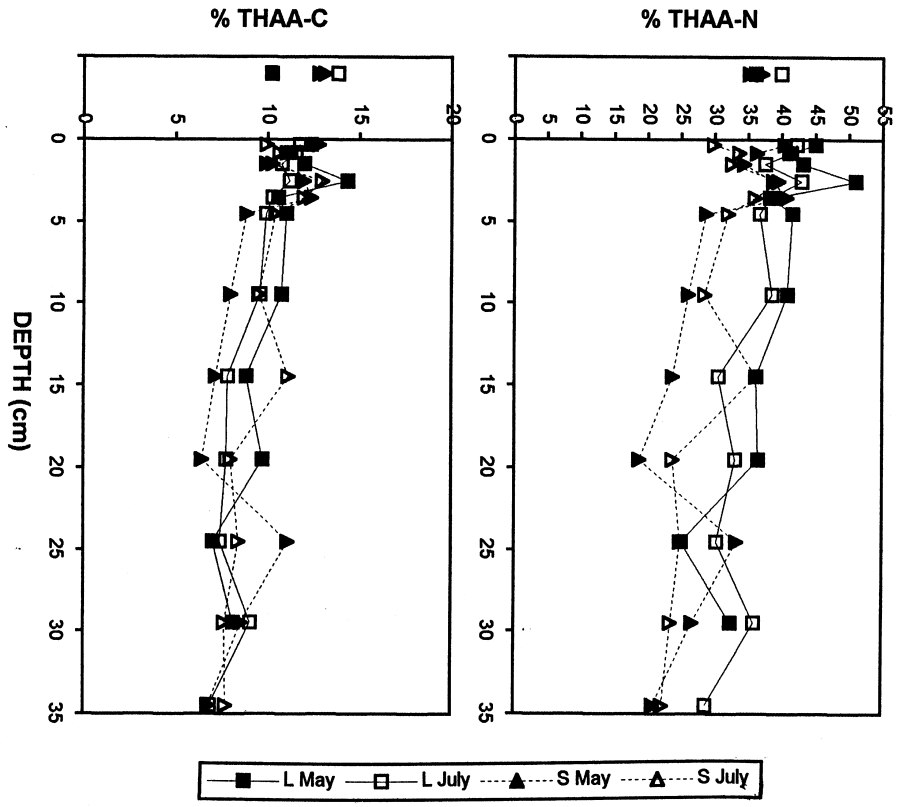

Fig. 3. Proportion of carbon and nitrogen present as THAA in sediments and settling particles (above 0 depth). Average conversion factors are 0.44 for C and 0.14 for N (n = 17).

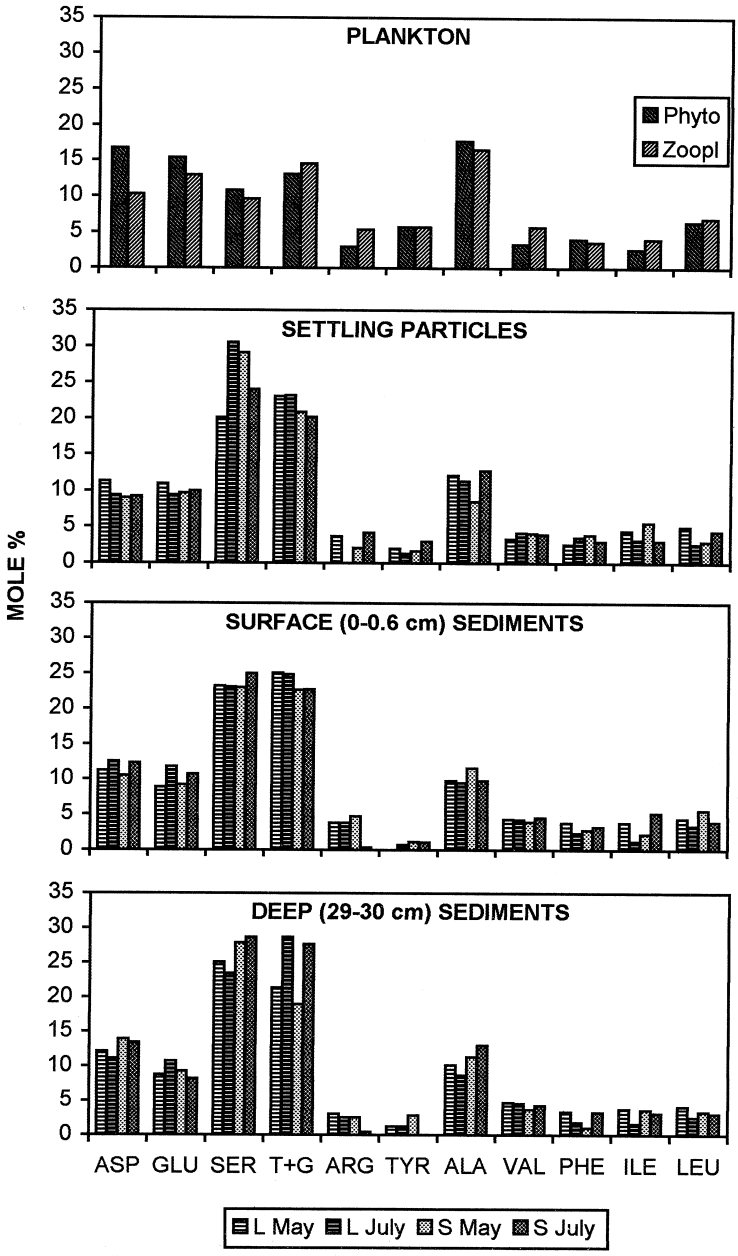

Fig. 4. Individual amino acid composition of THAA in fresh plankton, trap material, surface and deep sediments.

the trap material. From the three amino acids enriched in diatom cell-walls, Ser appears as the most sensitive tracer: its relative abundance covaried with those of diatom lipid biomarkers (heneicosahexaene, fatty acid 16:1) and the chlorophyll a/Pheopigment ratio (Colombo *et al.*, 1996c), which presented highest values in the traps of L July and specially S May (Fig. 4) when an early diatom bloom was sampled. This signal is also detectable in underlying sediments: as has been observed for marine lipids and diatom biomarkers (Colombo *et al.*, 1997), the proportion of Ser is generally higher at the seaward site, particularly in the core collected at S in July during the spring diatom bloom (Fig. 5, Table 2). This provides good field evidence for a diatom source of Ser. The increasing proportion of Ser with sediment depth indicates the selective preservation of the diatom protein–silica complex. The poorer sensitivity of Thr and Gly as diatom tracers might be related to their lower enrichment in the cell-walls. In the five species studied by Hecky *et al.* (1973), the difference between cell-wall and cell contents averaged $1.6 \pm 1.4\%$ for Thr, $4.8 \pm 4.2\%$ for Gly and $9.0 \pm 6.7\%$ for Ser.

Estimates of contribution of marine and terrestrial inputs to THAA in the sediments can be made

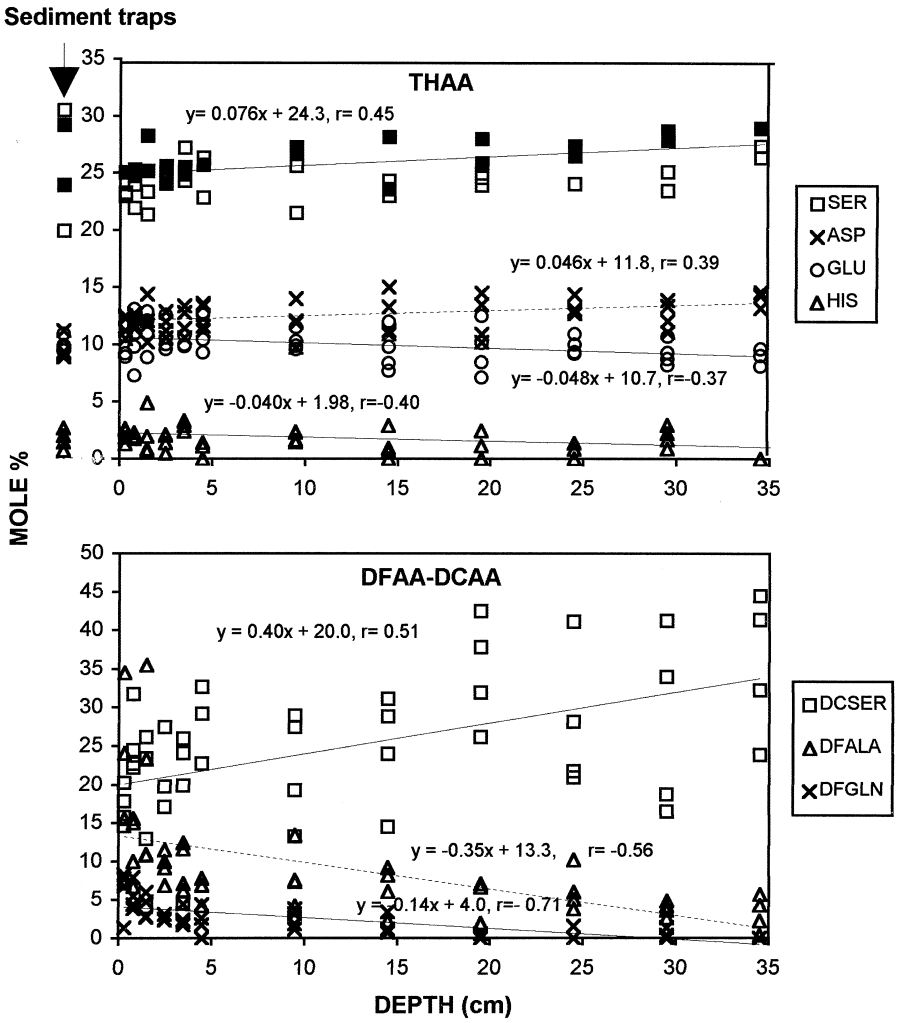

Fig. 5. Variation of the relative abundance of selected solid phase (THAA) and porewater amino acids (DCAA and DFAA) with sediment depth. Trap values are indicated for THAA. Filled points of THAA SER correspond to the cores collected at the seaward site.

by using the amino acid yields of Cowie and Hedges (1992) for phytoplankton, zooplankton and terrestrial vascular plants (55–112, 65–137 and 0.4–17.4 mg THAA/100 mg OC, respectively) and calculations from our previous work (Colombo *et al.*, 1996a) indicating 50% of TOC from terrestrial sources (equivalent to 22.3 mg TOC/g) and 29% from phytoplankton (12.9 mg TOC/g) in the trap material. This calculation shows that most THAA are of marine origin even if the relevant contribution of zooplankton is not estimated, i.e. from 50 to 100% of THAA would come from algae and only about 13% from terrestrial plants.

In coastal environments, the composition of THAA generally shows no clear change with depth in the sediment (Henrichs *et al.*, 1984; Henrichs and Farrington, 1987; Cowie and Hedges, 1992). However, some authors reported a preferential removal of acidic versus the more stable basic amino acids (Rosenfeld, 1979; Gonzalez *et al.*, 1983; Burdige and Martens, 1988). In the Laurentian Trough some subtle compositional changes can be discerned, notably the relative increase of Ser and Asp and slight decrease of Glu and His (Fig. 5). The other amino acids showed very weak and not significant trends ($p = 0.05$): Arg, Val, Phe, Ile and Leu tended to decrease, T + G and Tyr increased slightly and Ala showed more constant profiles (Table 2).

Serine seems to be the most stable amino acid. Its relative increase with depth in the sediments is more pronounced than that of Asp (overall concentration versus depth regression slopes = 0.08 and 0.05; $r = 0.45$ and 0.39, $n = 47$, respectively). In contrast, the proportion of Glu, which shows surface values similar to Asp, decreases with depth (slope = -0.05; $r = -0.37$). The protection of the cell-wall matrix may also explain the unusual relative persistence of Asp. Although Ser is one of the most abundant amino acids in diatom cell-walls,

Asp is also an important component, and in some cases it is enriched, i.e. *Cyclotella cryptica*, whereas Glu is more abundant in the cell contents (Hecky *et al.*, 1973).

Porewater amino acids: DFAA and DCAA concentrations and early diagenesis

The concentrations of DFAA in the sediment porewaters ranged from 1.4 to 16 μM, with the highest levels occurring in the 5–15 cm section. DCAA levels were low and similar to those of DFAA in the top 5 cm and also showed sub-surface maxima (5–32 μM) at 10–15 cm depth (Fig. 2; Table 2). Both amino acid fractions combined represented 2–32% of porewater DOC. DFAA accounted for 2–17% DOC in the first 10 cm and 1.4% at the bottom of the cores. DCAA contribution was higher at 10 cm (10–19% DOC) and decreased at the top and bottom of the cores. These DFAA concentrations are similar to those reported for the Limfjord, Denmark (1–21 μM) and Georgia salt marsh soils (0.4–8.8 μM), where the profiles also exhibited sub-surface maxima at 4–6 and 10–15 cm, respectively (Gardner and Hanson, 1979; Jorgensen *et al.*, 1981). Much higher DFAA levels have been reported for the Peru Upwelling region (1–5 to 10–200 μM), Buzzards Bay (5 to 30–60 μM) and Cape Lookout Bay (2–5 to 20–60 μM), where DFAA generally decreased exponentially with core depth (Henrichs *et al.*, 1984; Henrichs and Farrington, 1987; Burdige and Martens, 1990).

These exponentially decreasing profiles are interpreted in the context of a general model where DFAA and DCAA are important intermediates in the mineralization of OM (Henrichs *et al.*, 1984; Burdige and Martens, 1988, 1990). Near the oxic–anoxic interface, the hydrolysis of peptides and proteins from the solid phase results in higher concentrations of DFAA and DCAA in the porewaters. These amino acids are then converted by fermentative processes to volatile fatty acids, H_2 or methylated amines which are utilized by sulphate reducing and methanogenic bacteria. DFAA and DCAA can also be incorporated back to the solid phase by abiotic reactions (adsorption, condensation) or by inclusion into bacterial biomass (Burdige, 1989, 1991).

In sediments from the Laurentian Trough, however, the low levels of DFAA and DCAA coincide with the surficial zone of most intense solid phase decay (Fig. 2). This pattern indicates that removal mechanisms (i.e. consumption, irrigation, diffusion) are very intense in this suboxic–anoxic surficial sediment layers (the oxygenated layer is restricted to top 0.5 cm). The presence of clear near-surface (2–4 cm) minima was also observed in the profiles of total DOC and porewater carbohydrates and has been attributed to an intense consumption of DOM, probably enhanced by biologically mediated exchange of solutes within the sediment, and to bioirrigation to overlying waters (Colombo *et al.*, 1996b).

The mineralization of DFAA by bacteria is very intense and accounts for a significant fraction of the ammonium production in anoxic sediments (Burdige, 1991). Tracer experiments indicated that more than 70% of added alanine was metabolized in 2–4 h with turnover times of 5–9 min (Christensen and Blackburn, 1980). In addition to the catabolic uptake of DFAA, their anabolic incorporation into bacterial biomass can also play a significant role. This process was suspected to account for 20–40% of the added amino acids in sediment slurry experiments (Burdige, 1991). DCAA also constitute a source of carbon and nitrogen for bacteria (Coffin, 1989; Rosenstock and Simon, 1993), although DCAA usually show slower turnover times.

Another potentially important sink of DFAA is the transepidermal uptake by benthic organisms. This process occurs even against strong concentration gradients and could cover a major part of the organism energy requirements (Jorgensen, 1976; Stephens *et al.*, 1978). In Buzzards Bay, uptake by benthic organisms was considered insignificant because the calculated potential turnover time of amino acids was higher than the values currently measured in sediments (Henrichs and Farrington, 1987). A different conclusion is obtained for the Laurentian Trough. Using the same rate of uptake utilized for Buzzards Bay (0.5 μmol/g ww/h) and considering only the polychaete biomass in the first 13 cm (≈220 individuals/m^2*0.5 g each = 110 g ww/m^2; Ouellet, 1982), the rate of uptake would be 10 nmol/cm^3/d and the turnover time 19 h, in the range of those reported for marine sediments (<1 to 24 h). This suggests that macrofaunal uptake could be a complementary sink of DFAA in the Laurentian Trough. This conclusion would be reinforced if more recent, higher polychaete abundances (Nehr, 1991) and the presence of echinoderms (8–40/m^2), crustaceans (≈20/m^2) and bivalves (≈19/m^2) are taken into account.

Below 3–5 cm, increasing levels of dissolved amino acids (Fig. 2) indicate that the rates of production outstrip their removal by biological uptake, biodiffusion or adsorption. The presence of sub-surface maxima of DFAA has been related to enhanced microbial activity due to sulphate reduction or to the transition from sulphate reduction to methanogenesis (Jorgensen *et al.*, 1981; Burdige and Martens, 1990). In the Laurentian Trough the data do not allow any firm conclusion: at S the sub-surface amino acid maxima coincide with the depth (17 cm) of maximum sulphate reduction reported for an intermediate site (Edenborn *et al.*, 1987) but at station L the amino acid maxima seem

too shallow (10 cm) to be related with a peak of sulphate reduction.

At the bottom of the cores, microbial remineralization and adsorption onto particles probably predominate, resulting in lower amino acid levels. The consistently higher concentrations of DCAA indicate that they are produced at higher rates, adsorbed to a lesser degree or, more likely, that DCAA are removed more slowly than DFAA. This latter assumption is supported by the greater chemical complexity of DCAA. For estuarine waters, three different DCAA fractions have been proposed: labile proteins ($< 10\%$, bacterial turnover times $= 4 \pm 8$ h), protein–carbohydrate condensation products ($\approx 50\%$; turnover times $= 288 \pm 344$ h) and a nonproteinaceous fraction bound to colloids or small particles (Keil and Kirchman, 1993).

Porewater amino acids: DFAA and DCAA composition, sources and individual reactivity

The composition of DFAA and DCAA show remarkably different patterns (Table 2). DCAA resemble most the patterns of the source biopolymers from the solid phase (THAA) and show a marked abundance of Ser and T + G. In contrast the composition of DFAA show a predominant contribution of Glu and βGlu, probably originating from bacteria. This indicates that although DCAA may be considered as precursors of DFAA, the composition of this more reactive fraction is strongly influenced by other factors such as the abundance or activity of bacteria.

Previous studies in salt marshes and marine sediments reported similar Glu and βGlu-dominated DFAA patterns (Gardner and Hanson, 1979; Jorgensen *et al.*, 1981; Henrichs *et al.*, 1984; Henrichs and Farrington, 1987; Burdige and Martens, 1990). The most probable source of Glu in porewaters is bacteria because Glu is usually the major component of bacterial free amino acid pools. β-Aminoglutaric acid has also been found among the free amino acids of some marine bacteria (Henrichs *et al.*, 1984; Henrichs and Farrington, 1987). The high porewater levels of Glu have also been attributed to its preferential mobilization from the solid phase (Burdige and Martens, 1990). These authors suggested that the selective utilization of Glu and Ala and preservation of Gly in the solid phase (indicated by their opposing mol% trends in THAA) could explain the relative enrichment of Glu and Ala and the depletion of Gly in porewaters relative to THAA. Our amino acid patterns also show an enrichment of Glu and Ala and a depletion of T + G in surficial porewaters relative to THAA, but only Glu showed a moderate decrease in the solid phase (Table 2). Moreover, if DCAA are intermediaries in the formation of DFAA, a selective mobilization of Glu from the solid phase would also produce an enrichment of Glu in the DCAA pool and the proportion of Glu in this fraction is very low (Table 2). Another factor which could influence the distribution of DFAA is adsorption onto particles. However, this process would only contribute to decreasing porewater levels of basic amino acids (Lys, His, Arg, Orn) which react more rapidly with OM and are preferentially adsorbed by clay minerals (Rosenfeld, 1979; Hedges and Hare, 1987; Henrichs and Farrington, 1987; Henrichs and Sugai, 1993).

The selective uptake or release of amino acids by macrofauna could be another relevant process. The transepidermal absorption of amino acids involves the existence of specific membrane carriers, and a preferential uptake of Ala and Gly has been reported for polychaetes, echinoderms and mollusca (Stephens *et al.*, 1978; Stewart, 1979) whereas acidic amino acids (Glu and Asp) show very low or null rates of transport. Thus, when macrofaunal absorption is significant, as it seems to be for the Laurentian Trough, the selective uptake of amino acids could contribute to the abundance of Glu relative to Ala or Gly.

In contrast to THAA, which showed only subtle downcore trends, the composition of porewater amino acids showed marked changes with depth in the sediments, notably the relative increase of Ser in DCAA and of βGlu in the DFAA fraction and the decrease of Gln, Ala and Glu in the DFAA pool.

The relative contribution of Ser to DFAA increases between 9–25 cm and decreases towards the bottom of the cores (Table 2). A clearer downcore relative increase of Ser is observed in the DCAA fraction (Fig. 5) suggesting that this is the most stable amino acid, both in the solid phase and porewaters. The mol% contributions of Gln and Ala to DFAA show a significant decrease with sediment depth. Glutamine is seldom detected below 20 cm, whereas Ala shows a moderate decrease in the core collected at S in July (7–11 to 5–6%) and a strong decay in the other three cores (16–35 to 0.4–4%; Fig. 5). The marked decrease of Ala is consistent with its rapid biological uptake and turnover in marine sediments (Christensen and Blackburn, 1980). However, in the solid phase or in DCAA, Ala did not show any significant trend (Table 2), suggesting that polymerized Ala is not as readily bioavailable.

The opposing trends followed by the relative proportions of Glu (slope $= -0.28$, $r = -0.42$) and βGlu (slope $= 0.74$, $r = 0.80$, $n = 48$) in the DFAA pool (Table 2) strongly suggest the preferential degradation of Glu and its conversion into βGlu. According to Henrichs *et al.* (1984), the relative increase of βGlu in deeper porewaters could be related to (1) changes in the excretion of DFAA by bacteria due to varying chemical conditions of the sediments, (2) differences in the decomposition rates

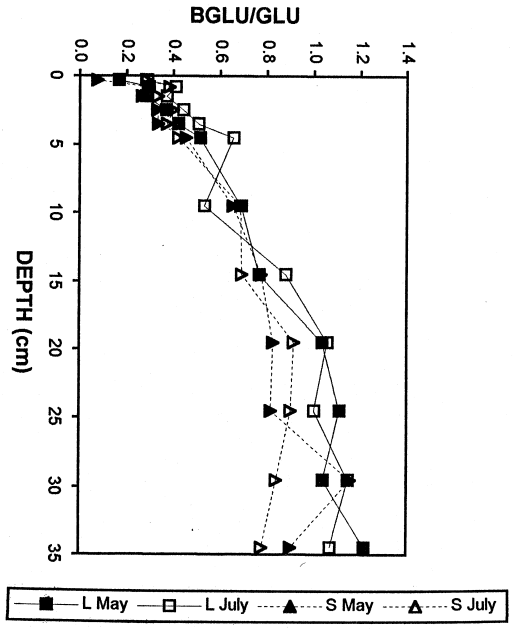

Fig. 6. Evolution of the ratio β-aminoglutaric acid (βGLU)/glutamic acid (GLU) in porewaters from both stations and sampling periods.

of both amino acids or (3) the biologically-mediated formation of βGlu from Glu. The fact that the βGlu/Glu values increase smoothly with depth in our cores regardless of whether the concentrations increase (0–10 cm) or decrease (10–35 cm; Fig. 6), suggests that preferential decay and conversion are coupled, i.e. some fraction of Glu is converted to βGlu during the utilization of the former. This is in agreement with sediment slurry experiments, where the addition of Glu lead to a small (1%) transient build-up of βGlu (Burdige, 1989).

The evolution of the βGlu/Glu values with sediment depth also indicates a geographical difference. The ratios show similar initial values and rates of increase in the first two cm at both stations. Below this depth, the ratios increase more rapidly at L and a clear divergence is observed below 10–15 cm (Fig. 6). These profiles suggest a deeper activity of bacteria with extended selective degradation and conversion of Glu at the landward site. These trends could be related to the higher sedimentation rates and bioturbation observed at the landward station which favor the downward transport of still undegraded OM (Colombo *et al.*, 1996b), thus allowing the continued metabolism of bacteria in deeper sediment layers.

CONCLUSIONS

Total hydrolysable (THAA), dissolved free (DFAA) and combined (DCAA) amino acids were analyzed in settling particles and the solid phase and porewaters of underlying sediments in the Laurentian Trough to evaluate their sources and individual reactivity during early diagenesis. THAA fluxes measured at mid-depth in the water column (234–980 μmol/m^2/d) represented 3.8% of the average daily primary production, comparable to other moderately productive deep coastal areas. The settling organic material showed relatively low %THAA-C and THAA-N indicating partial degradation. Surficial sediments presented an average 56% decrease of THAA levels but similar %THAA-C and %THAA-N compared to settling particles suggesting that TOC, TN and THAA decompose at similar rates. Deeper in the cores, however, THAA were preferentially degraded and accounted for 21% of TOC reduction and 67–80% of TN loss.

THAA composition in settling particles and sediments was relatively uniform and showed an enrichment of serine and threonine + glycine relative to fresh plankton, reflecting the selective preservation of diatom cell-walls. Serine was the most specific diatom tracer and its proportion covaried with that of diatom lipid biomarkers. Its relative abundance was higher at a seaward site, which receive stronger inputs of marine OM and increased downcore reflecting selective preservation of the diatom cell-wall matrix. Glutamic acid and histidine were preferentially degraded with depth in the sediments.

Porewater DFAA and DCAA accounted for 3–25% of total DOC. Low levels in the surface zone of most intense solid phase THAA decay point to strong biological uptake. Deeper in the cores, DFAA were preferentially consumed relative to DCAA. Both fractions showed remarkably different compositions: DCAA were dominated, as was solid phase THAA, by serine and threonine + glycine whereas DFAA were enriched in glutamic and β-aminoglutaric acids of bacterial origin. In contrast to the subtle trends observed for solid phase THAA, the relative abundance of porewater amino acids showed marked changes with sediment depth, reflecting their greater reactivity. βGlu increased and Ala and Glu decreased in the DFAA pool and Ser increased in DCAA. Increases of βGlu/Glu values with sediment depth are attributable to preferential degradation and conversion of Glu into βGlu. These processes were more intense at a landward station, where the higher sedimentation rates and bioturbation favor the burial of relatively undegraded OM, allowing the continued metabolism of bacteria in deeper sediment layers.

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