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Lipid biogeochemistry in the Laurentian Trough—II. Changes in composition of fatty acids, sterols and aliphatic hydrocarbons during early diagenesis

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Abstract—Interfacial sediments of the 300-m deep Laurentian Trough contained 3.2–11, 1.2–6.2, 0.4–2.4, 0.2–0.5 mg g^{-1} OC of fatty acids, unresolved hydrocarbons (UCM), sterols, and resolved aliphatic hydrocarbons, respectively, reflecting a 46–93% loss relative to settling particles intercepted at 150 m depth. A further 22–66% lipid loss was observed between 0–3 and 35 cm depth in the sediments. Lipid accumulation efficiencies in the top 3 cm sediment inventory averaged 21 ± 29% of water column fluxes, and indicated a clear reactivity trend: pheopigments > sterols > fatty acids ≈ total lipids > resolved hydrocarbons > UCM. However, within each lipid class, marine-derived components were as highly reactive as pheopigments, whereas terrestrial compounds behaved akin to the UCM. Extremely labile marine lipids that were enriched in settling particles, such as pristane, 24-methylcholesta-5, 22E-dien-3β-ol, and heneicosahexaene, were quickly lost near the sediment–water interface. Only moderately reactive components (16:0, 16:1 fatty acids, squalene) and the more stable 22:0 and 24:0 acids, fichtelite and UCM persisted deep enough to preserve the geographical trends observed for rapidly settling particles, i.e. predominance of terrestrial and petrogenic compounds at a landward site and prevalence of marine lipids at a station located 120 km further seaward. The preferential decay of marine components continued with depth in the cores, resulting in similar residual lipid patterns at 35 cm depth. However, each site could still be discriminated clearly by its fatty acid and hydrocarbon composition. *In situ* sedimentary processes, such as the vertical distribution of bacteria and the production of coprostanol, were also recorded in the lipid composition of these deep coastal sediments. © 1997 Elsevier Science Ltd

Key words—deep coastal sediments, lipid biomarkers, fatty acids, sterols, aliphatic hydrocarbons, early diagenesis, reactivity, Laurentian Trough

INTRODUCTION

Previous studies on the distribution of bulk organic components and amino acids in settling particles and sediments collected at two contrasting locations in the Laurentian Trough (Colombo *et al.*, 1996a,b,d) revealed clear geographical and temporal patterns in the vertical flux of organic matter (OM) that were effectively recorded in the underlying sediments. Higher fluxes and stronger terrestrial character of the settling material sampled at a landward station were reflected by higher C/N ratios and organic contents in the sediments. The higher sedimentation rates at this site resulted in a continuous decrease of organic matter down to 35 cm depth in the cores as opposed to a levelling off at 5 cm depth at a seaward station. The amino acid composition of settling particles and sediments was very uniform, reflecting a major marine origin at both sites. However, no evidence was found in these data of an unexpectedly important phytoplankton bloom sampled at the seaward site in May. The study of lipid biomarkers in settling particles confirmed the general trends observed for the bulk parameters and revealed specific OM contributions: algae, including diatoms (prevailing during the spring bloom at the seaward site) and dinoflagellates (more abundant during the summer); zooplankton (abundant in all the traps); bacteria, vascular land plants and anthropogenic hydrocarbons which predominated at the landward station (Colombo *et al.*, 1996c).

The detailed evaluation of lipid biomarkers in sediments provides specific information on the sources of organic matter, as well as on the particular conditions of deposition and burial (e.g. Nishimura, 1977, 1982; Barrick *et al.*, 1980; Smith *et al.*, 1983a; Gagosian *et al.*, 1983; Volkman *et al.*, 1981, 1987; Kawamura *et al.*, 1987). The compo-

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sition and depth distribution of lipids in sediments is determined by the relative importance of the different sources (marine, terrestrial, anthropogenic) and by a series of compound-specific (chemical structure, reactivity) and environment-specific (sedimentation rates, oxygen concentration, redox zonation) characteristics. The simultaneous study of different lipid biomarkers facilitates the interpretation of the patterns resulting from the interaction of these complex processes.

In this paper we follow the fate of lipids from water column sources by studying the distribution and composition of fatty acids, sterols and aliphatic hydrocarbons in detailed vertical profiles of underlying sediments.

MATERIALS AND METHODS

A detailed description of the study area, sampling methods and chemical analyses was presented in previous papers (Colombo *et al.*, 1996a,b,c). Briefly, undisturbed bottom sediments were recovered from 320 m at a landward site (L) and 280 m depth at a seaward site (S), using a 0.1 m^2 box corer during each period of sediment trap deployment. The cores were immediately sub-sampled in a glove box under a forced flow of N_2 by scraping successive $\approx$2 mm thick layers in the first centimetre, then taking 1 cm thick slices every 1–5 cm depth and at 5 cm intervals down to 35 cm depth. All samples were stored at −20 or −40°C until analysis. Fatty acids, sterols and hydrocarbons were analysed by high resolution gas chromatography on a 30 m DB5 capillary column with flame ionisation detection. The chemical procedures employed included ultrasonic extraction with 1:1 acetone–petroleum ether (3 × 40 ml for 20–30 g wet weight sediment), acid-catalysed derivatisation of fatty acids to methyl esters, purification and fractionation of hydrocarbons and sterols on silica gel–alumina columns, and derivatisation of sterols to trimethylsilyl ethers.

RESULTS AND DISCUSSION

Depth distribution of total lipids

Tables 1–3 give the total concentrations on a dry weight (DW) and organic carbon (OC) basis, of fatty acid methyl esters (FAMES), sterols, and aliphatic hydrocarbons, including resolved compounds (RESHC) and the unresolved complex mixture (UCM), for the four cores analysed. The concentrations in the top 0–3 cm decrease in the order FAMES (59–247 μg/g DW = 3.2–11.5 mg/g OC) > UCM (27–124 μg/g DW = 1.2–6.2 mg/g OC) > sterols (7.9–42 μg/g DW = 0.4–2.4 mg/g OC) > RESHC (3.7–10 μg/g DW = 0.2–0.5 mg/g OC).

These lipid concentrations lie within the range reported for other coastal environments, being intermediate between those of deep-sea (very low) and organic-rich sediments (very high). Fatty acid levels, for example, are similar to those reported for the Providence River, Narragansett Bay and Buzzards Bay, 30–300 μg/g DW (Farrington and Quinn, 1973; Farrington *et al.*, 1977; Van Vleet and Quinn, 1979), compared with 0.2–26 μg/g for the deep sea (Saliot *et al.*, 1988) and 3760 μg/g for the Peru upwelling (Smith *et al.*, 1983a). Our sterol values are also comparable with those found in Buzzards Bay, 1.4–23 μg/g (Lee *et al.*, 1977), whereas on the Namibian Shelf and off Peru the values rise up to 175–226 and 619 μg/g DW respectively (Smith *et al.*, 1982, 1983b; Volkman *et al.*, 1987). In terms of aliphatic hydrocarbons, the Laurentian Trough is comparable to Puget Sound and the San Nicolas Basin, other mildly polluted (45–115 μg/g DW, with ~75% UCM) deep coastal environments (Barrick *et al.*, 1980; Venkatesan *et al.*, 1980).

A conspicuous feature of the lipid profiles in the Laurentian Trough is the presence of irregular data in the bioturbated upper 5 cm of the cores (Fig. 1). This layer contains ~90% of the sediment macrofauna, including polychaetes, molluscs, echinoderms and bivalves which have been suspected to produce marked influences in early diagenetic processes (Ouellet, 1982; Bouchard, 1983; Sundby *et al.*, 1983; Silverberg *et al.*, 1986, 1987). For this reason, in previous calculations (Colombo *et al.*, 1996b), the top 3 cm sediments have been considered as an homogeneous layer. In addition to promote mixing and diffusion of OM, small (unremoved) burrowing animals could also be a source of lipids and their distribution may be reflected in the subsurface peaks observed in some profiles (Fig. 1).

In spite of these potentially confusing factors, clear differences are observed in the concentration of lipids from sinking particles to interfacial and deeper sediments. As has been observed for bulk organic matter components (Colombo *et al.*, 1996b), lipid levels in the top 3 cm sediments are much lower than those measured in settling particles (particularly fatty acids and sterols; Fig. 1), reflecting the different "freshness" of the OM in each reservoir. The continued loss of OM with depth in the sediments is less dramatic, but by the base of our cores (35 cm), lipid levels are further reduced down to 1.2–3.8 mg FAMES/g OC (17–55 μg/g DW), 0.1–0.5 mg sterols/g OC (2–8 μg/g DW), and 0.2–0.3 mg RESHC/g OC (2.1–4.3 μg/g DW). The low UCM levels at 35 cm depth (0.4–1.7 mg/g OC = 5–25 μg/g DW) would primarily reflect lower petrogenic inputs rather than decay.

The UCM is known to be resistant to degradation (Gough and Rowland, 1990) and its decrease with sediment depth has been related to decreasing anthropogenic inputs in other marine environments (Barrick *et al.*, 1980; Prahl *et al.*, 1980). UCM profiles at station L show a strong reduction down to

Table 1. Total concentrations and relative composition of fatty acids in sediment cores collected at landward (L) and seaward (S) sites in the Lower St. Lawrence Estuary

		Total conc.		% Total fatty acid																							
		μg/g	mg/g																								
Depth (cm)	Sample	DW	OC	12:0	a13:0	14:0	i15:0	a15:0	15:0	i16:0	16:1 (n − 7)	16:0	18:1 (n − 7)	18:1 (n − 9)	18:0	20:5	20:1	20:0	22:6	22:5	22:1	22:0	23:0	24:1	24:0	25:0	26:0	27:0
0–0.4	L May	247	11.5	0.4	0.6	3.1	2.1	2.9	0.9	0.8	11.0	13.3	6.2	7.5	5.0	0.8	3.1	2.3	0.3	0.8	3.3	6.9	—	2.0	11.2	1.7	6.9	1.3
	L July	71	3.1	0.2	0.5	3.7	1.9	2.9	1.0	0.5	11.2	15.5	6.5	7.0	4.0	1.3	3.8	1.8	0.6	0.8	3.8	5.9	1.8	2.1	10.2	1.4	5.9	1.1
	S May	97	5.4	0.2	0.5	5.6	2.5	4.1	1.2	0.9	23.0	18.0	7.6	5.8	2.9	1.0	2.0	1.5	0.5	0.6	2.4	4.1	—	2.1	4.0	1.0	4.8	1.2
	S July	70	3.8	0.9	0.5	5.4	2.8	4.5	1.2	0.3	18.0	17.1	7.8	7.5	3.1	1.9	1.9	1.4	0.7	—	0.7	3.7	—	1.6	6.8	1.6	5.4	0.5
0.4–0.6	L May	187	8.8	0.1	0.5	3.3	1.9	2.6	0.9	0.6	11.5	14.0	5.8	6.0	4.2	0.6	2.4	2.2	—	0.7	2.4	7.0	2.0	1.9	12.2	2.1	9.0	2.2
	L July	113	4.7	0.4	0.6	3.3	1.9	2.2	1.0	0.6	13.0	15.0	6.3	6.5	4.5	0.6	1.3	2.1	0.3	—	1.6	7.1	2.2	2.4	13.0	2.0	8.6	1.9
	S May	94	5.3	0.2	0.5	4.2	1.9	3.3	1.0	0.4	18.2	15.2	6.7	6.8	2.6	2.7	4.9	1.4	0.4	3.1	5.6	3.8	1.0	1.0	6.8	1.1	4.8	1.2
	S July	109	6.0	0.5	0.7	3.8	2.1	3.7	1.1	1.0	16.3	14.3	7.2	6.9	2.7	2.2	2.6	1.3	1.0	1.1	4.2	3.7	1.0	2.9	8.3	1.0	4.5	1.5
0.6–1	L May	124	5.9	0.2	0.7	3.7	1.9	3.5	1.0	0.2	10.3	14.4	6.0	6.8	4.6	0.6	1.5	2.4	—	—	2.0	7.3	2.1	2.3	13.0	1.6	7.9	1.2
	L July	97	4.1	0.2	0.6	3.3	2.3	3.7	1.1	0.2	10.3	13.5	5.9	5.9	4.2	0.6	2.5	2.1	0.2	—	1.8	7.0	2.1	2.2	12.2	1.7	8.1	3.4
	S May	83	4.5	0.7	0.4	4.7	2.7	4.7	1.3	0.5	19.4	17.1	7.2	5.3	3.1	1.2	1.4	1.3	—	—	1.8	4.7	—	1.7	8.3	1.3	5.7	1.1
	S July	102	4.7	0.3	0.5	4.3	2.6	4.9	1.3	0.4	17.0	16.2	8.6	7.4	3.8	2.0	1.6	1.3	0.5	—	0.7	4.2	1.2	1.3	7.6	1.1	5.7	1.3
1–2	L May	96	4.7	0.2	0.6	3.1	1.9	2.8	1.0	0.3	10.0	14.3	6.6	6.5	4.5	0.6	4.4	2.0	0.4	2.3	1.6	6.9	2.0	2.4	13.0	1.5	6.2	1.1
	L July	101	4.3	0.7	0.6	3.4	2.6	4.2	1.5	0.9	12.2	14.0	5.7	5.8	4.2	0.4	1.3	2.2	0.3	—	1.0	7.4	2.6	2.2	13.1	2.0	0.2	1.6
	S May	98	4.8	0.3	0.6	4.7	2.8	5.1	1.3	0.5	16.3	14.2	7.6	6.1	3.0	1.3	2.0	1.7	0.4	0.7	1.3	4.5	—	2.3	8.8	1.4	5.5	2.3
	S July	77	3.7	0.5	—	4.2	2.6	5.5	1.5	0.5	18.0	16.0	7.9	7.3	3.1	1.6	2.6	1.5	—	1.5	1.5	4.8	1.1	7.0	8.4	1.1	5.9	0.5
2–3	L May	123	6.2	0.2	0.6	3.5	2.1	2.7	1.2	1.8	10.2	14.4	6.3	5.9	4.5	0.9	1.5	2.3	0.4	—	2.7	6.9	2.0	2.4	11.5	1.4	6.4	4.2
	L July																											
	S May	163	9.0	1.0	0.6	4.3	2.7	5.5	1.4	1.0	18.2	13.2	7.2	6.2	3.1	1.6	2.3	1.7	0.6	1.1	2.0	4.8	1.2	1.7	7.8	1.2	5.5	1.2
	S July	59	3.2	0.1	0.9	4.0	2.6	6.2	1.5	0.7	15.0	15.2	7.5	7.3	3.3	1.1	1.5	1.8	—	—	0.9	5.1	1.3	2.2	8.8	1.3	5.5	1.5
3–4	L May	111	5.7	0.3	0.3	3.3	2.3	3.2	1.3	0.7	12.0	13.4	5.7	4.7	4.5	0.6	1.4	2.4	2.0	—	2.6	7.3	2.2	2.5	13.0	1.7	6.7	1.4
	L July	89	4.4	0.6	0.7	3.5	2.4	5.4	1.3	0.5	9.6	13.0	4.6	5.2	4.5	0.6	1.4	2.5	—	—	0.7	7.3	2.2	2.2	13.0	2.7	7.5	3.3
	S May	83	4.7	0.5	0.6	4.6	2.8	6.3	1.6	0.6	16.0	14.3	7.2	6.3	3.5	2.2	1.4	1.7	0.1	—	1.3	4.6	1.3	1.4	8.0	1.3	5.3	0.8
	S July	81	4.2	0.1	0.7	3.5	2.7	6.2	1.5	0.5	15.2	14.2	6.3	5.5	3.3	0.7	3.2	1.7	—	—	1.2	5.8	1.2	2.2	11.2	1.3	7.7	2.2
4–5	L May	195	10.3	0.4	0.6	3.4	2.8	5.2	1.7	0.8	11.0	12.5	4.8	5.7	4.5	0.4	1.3	2.4	0.2	—	1.6	7.4	2.4	1.7	14.1	1.8	7.3	1.6
	L July	73	3.8	0.6	0.7	4.0	2.5	5.9	1.4	0.6	9.6	14.0	4.1	5.0	4.5	1.1	1.7	2.3	—	—	1.3	6.9	2.3	2.3	13.0	2.0	8.2	1.6
	S May	92	6.0	0.4	0.5	4.2	3.4	7.8	1.8	1.2	18.0	13.0	6.5	5.5	2.8	1.7	1.8	1.7	0.6	0.5	0.8	4.2	1.2	1.5	7.8	—	5.1	0.9
	S July	56	3.4	0.2	0.2	4.0	2.7	6.7	1.6	0.7	12.4	15.0	7.3	7.1	3.8	2.9	3.1	2.0	0.4	—	1.8	4.7	1.1	1.8	8.4	1.1	5.5	0.9
9–10	L May	111	5.8	0.4	0.7	3.4	2.4	6.3	1.4	0.5	7.5	12.5	3.8	6.1	4.9	0.9	1.0	3.1	—	—	2.3	7.3	2.4	2.6	14.0	1.6	8.2	1.8
	L July	55	3.1	0.6	0.7	3.9	2.2	5.4	1.3	0.7	10.4	14.1	3.9	6.1	4.6	0.9	2.2	2.4	0.2	—	1.3	7.1	2.0	2.6	13.0	1.9	8.0	1.9
	S May	94	6.2	0.8	0.3	4.8	2.7	8.4	1.6	1.1	12.3	13.5	3.5	4.3	3.7	1.4	2.7	2.5	—	0.5	1.2	5.5	1.6	2.4	10.2	1.8	8.1	2.2
	S July	49	3.4	0.7	0.4	4.5	2.7	9.0	1.6	1.1	11.0	15.0	3.1	6.1	3.8	1.3	1.3	2.7	—	0.4	1.3	5.6	1.8	2.7	11.0	—	9.0	1.6
14–15	L May	99	5.5	0.5	0.2	3.0	2.1	6.4	1.1	0.7	5.2	11.0	2.6	5.9	4.4	—	1.5	4.0	—	0.3	1.6	8.1	2.5	2.8	15.0	2.2	11.0	3.6
	L July	48	2.8	0.6	0.8	3.7	2.1	6.2	1.2	0.6	7.9	13.3	2.9	5.8	5.0	—	1.2	3.1	—	—	1.2	8.5	2.5	2.9	15.0	2.1	8.7	2.9
	S May	61	3.9	0.7	0.7	4.6	3.0	9.4	1.3	0.7	5.8	14.5	2.8	5.4	3.6	0.3	1.7	3.0	—	—	1.3	6.1	1.7	3.5	12.0	2.1	10.1	1.8
	S July	25	1.9	0.3	—	4.0	2.2	7.0	1.3	0.9	7.9	16.0	2.2	4.4	4.0	—	1.8	3.1	—	—	1.8	6.2	1.8	3.5	13.0	2.6	12.0	2.6

Table 1—*continued*

Depth (cm)	Sample	Total conc. μg/g DW	Total conc. mg/g OC	% Total fatty acid 12:0	a13:0	14:0	i15:0	a15:0	15:0	i16:0	16:1 (n − 7)	16:0	18:1 (n − 7)	18:1 (n − 9)	18:0	20:5	20:1	20:0	22:6	22:5	22:1	22:0	23:0	24:1	24:0	25:0	26:0	27:0
19–20	L May	61	3.7	0.3	0.7	3.3	2.3	8.0	1.3	0.5	4.4	12.3	2.6	6.5	4.7	—	1.6	3.6	—	—	2.0	8.0	2.6	3.1	15.0	2.1	8.8	1.5
	L July	37	2.3	1.1	0.8	3.9	2.5	8.6	1.4	1.1	5.0	13.0	1.4	3.6	4.7	—	1.4	3.3	—	—	1.4	8.6	2.5	3.3	15.5	2.2	9.7	2.2
	S May	36	2.6	1.1	0.6	4.2	2.5	8.7	1.4	0.6	7.3	15.4	2.2	4.8	3.4	—	1.4	2.8	—	—	2.0	5.3	1.7	3.4	11.5	2.5	11.0	3.6
	S July	28	2.0	0.8	1.2	5.0	1.9	7.7	1.5	1.2	7.3	18.5	1.2	3.5	3.9	—	1.9	2.7	—	—	1.5	5.0	1.5	3.5	11.2	2.3	11.2	3.1
24–25	L May	47	2.8	0.4	0.8	3.4	1.9	5.7	1.3	0.6	5.1	13.3	2.1	5.5	4.9	—	1.9	3.6	—	—	1.5	8.7	2.5	3.4	15.4	2.3	9.1	3.6
	L July	40	2.4	0.5	0.8	3.2	2.2	8.1	1.1	0.5	3.8	12.4	1.9	5.7	4.6		1.9	3.2	—	—	1.9	8.4	2.4	3.8	16.0	2.2	10.5	2.2
	S May	36	2.8	1.4	—	4.7	2.2	8.0	1.4	0.5	6.3	16.2	1.9	6.3	3.3		5.2	2.7	—	—	3.6	4.7	1.1	4.4	10.2	2.2	9.6	2.2
	S July	26	1.9	0.8	—	4.9	1.6	6.1	1.6	0.4	5.7	18.4	1.2	3.7	3.7	—	1.6	3.3	—	—	2.0	6.1	1.6	4.1	13.1	2.9	13.1	2.4
29–30	L May	74	4.5	0.3	0.3	3.3	2.0	6.3	1.2	0.4	3.8	12.0	1.8	3.3	4.6	—	1.6	3.9	—	—	2.2	8.8	2.7	3.5	17.0	3.1	13.3	2.7
	L July	28	1.8	0.1	0.8	3.0	1.9	6.8	1.1	0.4	4.5	12.0	1.5	5.3	4.5	—	1.9	3.4		—	2.3	8.6	2.6	3.0	16.5	3.0	12.4	3.4
	S May	37	2.7	1.3	—	4.3	1.9	5.9	1.3	0.5	5.6	16.0	1.6	4.0	3.5		1.6	3.0		—	1.6	5.6	1.6	3.8	12.1	7.0	11.0	5.4
	S July	23	1.6	1.8	—	5.3	1.3	5.3	1.3	—	4.8	19.3	1.8	3.5	3.9	—	1.8	3.1	—		2.2	5.3	1.3	3.9	13.0	3.1	14.0	2.6
34–35	L May	55	3.8	0.7	0.7	3.8	1.8	5.5	1.3	0.5	4.2	13.1	2.0	6.7	4.7	—	2.0	3.3	—	—	2.6	7.5	2.2	4.4	15.0	2.6	10.4	1.8
	L July	35	2.3	0.9	0.9	3.3	1.8	7.2	0.9	0.6	3.6	12.0	1.8	5.7	4.2	—	1.8	3.3	—	—	2.1	8.1	2.4	3.9	16.1	3.0	12.0	2.4
	S May	21	1.6	1.4	—	4.3	1.9	6.2	1.4	1.0	5.7	19.0	1.9	4.8	4.3	—	1.4	2.9	—	—	2.4	6.2	1.9	3.8	12.4	2.4	11.4	1.9
	S July	17	1.2	0.3	0.4	3.6	1.2	3.6	1.8	—	4.2	20.5	1.8	4.2	3.6	—	2.4	3.0	—	—	2.4	5.4	1.8	4.8	13.3	3.0	14.5	3.0

DW: dry weight; OC: organic carbon; — below detection limits.

Table 2. Total concentrations and relative composition of sterols in sediment cores collected at landward (L) and seaward (S) sites in the Lower St. Lawrence Estuary

		Total conc.		% Total sterol												
Depth (cm)	Sample	μg/g DW	mg/g OC	A	C	E	G	H	I	J	L + M	P	S	T	U	X
0–0.4	L May	20.2	0.9	1.5	7.4	8.9	14.4	3.0	4.5	4.5	12.0	4.5	5.0	18.3	9.9	6.4
	L July	36.4	1.6	0.6	5.0	5.0	14.3	5.6	5.6	6.5	11.2	5.5	7.0	18.0	9.0	6.6
	S May	42.1	2.4	1.4	5.0	5.9	11.0	4.5	5.9	5.5	12.0	8.3	4.8	17.1	8.8	10.2
	S July	20.0	1.1	1.8	3.7	7.9	16.0	6.7	5.7	5.5	13.4	2.4	5.4	17.0	7.3	7.3
0.4–0.6	L May	18.1	0.9	2.4	7.7	13.0	12.2	7.7	2.9	2.2	12.0	4.0	4.4	18.0	8.5	5.0
	L July	19.2	0.8	1.2	6.1	6.0	16.0	7.9	4.3	6.5	12.0	3.0	7.5	17.0	7.5	5.5
	S May	10.2	0.6	2.0	6.9	6.8	15.0	7.0	6.9	5.9	8.8	2.0	5.9	18.0	8.8	6.9
	S July	15.0	0.8	1.2	6.5	5.4	14.4	6.7	6.2	5.9	12.4	2.3	6.4	16.0	7.9	8.5
0.6–1	L May	16.0	0.8	2.6	6.4	9.6	12.2	7.1	3.8	5.1	7.7	6.4	4.5	16.0	12.2	6.4
	L July	30.0	1.3	0.4	5.2	5.0	10.1	5.6	3.6	5.2	12.0	4.5	7.7	18.1	14.0	8.5
	S May	7.9	0.4	1.3	7.6	5.1	15.2	6.3	7.6	6.3	15.2	6.3	6.3	13.0	5.1	5.1
	S July	36.2	1.7	0.7	5.6	6.3	11.0	5.2	5.2	5.2	9.7	5.2	7.8	17.5	8.9	12.0
1–2	L May	14.0	0.7	0.8	1.4	5.0	24.0	4.3	2.8	4.0	7.9	2.9	5.7	25.0	11.4	5.0
	S May	11.0	0.5	0.9	5.6	7.4	16.0	5.6	3.7	4.7	12.0	7.4	6.0	16.0	8.6	6.5
	L July															
	S July	15.0	0.7	1.9	6.5	4.7	17.0	4.7	5.5	5.7	8.4	3.7	5.7	17.0	9.0	10.3
2—3	L May	24.0	1.2	0.8	6.6	8.2	15.5	5.0	4.2	4.6	12.0	5.0	6.2	18.0	10.1	4.2
	S May															
	L July	7.9	0.4	1.3	7.6	7.0	13.0	6.3	5.1	5.1	13.0	6.3	6.7	14.0	6.7	8.0
	S July	9.0	0.5	—	1.4	4.3	16.0	1.4	—	8.7	8.7	4.3	11.6	25.0	16.0	2.9
3—4	L May	18.0	0.9	0.5	5.6	6.7	11.1	5.6	3.3	3.9	15.0	3.9	6.0	18.3	12.0	8.3
	L July	14.0	0.7	0.5	6.1	4.5	15.2	7.6	3.5	6.1	14.0	2.3	7.6	19.0	10.0	3.8
	S May	19.4	1.1	0.5	5.2	7.3	22.0	4.1	4.2	3.6	9.2	6.2	6.6	13.4	6.2	11.0
	S July	12.0	0.6	—	1.1	5.7	22.0	1.2	—	9.0	8.0	—	11.4	20.5	11.4	10.2
4–5	L May	13.3	0.7	0.7	6.0	4.5	16.5	6.8	3.9	6.0	14.0	3.8	5.3	17.3	7.7	7.5
	L July	26.2	1.4	0.4	5.0	3.4	20.5	5.9	4.7	5.5	13.0	3.9	7.2	16.0	10.0	4.3
	S May	7.3	0.5	1.0	9.6	7.0	18.0	5.5	2.7	5.5	11.0	4.1	6.0	13.0	6.4	10.0
	S July	10.0	0.6	0.6	6.2	6.0	26.0	5.0	4.2	3.7	12.3	6.2	4.7	12.3	7.3	6.2
9–10	L May	16.0	0.8	0.5	5.7	3.8	20.3	6.3	2.5	5.7	10.1	3.2	6.3	16.5	15.0	4.4
	L July	16.0	0.9	0.6	3.8	3.3	15.0	5.7	3.8	5.7	16.0	6.4	6.9	16.0	10.5	5.7
	S May	5.9	0.4	1.0	10.2	6.1	12.0	6.8	3.7	5.1	9.5	5.3	8.6	14.0	9.2	8.5
	S July	7.4	0.5	—	10.3	3.4	15.0	5.9	—	2.9	4.4	—	11.8	18.0	13.0	15.0
14–15	L May	7.3	0.4	—	2.4	6.8	14.0	5.5	1.4	2.7	4.1	4.1	8.2	26.0	19.2	5.5
	L July	19.3	1.1	0.4	6.7	3.6	5.2	6.2	—	6.8	9.8	7.8	9.3	19.0	17.1	8.3
	S May	5.8	0.4	0.9	12.0	5.9	6.9	6.9	2.2	8.0	6.5	5.5	10.0	15.5	9.5	10.3
	S July	8.2	0.6	—	11.0	2.7	8.1	4.1	—	8.0	6.7	5.5	15.0	16.2	11.0	12.2

Table 2—*continued*

Depth (cm)	Sample	Total conc.		% Total sterol												
		μg/g DW	mg/g OC	A	C	E	G	H	I	J	L + M	P	S	T	U	X
19–20	L May	6.5	0.4	—	2.8	6.2	11.0	6.2	1.5	3.1	6.2	3.1	6.2	27.0	20.0	6.2
	L July	9.7	0.6	0.6	7.3	3.1	4.2	5.3	—	7.5	8.4	4.2	12.0	19.0	18.0	10.0
	S May	3.6	0.3	0.4	17.0	5.6	5.6	5.6	—	8.3	5.6	4.3	14.0	14.0	11.0	8.3
	S July	3.9	0.3	—	16.7	8.3	8.3	5.6	—	5.6	4.8	—	13.0	15.0	11.0	11.1
24–25	L May	6.8	0.4	0.4	7.4	4.4	4.4	5.9	2.9	7.4	8.8	2.9	8.8	21.0	20.0	5.9
	L July	12.3	0.7	0.5	9.7	4.2	4.4	6.2	—	7.0	8.3	4.1	14.0	18.0	15.0	8.0
	S May	2.0	0.2	—	4.5	5.0	15.0	5.0	—	4.6	3.3	5.0	15.0	19.0	20.0	4.0
	S July	4.5	0.3	—	18.6	1.6	7.0	4.7	—	6.3	4.4	—	16.0	14.0	13.0	12.0
29–30	L May	8.6	0.5	0.6	8.1	3.5	3.5	8.1	0.3	4.7	8.1	3.5	12.0	21.0	20.0	7.0
	L July	8.6	0.6	1.2	9.2	4.6	6.0	6.0	—	8.4	9.6	—	13.5	17.0	14.0	9.6
	S May	1.4	0.1	—	21.4	7.1	5.0	5.0	—	5.7	3.6	4.0	14.3	17.0	9.3	7.1
	S July	4.4	0.3	—	18.2	5.1	6.8	4.5	—	9.0	4.5	—	16.0	14.0	12.0	9.1
34–35	L May	4.4	0.3	1.5	7.8	2.3	4.5	5.8	0.9	2.5	9.0	4.5	11.0	19.0	20.0	11.0
	L July	8.0	0.5	0.8	9.1	6.5	5.2	6.5	—	7.4	8.5	2.6	14.0	16.0	14.0	9.1
	S May	2.0	0.1	—	20.0	3.5	5.0	5.0	—	7.0	4.5	4.0	10.0	15.0	15.0	10.0
	S July	4.3	0.3	—	19.0	4.9	7.3	4.9	—	7.3	3.4	7.3	16.0	9.8	9.0	11.0

DW: dry weight: OC: organic carbon; — below detection limits.
A: 24-norcholestra-5, 22E-dien-3β-ol.
C: 5β-cholestan-3β-ol (coprostanol).
E: cholesta-5, 22E-dien-3β-ol.
G: cholest-5-en-3β-ol (cholesterol).
H: 5α-cholestan-3β-ol (cholestanol).
I: 24-methylcholesta-5, 22E-dien-3β-ol (24α: crino-diatomsterol; 24β: brassicasterol).
J: 24-methyl-5α-cholest-22E-en-3β-ol.
L: 24-methylcholesta-5, 24(28)-dien-3β-ol (24-methylenecholesterol).
M: 24-methyl-5α-cholest-24(28)-en-3β-ol + 24-methylcholest-5-en-3β-ol (24α campesterol; 24β dihydrobrassicasterol).
P: 23, 24-dimethyl-5α-cholest-22E-en-3β-ol + 24-ethylcholesta-5, 22E-dien-3β-ol (24αstigmasterol; 24β poriferasterol).
S: 23, 24-dimethylcholest-5-en-3β-ol.
T: 23, 24-dimethyl-5α-cholestan-3β-ol + 24-ethylcholest-5-en-3β-ol (24αsitosterol; 24β clionasterol) + 24-ethylcholesta-5, 24(28)E-dien-3β-ol (fucosterol).
U: 24-ethyl-5α-cholestan-3β-ol (stigmastanol) + 24-ethyl-5-cholest-24(28)E-en-3β-ol + 24-ethylcholesta-5, 24(28)Z-dien-3β-ol (isofucosterol).
X: 4α, 23, 24-trimethyl-5α-cholest-22-en-3β-ol (dinosterol).

Table 3. Total concentrations and relative composition of aliphatic hydrocarbons in sediment cores collected at landward (L) and seaward (S) sites in the Lower St. Lawrence Estuary

		Total conc.				% Total hydrocarbon																							
		μg/g DW		mg/g OC																									
Depth (cm)	Sample	RESHC	UCM	RESHC	UCM	C14	C15	C16	C17	Pris	C18	Phyt	C19	Ficht	C20	HEH	C21	C22	C23	C24	C25	C26	C27	C28	Squal	C29	C30	C31	C32	C33
0–0.4	L May	6.7	80	0.3	3.7	0.7	0.9	1.0	3.9	4.2	1.2	1.2	1.8	1.9	1.3	—	2.5	4.0	6.9	2.2	8.5	3.6	11.2	4.9	0.6	12.0	3.0	8.4	2.2	3.4
	L July	8.1	69	0.4	3.0	0.7	1.0	1.1	4.3	3.2	1.4	0.4	1.7	2.0	1.5	0.3	2.9	2.4	6.0	2.7	8.1	3.8	12.3	4.2	1.8	13.1	3.5	8.4	1.7	4.5
	S May	3.9	38	0.2	2.1	0.5	0.8	1.3	3.6	4.6	1.5	0.5	1.8	0.8	1.5	0.8	2.8	2.3	5.7	2.8	8.2	3.4	12.4	4.9	2.8	13.0	3.4	9.5	1.8	3.6
	S July	4.3	35	0.2	1.9	—	0.9	0.9	3.7	2.6	1.4	0.6	1.7	0.9	1.4	0.4	2.9	2.3	6.3	2.9	7.7	2.9	12.0	3.4	3.1	13.0	3.4	9.1	2.0	4.0
0.4–0.6	L May	10.1	124	0.5	5.8	1.0	1.0	1.2	4.1	4.1	1.4	0.5	1.9	2.0	1.3	0.1	3.1	2.2	7.8	2.5	3.0	3.4	12.2	4.8	0.3	12.0	4.1	9.3	4.0	4.9
	L July	9.1	111	0.4	4.7	0.6	0.9	1.2	4.3	3.2	1.5	0.5	1.5	1.8	1.4	—	2.6	2.2	6.2	2.7	8.0	3.7	12.2	4.9	1.5	13.0	2.4	9.0	2.3	4.9
	S May	7.2	60	0.4	3.4	0.7	1.0	1.2	3.5	4.4	1.7	0.6	1.8	0.8	1.3	0.4	2.6	2.2	5.2	2.3	8.0	2.9	12.0	5.4	1.1	12.4	3.9	9.5	2.1	4.3
	S July	3.7	37	0.2	2.0	0.6	0.9	0.9	3.5	2.2	1.3	0.3	1.6	0.6	1.6	0.5	2.8	1.6	5.7	2.5	7.0	2.8	12.0	3.5	3.2	12.3	3.5	9.5	1.9	4.1
0.6–1	L May	7.9	86	0.4	4.1	0.8	0.9	1.0	4.3	3.9	1.4	0.6	1.6	1.9	1.5	0.3	3.0	1.9	6.3	2.7	8.6	3.4	12.5	4.9	1.5	12.4	3.4	8.7	1.8	3.3
	L July	8.5	111	0.4	4.7	0.6	1.0	1.1	4.5	2.8	1.4	0.6	1.7	1.8	1.4	—	2.3	1.6	6.5	2.7	7.8	2.5	12.0	5.2	0.5	12.0	3.8	8.4	2.5	6.2
	S May	5.4	68	0.3	3.7	0.7	1.1	1.1	3.9	3.5	1.5	0.4	1.7	0.9	1.5	0.2	2.8	2.2	6.1	2.4	7.6	3.5	12.4	4.1	1.6	12.0	5.7	9.2	2.4	7.4
	S July	4.4	27	0.2	1.2	0.6	0.9	0.9	3.0	1.8	1.2	0.3	1.5	0.3	1.5	0.6	2.7	1.8	5.5	2.4	7.3	3.0	12.2	4.0	3.1	12.5	3.4	9.8	2.4	4.3
1–2	L May	8.8	75	0.4	3.7	0.8	1.0	1.3	4.9	3.8	1.6	0.6	1.8	2.5	1.6	0.1	3.3	2.0	6.0	3.0	7.5	4.3	11.0	5.0	0.8	11.4	3.8	8.6	2.3	3.1
	L July	8.0	95	0.3	4.1	0.6	1.0	1.3	4.7	2.8	1.6	0.8	1.8	2.1	1.3	—	3.2	2.5	6.5	3.0	8.0	3.1	12.0	6.1	0.8	13.0	3.5	9.0	2.0	3.9
	S May	4.8	54	0.2	2.6	0.6	0.8	1.3	3.8	2.9	1.3	0.4	1.7	0.8	1.1	—	2.5	1.9	6.3	2.3	8.4	2.5	12.0	4.8	2.3	12.0	3.8	8.8	2.1	7.8
	S July	4.5	42	0.2	2.0	0.6	0.9	1.2	4.0	2.2	1.2	0.3	1.5	0.9	1.5	0.7	2.8	1.9	5.3	2.8	7.4	2.8	12.0	4.3	3.4	12.4	3.7	9.0	1.9	5.0
2–3	L May	9.6	124	0.5	6.2	0.8	1.1	1.4	4.9	3.1	1.6	0.6	2.0	2.2	1.7	0.1	3.2	2.2	6.5	2.8	7.5	2.9	11.5	4.8	0.6	11.5	4.3	8.6	2.2	3.8
	L July																													
	S May	6.0	57	0.3	3.1	0.7	1.0	1.2	4.0	2.7	1.5	0.5	1.7	1.0	1.2	0.3	2.5	2.0	6.7	2.5	7.2	2.5	13.0	5.2	1.8	13.0	3.7	9.3	2.2	5.3
	S July	4.4	38	0.2	2.0	0.9	0.9	1.2	3.6	1.5	1.5	0.6	1.8	0.9	1.5	—	3.0	2.1	5.6	2.7	7.1	3.0	13.0	3.6	2.4	13.3	3.8	10.4	2.4	3.3
3–4	L May	12.1	154	0.6	7.9	0.7	1.1	1.2	4.6	2.4	1.5	0.6	2.2	2.9	1.6	0.2	3.2	1.7	6.9	2.7	7.8	3.6	11.0	4.7	0.9	12.0	4.0	8.3	2.3	3.9
	L July	8.7	77	0.4	3.8	0.9	0.8	1.2	4.8	2.5	1.7	0.6	2.1	—	1.7	—	3.4	2.5	6.4	2.1	7.6	2.7	11.5	5.9	1.1	12.0	3.2	8.3	1.5	8.5
	S May	5.1	42	0.3	2.4	0.8	1.0	1.2	3.9	2.4	1.4	0.4	1.8	1.2	1.4	0.6	2.6	1.8	6.1	2.4	7.9	2.9	12.2	4.1	5.9	12.0	3.7	9.2	2.2	4.1
	S July	4.5	28	0.2	1.5	0.9	0.9	1.2	3.9	1.5	1.8	0.3	1.8	1.2	1.2	—	2.7	1.8	5.1	2.1	8.7	3.0	12.0	4.5	3.0	13.2	4.8	9.3	2.1	6.0
4–5	L May	10.0	152	0.5	8.0	0.8	1.1	1.2	4.7	2.1	1.4	0.6	2.0	2.9	1.6	0.1	3.1	2.3	6.0	2.5	6.9	2.3	11.1	6.5	0.5	11.1	4.1	8.2	2.3	6.7
	L July	7.5	100	0.4	5.3	0.6	1.0	1.2	4.3	2.1	1.7	0.7	1.8	2.8	1.4	—	3.0	3.4	6.1	2.6	8.1	3.3	11.0	6.1	1.2	12.1	4.7	8.8	2.1	3.3
	S May	4.0	38	0.3	2.5	—	1.2	1.2	4.2	2.5	1.5	0.5	2.0	1.2	1.2	0.2	3.0	2.2	5.7	2.5	8.7	3.5	7.2	5.2	2.7	13.0	4.0	9.7	2.0	7.7
	S July	4.1	33	0.2	2.0	0.9	0.9	1.2	3.9	1.5	1.5	0.3	1.8	1.2	1.5	0.2	2.4	1.8	5.8	2.4	7.6	2.7	11.0	8.2	3.3	12.0	3.6	9.4	2.1	5.2
9–10	L May	12.0	147	0.6	7.7	0.6	0.9	1.0	3.7	1.7	1.2	0.6	1.8	3.1	1.3	0.2	2.6	2.1	5.6	2.4	8.2	4.3	11.0	4.8	0.3	11.0	3.9	8.8	2.6	5.0
	L July	8.0	93	0.4	5.2	0.6	0.9	1.0	3.8	1.7	1.3	0.6	2.2	2.9	1.4	—	2.8	2.3	5.5	2.7	7.3	3.4	11.0	6.4	1.3	13.2	4.7	8.5	2.7	4.2
	S May	7.1	43	0.5	2.8	0.6	0.8	1.1	4.0	1.7	1.6	0.4	2.0	1.1	1.6	—	2.7	2.1	5.5	2.7	8.5	3.1	12.1	5.1	1.0	12.4	3.5	10.0	1.6	7.8
	S July	2.0	5	0.1	0.3	0.6	1.1	1.1	4.4	1.1	2.2	0.6	2.2	—	2.2	—	3.9	2.8	7.2	3.3	9.4	3.9	14.4	2.8	1.6	14.4	2.2	11.0	1.7	3.9
14–15	L May	10.0	118	0.6	6.6	0.6	0.9	1.1	4.5	1.3	1.3	0.5	1.9	2.9	1.4	—	2.6	1.9	5.5	2.7	7.2	3.4	11.0	6.4	0.2	11.0	3.5	8.5	2.4	8.3
	L July	6.4	62	0.4	3.6	0.5	1.1	1.4	5.9	2.0	1.9	0.5	1.6	4.2	1.6	—	3.3	2.2	5.9	2.3	7.5	3.1	11.0	5.0	1.7	12.0	3.4	8.1	2.2	3.4
	S May	6.6	20	0.4	1.3	0.8	1.1	1.4	4.5	1.4	1.7	0.5	2.1	0.8	1.8	—	3.3	2.6	6.6	3.2	8.3	3.5	14.0	3.6	0.9	14.0	3.0	10.5	1.5	3.8
	S July	2.9	8	0.2	0.6	0.8	1.2	1.5	5.0	1.5	1.9	0.4	2.3	0.8	1.9	—	3.1	2.3	6.2	3.1	9.7	3.1	14.3	4.2	1.2	13.1	1.9	9.7	1.2	5.4

Table 3—*continued*

Depth (cm)	Sample	Total conc. µg/g DW RESHC	UCM	mg/g OC RESHC	UCM	% Total hydrocarbon C14	C15	C16	C17	Pris	C18	Phyt	C19	Ficht	C20	HEH	C21	C22	C23	C24	C25	C26	C27	C28	Squal	C29	C30	C31	C32	C33
19–20	L May	8.3	50	0.5	3.0	1.1	1.2	1.6	6.1	1.7	1.9	0.6	2.4	3.2	1.8	—	3.2	2.4	5.5	2.9	6.9	3.0	10.1	4.8	0.9	11.3	3.2	7.7	2.6	3.5
	L July	3.3	29	0.2	1.8	0.6	1.2	1.5	7.1	1.8	2.1	0.9	2.8	5.2	2.1	—	3.4	2.1	5.8	2.8	7.1	3.4	11.0	5.2	1.5	11.0	3.4	8.6	1.8	2.5
	S May	6.0	13	0.4	0.9	0.7	1.0	1.3	4.1	1.3	1.7	0.5	2.2	0.5	1.7	—	2.8	2.3	6.0	3.3	8.6	3.3	13.4	4.5	0.7	13.0	2.7	9.1	1.3	9.0
	S July	2.1	3	0.2	0.2	0.5	1.0	1.0	4.1	1.0	1.5	0.5	2.1	—	1.5	—	3.6	2.6	6.2	3.6	9.3	3.6	15.5	3.1	1.6	15.5	1.5	11.0	1.5	3.6
24–25	L May	4.6	34	0.3	2.0	0.9	1.3	1.5	6.3	1.1	1.7	0.7	2.2	1.7	2.0	—	3.3	2.6	6.1	2.8	7.6	3.5	11.5	3.7	0.5	12.1	3.3	9.3	1.7	4.3
	L July	6.0	40	0.4	2.4	0.9	1.1	1.5	7.1	1.5	1.8	0.7	2.4	3.8	1.6	—	3.8	2.4	6.4	3.6	8.4	3.3	11.3	4.6	1.1	12.0	3.8	8.4	2.0	2.6
	S May	3.3	7	0.3	0.6	0.6	1.2	1.5	5.1	1.5	2.1	0.6	2.4	0.6	2.1	—	3.6	3.0	6.6	3.6	8.4	3.0	15.0	4.2	1.5	14.0	1.5	9.9	1.2	2.1
	S July	2.0	3	0.2	0.2	0.5	1.0	1.5	4.6	1.0	1.5	0.5	2.0	—	1.5	—	3.6	3.0	6.6	3.6	9.1	3.0	15.2	3.0	1.5	15.0	2.0	11.0	1.0	3.6
29–30	L May	5.4	44	0.3	2.7	0.7	0.9	1.3	6.0	1.3	1.5	0.2	2.0	2.6	1.5	—	3.0	2.4	6.7	3.0	6.9	3.4	11.0	4.3	0.8	12.0	3.2	9.5	1.9	5.6
	L July	4.2	17	0.3	1.1	0.8	1.3	1.5	7.3	1.3	2.0	0.5	2.5	1.5	2.0	—	3.5	2.8	6.8	3.0	8.0	3.3	12.5	3.8	1.5	12.5	2.3	9.0	1.3	3.3
	S May	4.5	5	0.3	0.3	0.7	0.9	1.1	4.2	1.3	1.8	0.7	2.2	—	2.0	—	3.3	2.4	6.4	3.1	8.8	3.5	14.3	4.2	0.2	13.0	1.8	8.6	0.9	9.9
	S July	3.7	3	0.3	0.2	0.6	0.8	1.1	5.2	1.4	1.7	0.6	1.9	—	1.7	—	2.8	2.2	5.5	2.8	8.8	3.6	15.0	4.1	1.4	14.0	1.7	9.1	1.1	8.8
34–35	L May	4.2	25	0.3	1.7	0.9	1.2	1.4	7.6	1.2	1.7	0.7	2.6	1.7	2.1	—	3.8	2.8	7.1	3.3	8.3	3.3	12.0	3.6	0.7	12.0	3.1	8.8	1.2	3.3
	L July	4.3	19	0.3	1.2	1.0	1.2	1.4	7.7	1.2	1.9	0.5	2.4	1.4	2.2	—	3.6	2.7	6.3	3.1	8.5	3.4	12.1	3.1	2.0	13.0	2.4	8.9	1.0	3.6
	S May	3.5	8	0.3	0.6	0.9	1.2	1.4	4.6	1.2	2.0	0.6	2.6	—	2.0	—	3.5	2.6	6.7	3.5	9.3	3.2	14.5	3.8	1.2	14.0	1.7	9.6	1.2	3.5
	S July	2.1	5	0.2	0.4	0.5	1.0	1.0	3.5	1.0	1.5	0.5	2.0	—	2.0	—	3.0	2.5	6.6	3.5	9.1	3.5	16.0	3.0	1.5	16.2	2.0	11.0	1.5	3.5

DW: dry weight; OC: organic carbon; C14 to C35: *n*-alkanes; Pris: pristane; Phyt: phytane; Ficht: fichelite; HEH: heneicosahexaene; Squal: squalene; RESHC: resolved hydrocarbons; UCM: unresolved complex mixture; TOT.Fl: total aliphatic fraction. — below detection limits.

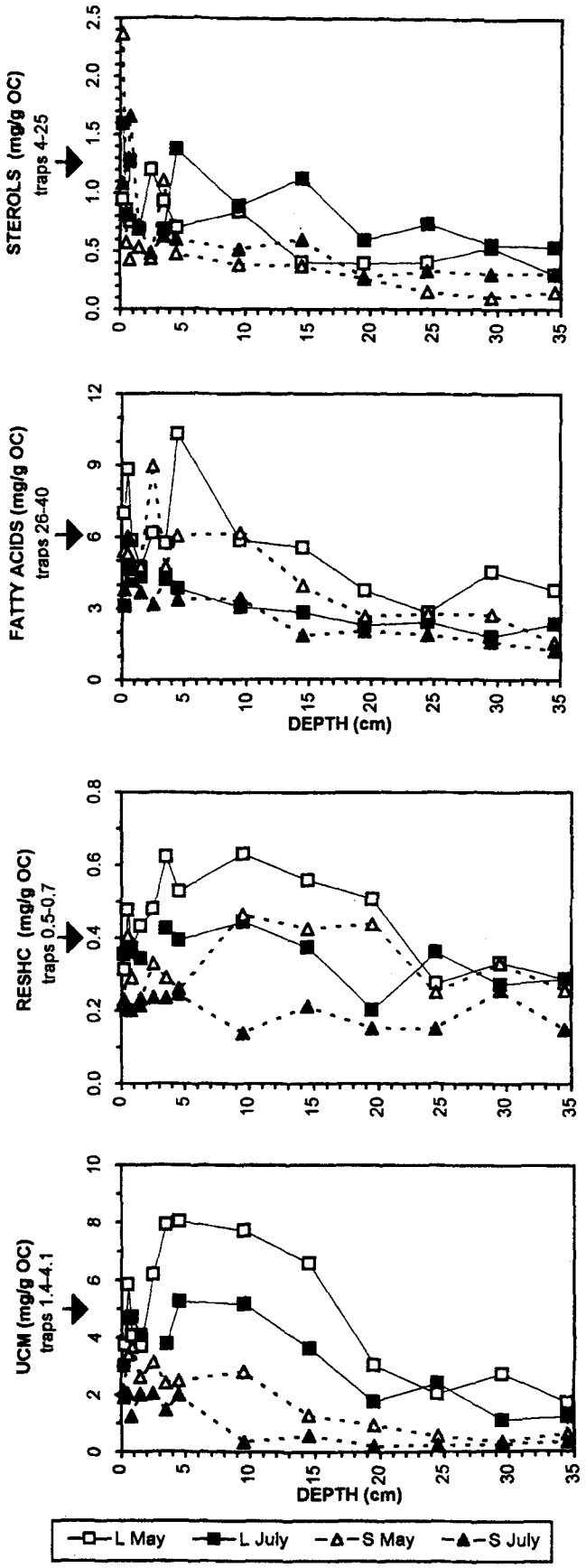

Fig. 1. Sediment profiles of fatty acids, sterols, UCM and resolved aliphatic hydrocarbons. The ranges measured in settling particles are also shown (arrows).

about 20 cm or 25–40 yr before the present (sedimentation rates = 0.6–1.2 cm/yr; Colombo *et al.*, 1996b). An unexpected decreasing trend is also apparent in the top 4–5 cm but the intense bioturbation in this layer complicates the interpretation of the data. At site S, due to the much lower sedimentation rates (≈ 0.2 cm/yr; Colombo *et al.*, 1996b), the recent history of pollution is compressed in the top 5 cm, which represent sediments younger than about 1960. The longer time interval represented by these cores permits a clearer record of pre-industrial baseline levels: the very low (0.2–0.9 mg/g OC = 3–13 μg/g DW), almost constant UCM levels below 20 cm (> 100 yr ago), indicate the virtual absence of anthropogenic contamination.

Relative reactivities of lipids during early diagenesis

A first indication of the differential degradation of the lipid classes studied is shown in Fig. 1, which include the concentrations in the settling material collected 150 m above the bottom. Comparing these values with those in the 0–3 cm surficial sediment layer, the parameter showing the least change is the UCM, whereas sterols evidence the greatest decrease. The percentage "loss" relative to the original trap concentration (OC-based) decreases in the order: sterols (93%) > FAMES (83%) > RESHC (46%) whereas the UCM actually increases from the traps to the top 3 cm sediments (35%, from an average of 2.5–3.4 mg/g OC).

Within the sediments, there remain considerable divergence in the loss rates, with the different "natural" lipids (excluding the UCM) decreasing in a similar relative order. Between the top 3 cm and the base of our cores sterols show the strongest decay, 66% (from an average of 0.97–0.33 mg/g OC), FAMES decrease by 58% (5.4–2.2 mg/g OC), while RESHC drop by 22% (0.32–0.25 mg/g OC). The strong decrease observed for the UCM, 71% (3.4–0.98 mg/g OC) reflects the reduction of anthropogenic inputs in the past (see previous section).

Another more precise quantitative estimate of the relative reactivities was obtained by comparing the inventories of lipids in surficial sediments with the average input from the water column (Colombo *et al.*, 1996d). The inventories of each lipid class and selected individual compounds, as well as of the mineral fraction (residual after subtraction of OM = TOC*1.8) were calculated for the top 3 cm layer. Lipid inventories were then normalised to represent one years' average accumulation according to the following equation:

$$\textit{one year inventory} = \text{0-3 } \textit{cm inventory}^* \frac{\textit{annual mineral flux}}{\text{0-3 } \textit{cm mineral inventory}}$$

The total amount of lipids remaining in this 1-year inventory was then divided by the annual influx to obtain an accumulation efficiency. The results are presented in Table 4. Previously reported TOC, total lipid and pheopigment data (Colombo *et al.*, 1996b) are also included for comparison.

The calculations indicate that a mean of 79 ± 29% of water column lipid fluxes (72 ± 37% at station L and 87 ± 18% at S) is degraded in the top 3 cm sediment layer. The relative reactivity deduced from the accumulation efficiencies confirm that pigments and sterols are the most labile lipids and the UCM the most recalcitrant (even more than TOC). This enhanced persistence of the UCM explains the increase of the OC-based concentrations from the traps to the sediments. The consistently lower efficiencies (greater apparent decay) at the seaward station are related to the predominance of marine inputs and lower sedimentation rates at this site (Colombo *et al.*, 1996b). Significantly higher burial efficiencies and a different reactivity trend have been reported for the top 2 cm of Black Sea sediments: fatty acids (18–19%) < sterols (33%) < C_{23-32} *n*-alkanes (44%; Sun and Wakeham, 1994). This higher lipid preservation is probably related to the anoxic conditions and decreased consumption and bioturbation in this deeper (2100 m) environment.

The average reactivity of each lipid class is a composite result of the reactivities of the individual compounds which vary over a wide range. Pristane, HEH and 14:0 fatty acid are about as labile as total sterols, whereas C_{27} *n*-alkane and 24:0 fatty acid are as persistent as the UCM. According to the accumulation efficiencies three main lipid groups may be distinguished: pheopigments, diatomsterol, cholesterol, stigmastanol, total sterols, 14:0, HEH and pristane (2.5 ± 1.4%); 16:1, 16:0, total FAMES, total lipids and squalene (7.1 ± 2.8%); and 24:0, *n*-C_{27}, RESHC and UCM (63 ± 18%). As suggested for bulk OM components (Colombo *et al.*, 1996b), this reactivity trend would be primarily related to the metabolic utilisation of the components by benthic organisms or bacteria. These organisms could also contribute to the sedimentary lipid reservoir, thus artificially increasing the accumulation efficiencies (e.g. 16:1, 16:0 and squalene are labile and widely distributed compounds).

Individual lipid behaviour during early diagenesis.

The multivariate study of lipid biomarkers in settling particles (Colombo *et al.*, 1996d) evidenced marked spatial and temporal trends of the sources of organic matter contributing to Laurentian Trough sediments. The most conspicuous patterns were the strong diatom signature (14:0, 16:1, 16:0 FAMES, HEH, squalene, campesterol, diatomsterol) of the samples collected at the seaward site in May and the predominance of higher plant biomarkers (22:0, 24:0, 26:0 FAMES; *n*-$C_{25,27,29,31}$; stigmastanol) and petrogenic hydro-

Table 4. "One-year" inventories of different lipids and TOC in the top 3 cm sediments compared with the average water column fluxes

Compound	Station	Inventory μg/cm²/yr	Trap flux μg/cm²/yr	Acc. effic. % trap flux
UCM	L	37.0	38.0	97.0
	S	5.4	11.0	49.0
TOC	L	7970.0	12600.0	63.0
	S	2240.0	6888.0	33.0
RESHC	L	3.2	7.7	42.0
	S	0.6	3.4	17.0
Pristane	L	0.1	2.2	4.5
	S	0.01	1.5	0.7
HEH	L	0.003	0.2	1.5
	S	0.002	0.2	1.0
Squalene	L	0.030	0.4	7.5
	S	0.010	0.2	5.0
n-C27	L	0.4	0.7	57.0
	S	0.1	0.2	50.0
Total Lipids	L	530.0	4730.0	11.0
	S	100.0	1960.0	5.1
Total FAMES	L	44.0	407.0	11.0
	S	11.0	195.0	5.6
14:0	L	1.5	32.0	4.7
	S	0.5	20.0	2.5
16:1	L	4.7	57.0	8.2
	S	2.0	37.0	5.4
16:0	L	6.3	69.0	9.1
	S	1.7	62.0	2.7
24:0	L	5.3	7.5	71.0
	S	0.9	1.7	53.0
Total sterols	L	7.5	219.0	3.4
	S	1.6	93.0	1.7
Diatomsterol (I)	L	0.4	13.0	3.1
	S	0.1	8.6	1.2
Cholesterol (G)	L	1.1	53.0	2.1
	S	0.2	12.0	1.7
Stigmastanol (U)	L	0.7	15.0	4.7
	S	0.1	2.6	3.8
Pheopigments	L	5.7	200.0	2.9
	S	1.3	100.0	1.3

Inventories are the average of both cores taken at each station and have been calculated according to: $C^*p\ (1-\phi)$, where C = concentration: p = sediment density (2.65 g/cm³) and ϕ = porosity. The "one-year" normalisation was performed with the one year flux to inventory ratio of the mineral fraction (residual after sustraction of OM = TOC*1.8: see text).

carbons (n-$C_{24,26,28,30}$, UCM) at the landward site. These trends are effectively preserved in underlying sediments. However, due to the contrasted reactivities of the components, lipid patterns show marked changes from settling particles to deeper sediments, becoming more alike at 35 cm depth in the cores. The prevailing trend is the preferential utilisation of marine lipids and relative enrichment in terrestrial compounds. The molecular structure (degree of unsaturation, chain length) and the depth variation of *in situ* sedimentary sources also contributed to the compositional changes observed.

Fatty acids. Sedimentary fatty acids show a decrease in the proportion of unsaturated and shorter chain FAMES that are more prominent in planktonic sources, and a sharp increase of long-chain terrestrial (>20:0) and bacterial branched acids relative to settling particles (Fig. 2A). This reflects the preferential utilisation of marine OM and of unsaturated and shorter chain FAMES which are primary substrates for organisms, whereas higher molecular weight acids are not (Matsuda and Koyama, 1977; Nishimura and Baker, 1987). The preservation of terrestrial FAMES may also be enhanced by their inclusion in

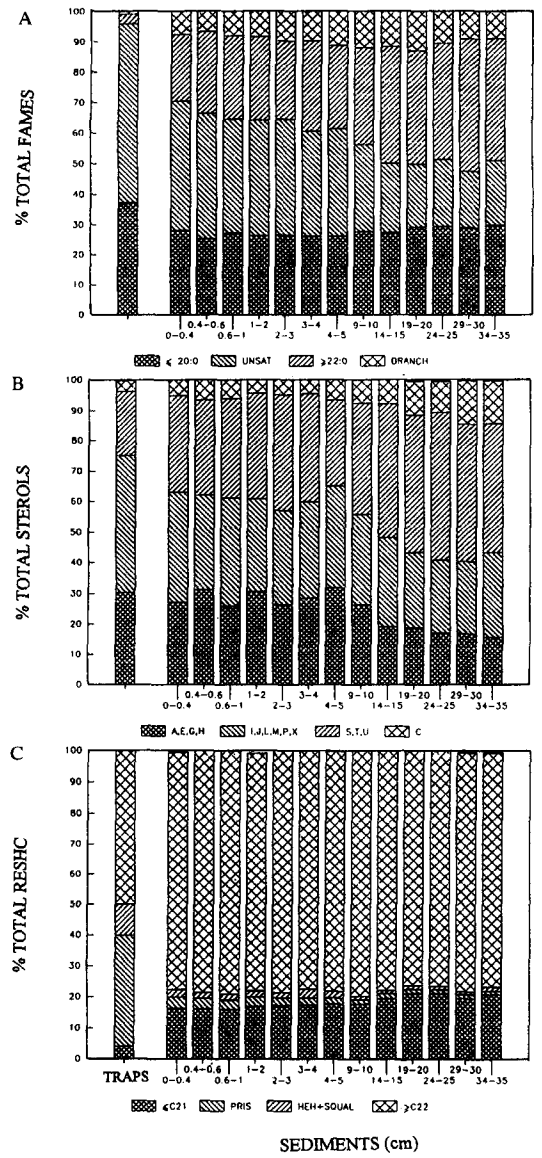

Fig. 2. Changes in the relative composition of fatty acids (A), sterols (B) and hydrocarbons (C) going from settling particles to surficial and deeper sediments. Group identification: ≤20:0 = low molecular weight FAMES; UNSAT = unsaturated FAMES; ≥22:0 = high molecular weight FAMES; BRANCH = branched FAMES; Sterol identification as in Table 2; $\leq C_{21}$ = low molecular weight hydrocarbons; PRIS = pristane; HEH + SQUAL = heneicosahexaene + squalene; $\geq C_{22}$ = high molecular weight hydrocarbons.

resistant and microbially inaccessible higher plant matrices (Kawamura and Ishiwatari, 1984; Nishimura and Baker, 1987; Volkman *et al.*, 1987; Haddad *et al.*, 1992).

Figure 3 summarises the most important trends observed in the fatty acid composition of settling particles and sediments: (a) the preservation of the diatom signature of the spring bloom in the top centimetres of the core collected at station S; (b) the prevalence of marine FAMES at site S and of terrestrial acids at station L; (c) the different reactivity of unsaturated and long chain terrestrial acids; and (d) the relative increase of bacterially-derived a15:0 with depth in the sediment.

The consistent pattern of diatom-derived 14:0, 16:1 ($n-7$) and 16:0 FAMES observed in the traps (values peaking during the spring bloom at the seaward site) is reproduced in the top cm of the concurrently sampled cores. This indicates a rapid transfer of the pulse observed 150 m above the bottom and its effective mixing by benthic organisms into the top centimetre sediments. The stronger pattern of 16:1 ($n-7$) is surprising because 16:0, which showed a greater increase during the diatom bloom and is more persistent than 16:1 ($n-7$), did not present as intense a signal. This may be related to the existence of other marine sources contributing 16:1 ($n-7$) at the seaward site. The different proportions of marine and terrestrial sources at both stations are clearly reflected by 14:0, 16:0 and 16:1 ($n-7$), most abundant at the seaward site, and 22:0 and 24:0 which predominate at the landward station. However, the preservation of the input signals with depth is affected by the individual reactivities: the differences in the proportion of 16:1 ($n-7$) disappear below 10 cm while those of 16:0, 22:0 and 24:0 are maintained throughout the cores. The preferential decay of unsaturated FAMES is also indicated by the decreasing trend of 16:1 ($n-7$) and 18:1 ($n-9$), whereas terrestrially-derived 22:0 and specially 24:0 increase with depth in the cores.

Sedimentary bacteria are the principal source of branched fatty acids whose contribution is thus much higher in sediments than in settling particles (Figs 2 and 3). A clear downcore increase is observed for a15:0. The maxima at 14–20 cm coincide with the depth of a sulphate reduction peak reported for an intermediate site, ≈17 cm (Edenborn *et al.*, 1987), suggesting that sulphate-reducing or fermenting bacteria might be the source. A similar hypothesis has been invoked to explain the abundance of n-$C_{15:0}$ fatty acids in the top 10 cm of Cape Lookout Bight sediments (Haddad *et al.*, 1992). However, further studies are needed in St Lawrence to explain why there is no clear pattern for i15:0 and 17:0, which are also dominant fatty acids in sulphate reducing bacteria (Boon *et al.*, 1977). A combination of lower contents in bacteria and greater reactivity may explain the much less-marked trend of i15:0 (Fig. 3). The more rapid decrease of the iso homolog has been invoked to explain the reduction of the i15:0/a15:0 ratios with sediment depth in other marine environments (Fukushima *et al.*, 1992).

Sterols. The composition of sedimentary sterols also show a higher proportion of terrestrial components (sitosterol = T, stigmastanol = U) com-

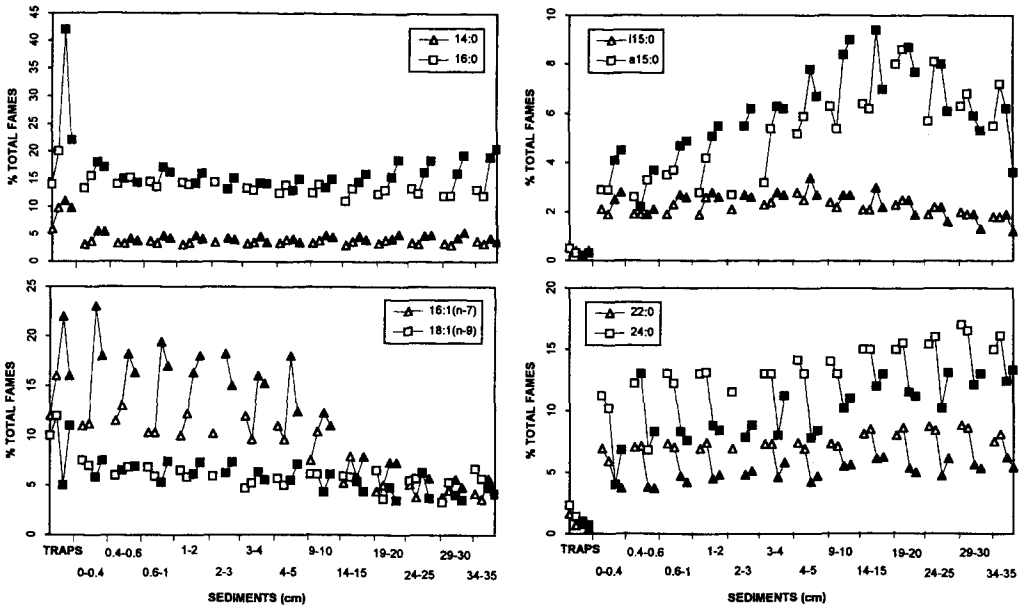

Fig. 3. Variation of the relative abundance of individual fatty acids in settling particles and sediment cores. The order of the traps and sediment samples at each depth is L May, L July, S May and S July. Samples from the seaward site (S) are represented with filled points.

pared with settling particles, which are enriched in marine sterols (diatomsterol = I, 24-methyl-5α-cholest-22E-en-3β-ol = J, 24-methylenecholesterol = L, campesterol = M, stigmasterol = P, dinosterol = X; Fig. 2B). The differential degradation of both fractions continues with depth in the sediments; marine sterols which include algal (I,J,L,M,P,X) and zooplanktonic biomarkers (24-norcholesta-5,22E-dien-3β-ol = A, cholesta-5,22E-dien-3β-ol = E, cholesterol = G, cholestanol = H), decrease while terrigenous C_{29} sterols (S,T,U) increase. However, not all algal sterols show the same behaviour, e.g. dinosterol is resistant and persists down the cores (Table 2). Coprostanol (C) also increases downcore but this is chiefly due to *in situ* production (see below). In Peru upwelling sediments, the persistence of terrestrial sterols has been also related to the presence of biologically-resistant biopolymers (Gagosian *et al.*, 1983; Volkman *et al.*, 1987).

In contrast to fatty acids, which clearly reflected the geographical and temporal trends observed in settling particles, the sterol composition does not preserve this information very well (Fig. 4). This is probably related to the greater reactivity of these compounds which are preserved with very low efficiencies, similar to pheopigments (see previous section).

The diatom signature of station S May traps, high in diatomsterol (I), 24-methylenecholesterol (L) and campesterol (M), is poorly reflected in the sediments. Only in the first centimetre do some patterns similar to the traps appear, particularly in the 0.6–1 cm sample which might reflect inhomogeneous and rapid infaunal mixing of these labile compounds. Geographical distinctions are not preserved in the sterol composition of the sediments. None of the marine or terrestrial components show consistent differences between sampling sites. In North Atlantic abyssal sediments, most early diagenetic losses of sterols also occurred at or near the sediment–water interface and the penetration of labile components was controlled by advective processes associated with infaunal feeding (Conte *et al.*, 1994).

The selective decay of marine sterols and preservation of terrestrial components is illustrated by the decreasing concentrations with depth of I, L, M and G, and the increasing trend of 23,24-dimethylcholest-5-en-3β-ol (sterol S; Fig. 4). As has been observed for 16:1 ($n-7$) fatty acid, the highest proportions of the most labile sterols are found in the first cm. Below 10 cm they show a rapid decrease whereas sterol S and U increase (Table 2). Sitosterol (T), which is also abundant in higher plants, show more constant profiles, probably reflecting its mixed terrestrial–algal origin in the Laurentian Trough (Colombo *et al.*, 1996d).

The other major trend observed in the composition of sterols is the relative increase of 5β-cholestan-3β-ol (coprostanol = C) with sediment depth (Fig. 4). This β stanol and its 5α homologue (cholestanol = H) are produced by hydrogenation of cholesterol in marine sediments (Gaskell and Eglinton, 1974, 1976; Nishimura and Koyama,

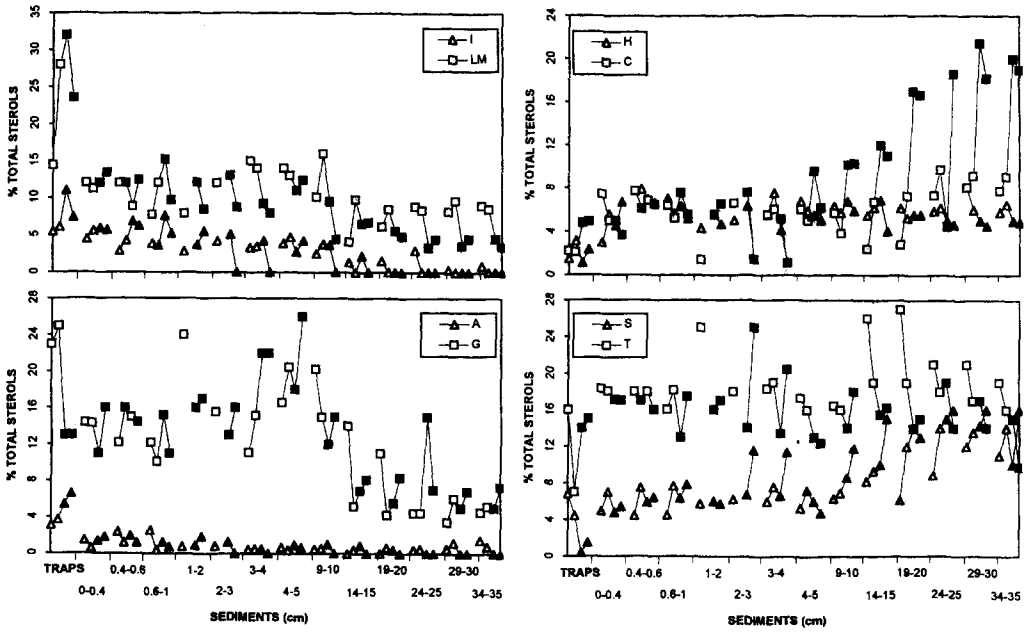

Fig. 4. Variation of the relative abundance of individual sterols in settling particles and sediment cores. Same order of points and codes as in Fig. 3.

1977; Smith *et al.*, 1982). A selective preservation of coprostanol could also produce an increasing trend. However, the α epimer is usually more stable in marine sediments (Grimalt *et al.*, 1990). The almost constant profiles of cholestanol and the marked relative increase of coprostanol below 10 cm at station S, in the zone where cholesterol shows the lowest values, suggest that the *in situ* reduction to coprostanol is the prevailing process.

The rate of conversion of stenols to 5β stanols in sediments seems to be controlled by a series of environmental factors (microbiological activity, redox potential) directly related to the contribution of autochthonous OM (Nishimura, 1978, 1982). The stronger relative increase of coprostanol at site S, which receives a higher proportion of marine OM, agrees with this observation. At the landward station, characterised by stronger terrestrial inputs and higher sedimentation rates and bioturbation, the biohydrogenation of cholesterol to coprostanol is less important and seems to be apparent only below 20 cm.

Hydrocarbons. The composition of resolved hydrocarbons also shows evidence of rapid decay of marine compounds (pristane, HEH and squalene) and selective preservation of terrestrial components ($\geq C_{22}$ *n*-alkanes) in sediments relative to settling particles (Fig. 2C). This results in a marked predominance of the odd *n*-alkanes $C_{23,25,27,29,31}$ characteristic of vascular plant waxes (Table 3). Sediments are also enriched in lower molecular weight *n*-alkanes relative to settling particles. This group seems to contain both petrogenic and biogenic components (see below).

Hydrocarbons appear to be intermediate between fatty acids and sterols in terms of their ability to reflect the patterns observed in settling particles. Marine components seem to be too labile to reflect the diatom bloom sampled at the seaward site in May, but some parameters preserve the terrestrial–marine and polluted–unpolluted differences throughout the cores (Fig. 5).

The clear diatom signature of the traps collected during the spring bloom at station S (high HEH and squalene) is completely lost in the sediments. HEH is very labile and disappears rapidly in the first centimetre. According to the inventory calculations (Table 4), the reactivity of HEH is about five times higher than that of 16:0 and 16:1 ($n-7$) fatty acids which preserved the diatom signal. Squalene is more persistent and retains geographical differences in the top 5 cm (higher proportions at site S). However, this compound is not as specific as HEH, and other non-diatom sources, including faecal matter from higher level consumers, are suspected to exist (Colombo *et al.*, 1996d).

Pristane is another very reactive marine component which does not preserve the pattern observed in the traps and shows a sharp decrease in the sediments. The strongest loss of pristane occurs between particles and surficial sediments (from ~0.2–0.3 to ~0.01 mg g^{-1} OC; 30–50 to 3–4% RESHC); afterward, its relative abundance

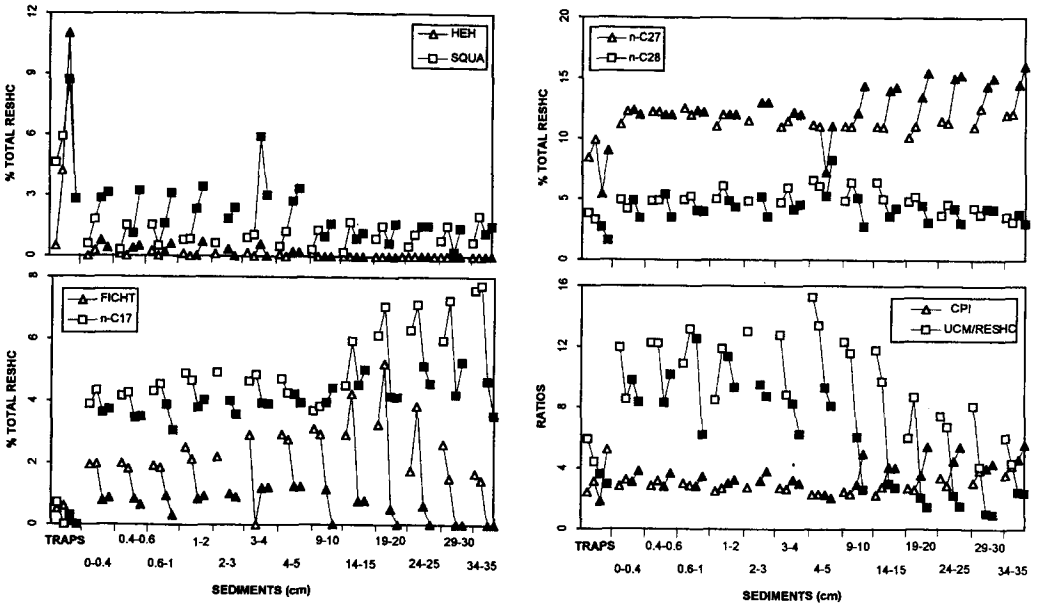

Fig. 5. Variation of the relative abundance of individual hydrocarbons, CPI and UCM/resolved hydrocarbon ratios in settling particles and sediment cores. Same order of samples and codes as in Fig. 3.

decreases slowly down to about 5–10 cm and remains more or less constant in deeper layers (Table 3). According to the inventory calculations, the reactivity of pristane is comparable with that of HEH or sterols in the top 3 cm sediments (Table 4). This contrasted behaviour of pristane (rapid loss in surficial sediments and persistence of residual values down to 35 cm depth) has been observed in other marine environments (Barrick *et al.*, 1980; Prahl *et al.*, 1980), and suggests the existence of at least two sources of pristane: a labile, zooplanktonic source and a more recalcitrant petrogenic component. This different reactivity of fresh and fossil pristane could be related to the presence of a protective physical matrix in crude oils, and/or to a different stereochemistry: zooplanktonic RS meso-pristane is changed to mixtures of RS, RR and SS isomers during maturation (Patience *et al.*, 1978; Mackenzie *et al.*, 1980; Volkman and Maxwell, 1986).

Contrasting with the marked decrease of pristane, the relative abundance of the other low molecular weight hydrocarbons ($\leq n$-C_{21}) increases from settling particles to surface and bottom sediments (Fig. 3c). Petrogenic sources are suspected for some of these components (Colombo *et al.*, 1996d). Algae are rich in n-C_{17} (Blumer *et al.*, 1971) which forms about one-third of $\leq n$-C_{21} in our cores. However, the relative abundance of n-C_{17} is very low in the traps, increases with depth in the sediments and is higher at the landward site, the same as fichtelite, a terrestrial tracer (Fig. 5). This behaviour is probably related to the predominance of the more recalcitrant acyclic multibranched 20:0 (Robson and Rowland, 1988) coeluting with n-C_{17}. Highly branched isoprenoid alkenes are abundant in marine sediments (Gearing *et al.*, 1976; Barrick *et al.*, 1980) and have been also found in diatoms (Volkman *et al.*, 1994). The higher proportion of n-C_{17} + Br20:0 at the landward site, where higher plant markers predominate, is puzzling. These data suggest the existence of an unidentified algal or terrestrial source predominating at station L.

Terrestrially-derived hydrocarbons preferentially preserved in sediments relative to settling particles include the high molecular weight n-alkanes ($\geq n$-C_{22}) and the C_{19} diterpenoid hydrocarbon fichtelite. This compound has been identified as a terrestrial tracer in Puget Sound, although it was not correlated with n-alkanes (Barrick and Hedges, 1981). The consistently higher relative abundance of fichtelite in settling particles and sediments from site L (Fig. 5) supports this observation. Pollution sources, including pulp and paper mills, have also been indicated in the St Lawrence (Gearing *et al.*, 1991).

The suite of high molecular weight odd carbon n-alkanes (n-C_{23-31}) characteristic of higher plant waxes, show no geographical distinctions in Laurentian Trough sediments. The proportion of n-C_{27} is similar at both stations in the top 5 cm and increases at the seaward site in deeper layers (Fig. 5). This unexpected pattern supports the hypothesis of additional sources for these long-chain alkanes (Colombo *et al.*, 1996d). Another factor which could contribute to explain this trend is the more rapid downcore reduction of the petrogenic signal at site S. The carbon preference indexes

(CPI = $2[C_{27} + C_{29}]/C_{26} + 2C_{28} + C_{30}$) are relatively low near the surface (2.8–3.8) suggesting the presence of petrogenic (CPI < 2) hydrocarbons. With depth in the cores the CPI increase, particularly at S, reflecting the reduction of fossil residues and persistence of higher plant alkanes. UCM/RESHC ratios further support this interpretation (Fig. 5). The values are low in settling particles due to the abundance of labile pristane, HEH and squalene; increase sharply in near-surface sediments reflecting the rapid decay of these compounds; and decrease below 10 cm, coinciding with the CPI increase, indicating lower petrogenic inputs. A clear geographical difference is observed; sediments from the landward site are more polluted and present lower CPI and higher UCM/RESHC ratios.

CONCLUSIONS

The concentrations of lipids in interfacial Laurentian Trough sediments (fatty acids: 3.2–11, UCM hydrocarbons: 1.2–6.2, sterols: 0.4–2.4, resolved aliphatic hydrocarbons: 0.2–0.5 mg g^{-1} OC) indicated a 46–93% loss relative to settling particles. The subsequent decay down to 35 cm depth in the sediments was less marked but showed a 22–66% loss. Lipid accumulation efficiencies in interfacial (0–3 cm) sediment inventories averaged $21 \pm 29\%$ of water column fluxes and revealed a clear reactivity trend: pheopigments > sterols > fatty acids $\approx$ total lipids > resolved hydrocarbons > UCM. However, large fluctuations were observed for the individual components: marine lipids were almost as reactive as pheopigments whereas terrestrial compounds behaved like the UCM. Extremely labile marine components enriched in settling particles (pristane, diatomsterol, heneicosahexaene), were rapidly lost near the sediment–water interface. Only moderately reactive marine components (16:0, 16:1 $(n-7)$ fatty acids; squalene) and the more stable terrestrial fatty acids (22:0, 24:0) and hydrocarbons (fichtelite, UCM), persisted deep enough in the sediments to preserve the geographical trends observed in the water column; a higher contribution of terrestrial and petrogenic compounds at a site located at the beginning of the maritime estuary (L) and prevalence of marine biomarkers at a station situated 120 km farther seaward (S). The signature of a spring diatom bloom sampled at site S was also preserved by fatty acids 14:0, 16:0 and 16:1 $(n-7)$ in the top 0–3 cm sediments.

The preferential decay of marine components continued with depth in the sediments and lipid patterns become more alike at 35 cm depth. However, the geographical difference observed in C/N ratios (11.6 ± 0.5 at L vs. 9.8 ± 0.4 at S; Colombo *et al.*, 1996b) was also preserved by fatty acids 16:0, 22:0, 24:0, the UCM/Resolved hydrocarbon ratios and the CPI index of *n*-alkanes over the entire length of the cores. The contrasted conditions of organic matter diagenesis resulting from the different rates of sedimentation, bioturbation and quality of organic matter inputs at each site, were also reflected by the depth distribution of bacterial fatty acids and coprostanol.

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