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Contrasting fates of organic matter in locations having different organic matter inputs and bottom water O_2 concentrations

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ABSTRACT

The goals of this work were to study sedimentary organic matter (OM) composition and transformation since the end of the last deglaciation and to evaluate the influence of contrasting depositional conditions on these parameters. One station was located in the Lower St. Lawrence Estuary (LSLE) where the current bottom waters are hypoxic and receive terrigenous and marine OM. The other station, located in the Gulf of St. Lawrence (GSL), has more oxygenated bottom waters and almost only marine OM inputs. Analyses included enantiomers of amino acids (L and D-AA) and muramic acid that provide different markers of OM alteration state and reactivity and of bacterial contribution to OM composition and diagenesis. The markers clearly indicated the increase in OM alteration state with depth in the sediments of the LSLE and the GSL. The steady decrease in AA yields with depth confirmed the preferential degradation of AA compared to the rest of the OM. The OM in the surface sediment of the LSLE was less altered than that of the GSL and was enriched in bacterial biomass as indicated by much higher muramic acid yields. Results indicated that an important degradation of particulate organic matter occurs in the water column in the GSL, while it takes place mostly in the sediments in the LSLE. The presence of heterogeneous OM and hypoxic conditions in the LSLE likely reduce OM degradation rate in its deep water layer. However, the zone near the water-sediment interface is responsible for large variations in AA composition at both locations. A relatively new redox index, based on AA composition, was tested and appeared robust. This study highlights the importance of ambient conditions in determining the fate of OM and in the biogeochemical cycles of vital elements.

1. Introduction

Although only a small part of the organic matter (OM) produced by primary producers escapes rapid remineralization, the persistence of some OM has major consequences on the cycles of vital elements such as carbon, nitrogen and oxygen. For instance, OM burial in sediments represents a mechanism for the removal of atmospheric CO_2 and for the accumulation of O_2. It was estimated that 10–15% of the world net annual primary production and over 80% of all OM burial in the ocean occur in coastal regions (Hedges and Keil, 1995; Muller-Karger et al., 2005). Despite the importance of these processes on the global scale, there are still debates over the factors governing sedimentary OM (SOM) preservation or degradation (e.g., Burdige, 2007). For instance, there is an emerging view that ambient conditions might be more important in determining the fate of OM than its molecular composition (Bianchi, 2011; Schmidt et al., 2011). However, coastal environments and estuaries in particular are among the most challenging study areas on earth considering the many possible sources and sinks of elements and the drastic spatial changes in parameters such as temperature, salinity, pH, and dissolved O_2 concentrations (Hedges and Keil, 1999). Exposure time to O_2 is an important parameter promoting the degradation of OM (Hartnett et al., 1998; Niggemann et al., 2007).

The St. Lawrence Estuary (Canada) is one of the largest and deepest estuaries in the world (El-Sabh and Silverberg, 1990). It is located downstream of the St. Lawrence River, linked to the Great Lakes, and upstream of the Gulf of St. Lawrence (GSL), connected to the Atlantic Ocean. The origin of the OM changes with distances downstream. Estimates indicate that between 40 and 70% of the SOM is terrigenous in the Lower St. Lawrence Estuary (LSLE) while

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the GSL receives almost exclusively marine SOM (e.g., Lucotte et al., 1991; Muzuka and Hillaire-Marcel, 1999; Tremblay and Gagné, 2007). Although the average annual primary production in the LSLE and the GSL is similar (i.e., 90–200 g C m^{-2} yr^{-1}, Steven, 1974; Therriault and Levasseur, 1985), the flux of organic carbon measured at 150 m by sediment traps is much higher in the LSLE (i.e., ~400 vs. ~20 μmol cm^{-2} yr^{-1}, Lucotte et al., 1991; Muzuka and Hillaire-Marcel, 1999) due mostly to an important contribution of terrigenous OM in the LSLE and a more intense degradation of the OM produced in the surface waters of the GSL (Bourgoin and Tremblay, 2010). Another important difference between the LSLE and the GSL is the dissolved O_2 concentrations of the bottom water layer. The bottom waters of the LSLE have recently displayed a decrease in dissolved O_2 concentrations, like other coastal areas (Conley et al., 2011). These concentrations have decreased by about 50% over the last century and the waters below 250 m depth have been hypoxic (<62.5 μM) since the mid-1980s in parts of the LSLE (Gilbert et al., 2005).

In the present study, SOM composition and transformations since the last deglaciation were evaluated with the goal of providing information on the impacts of contrasting depositional inputs and conditions on the fate of SOM. Two stations were considered, one in the LSLE having present day deep-water O_2 concentrations of about 65 μM (Hébert and Tremblay, 2017) and the other in the GSL having deep-water O_2 concentrations of approximately 160 μM (Gilbert et al., 2005). Bulk and molecular parameters were measured, including the enantiomers of amino acids (L and D-AA) and muramic acid (Mur). Most of the nitrogen in living organisms is contained in AA (Cowie and Hedges, 1992). However, after the death of these organisms, AA are generally selectively degraded compared to the rest of the OM, with some AA being more labile than others (Dauwe et al., 1999). As a result, AA yields in OM and the relative composition of individual AA can be used as markers of OM alteration state (e.g., Cowie and Hedges, 1994; Jennerjahn and Ittekkot, 1997; Dauwe et al., 1999; Menzel et al., 2013).

Heterotrophic microorganisms are the primary contributors of OM decomposition (Madigan and Martinko, 2006), and thus they control both the amount and composition of the SOM. One way to estimate microbial contribution to OM composition and diagenesis is to quantify source-specific biomarkers. Among these biomarkers are the amino sugar, Mur, and the D-AA. Mur is a very labile molecule, only found in bacteria, and thus Mur yields has been shown to be representative of bacterial cells or relatively unaltered cell debris contribution to bulk OM (e.g., Moriarty, 1977; Tremblay and Benner, 2006; Kaiser and Benner, 2008). D-AA, are only abundant in bacteria and their yields in OM have been shown to be representative of OM of bacterial origin which is mostly made of altered detritus in SOM (Tremblay and Benner, 2006; Kaiser and Benner, 2008). The molar percentage of D-AA (vs total AA) has been shown to increase during OM diagenesis (Tremblay and Benner, 2009), in part because proteins, containing only L-AA, are degraded faster than compounds with D-AA such as cell wall debris (Nagata et al., 2003).

Sediment total iron content was also measured. A recent study revealed that between 15 and 28% of the SOM is bound to reactive iron phases in the LSLE and the GSL, with the higher average values measured in the deep sediments of the GSL (Lalonde et al., 2012).

2. Materials and methods

2.1. Environmental setting and sampling

The St. Lawrence Estuary is divided at the mouth of the Saguenay Fjord into two parts: upper and lower estuaries. The GSL is semi-enclosed and covers an area of 226,000 km^2. The GSL is connected to the Atlantic Ocean through the Cabot Strait, between the provinces of Nova Scotia and Newfoundland, and the Strait of Belle-Isle, between the provinces of Québec and Newfoundland.

The main morphological characteristic of the LSLE and GSL is the Laurentian Channel which is 250–550 m in depth. The surface water has a salinity between 27 and 32 and flows towards the ocean. In contrast, the deep water layer enters the GSL and slowly moves landward in the Laurentian Channel. The deep water layer is a mixture of the Labrador Current Water and the North Atlantic Central Water (Saucier et al., 2003; Gilbert et al., 2005). The North Atlantic Central Water is saltier, warmer and poorer in O_2 than the Labrador Current Water. An increase in the proportion of the North Atlantic Central Water has been identified as the main cause of the recent hypoxic conditions in the deep water of the LSLE (Gilbert et al., 2005; Bourgault et al., 2012). In addition, the decrease in O_2 concentration was associated with an increase in water temperature (1.7 °C) which increases the OM respiration rate (Genovesi et al., 2011). The deep waters of the Laurentian Channel are separated from the atmosphere by the low density surface water layer (Petrie et al., 1996). As a result, when the water at the bottom of the Laurentian Channel moves landward, its O_2 concentration gradually decreases due to OM remineralization by respiration which is enhanced by an increase in nutrient concentrations (Yeats, 1988).

During the last deglaciation, the Goldthwait Sea invaded the St. Lawrence Estuary and Gulf and caused an increase in the deposition of glaciomarine sediments (from ~12,500 to ~8500 cal BP) composed mostly of relatively homogenous clayey silts to silty clays, while subsequent postglacial sediments (<~8500 cal BP) are mostly composed of bioturbated silty clays to sandy mud (St-Onge et al., 2008; Barletta et al., 2010).

Two sediment piston cores were collected during two expeditions on the R/V Coriolis II, as described by Barletta et al. (2010). The first core was taken in the Cabot Strait of the GSL (47°40.286′ N, 59°59.985′ W; named COR0503-CL04-36PC) in June 2005 at a water depth of 544 m. The second core was collected in the LSLE (48°24.031′ N, 69°14.328′ W; named COR0602-36PC) in June 2006 at a depth of 315 m. The GSL and LSLE cores were 7.71 m and 6.97 m long, respectively. A companion trigger weight core was collected at each site to ensure the sampling of surface sediments (Barletta et al., 2010). By comparing the physical properties of the piston and companion trigger weight core, Barletta et al. (2010) identified that 30 cm of sediments are missing from the top of COR0602-36PC and none from core COR0503-CL04-36PC. The results presented here for the first 30 cm of sediments in the LSLE are thus from the trigger weight core. After recovery, the cores were separated into sections of 1.5 meter and stored at 4 °C in a sealed LDPE bag to reduce gas exchanges and contamination. The chronostratigraphy of the cores was determined using AMS-^{14}C ages on marine shell fragments found in several sediment sub-samples as detailed by Barletta et al. (2010). The oldest sediments represent glaciomarine sediments deposited at approximately 10,400 cal BP and 9300 cal BP in the GSL and LSLE, respectively. Subsamples of approximately 1 g of sediment were collected from each core, using a spatula washed with methanol and rinsed with ultrapure water. These subsamples were then placed in pre-combusted 20 ml glass vials. The sediments were freeze-dried and milled in a Wig-L-Bug mill using a stainless steel vial and ball (Tremblay and Gagné, 2002). They were kept in a desiccator (with $CaSO_4$ as desiccant) until analysis.

2.2. Elemental analyses

The weight percentages of total carbon, organic carbon (%OC), and total nitrogen (%N) in sediments were measured by an

elemental analyzer Vario MICRO cube (Elementar). Before the analyses of OC, carbonates were removed under HCl vapor overnight (Hedges and Stern, 1984). Two blanks and three standards of acetanilide were prepared and analyzed after each set of 15 samples. The relative standard deviation (RSD) obtained with replicates of the same sediment represented 2% for %OC (n = 3) and 4% for %N (n = 13).

Total iron content in sediment was analyzed by energy dispersive X-ray fluorescence (EDXRF) spectrometry using a PANalytical Epsilon 3-XL. Before EDXRF analysis, loss on ignition was determined gravimetrically by heating the dried samples up to 950 °C for two hours. Subsequently, samples were treated by borate fusion in an automated fusion furnace (CLAISSE® M4 Fluxer). Samples weighing ~0.6 g were mixed with ~6 g of lithium borate flux (CLAISSE, pure, 49.75% $Li_2B_4O_7$, 49.75% $LiBO_2$, 0.5% LiBr). The mixtures were melted in Pt-Au crucibles (95% Pt, 5% Au), and after fusion the melts were cast to flat disks (diameter: 32 mm; height: 3 mm) in Pt–Au moulds. Analytical accuracy and precision were found to be better than 1–5%, as checked by an international standard (USGS SDC-1) and analysis of replicate samples.

2.3. Amino acid and muramic acid analyses

The methods of AA and Mur quantifications are described in Kaiser and Benner (2005) and Tremblay and Benner (2009). For these analyses, the quantity of sediment was adjusted to represent about 2 mg of OC. 23 AA, including D-AA, L-AA, and achiral AA, and Mur were measured by an Agilent 1200 HPLC equipped with a fluorescence detector. A Merck C-18 LiChrospher 100 RP-18 column (4 × 250 mm, 5 μm) and a LiChrospher 100 RP-18 (4 × 4 mm, 5 μm) guard column were used for AA separation. The column was replaced by a Merck C-18 Superspher 100 RP-18 column (4 × 125 mm, 4 μm) for Mur analysis. External standards were used for calibration and quantification. For AA analysis, two injections were performed for samples, blanks, and standards. The first injection was done using an automated precolumn derivatization with *o*-phthaldialdehyde (OPA) and *N*-isobutyryl-L-cysteine (IBLC) while the second one was done with OPA and *N*-isobutyryl-D-cysteine (IBDC). Chiral AA produce different diastereoisomers when derivatized with IBLC and IBDC, and these diastereoisomers have different retention times. As a result, the two injections allow resolving peak coelutions and greatly increase the accuracy of peak identification and quantification. For Mur, only IBLC was used with OPA because Mur is an achiral molecule.

Replicate analyses showed a RSD of 5%–12% for individual AA concentration (n = 3, Kaiser and Benner, 2005) and of 9.5% for Mur concentration (n = 6, Bourgoin and Tremblay, 2010). The RSD for THAA concentrations (n = 7) was 5.3% at the 65 μM level and 6.4% at the 16 μM level. The RSD for degradation index (see below) (n = 5) was lower than 18% at the THAA concentrations studied here. Considering the uncertainty of the OC analysis and the %OC of the sediments, the RSD for values in nmol $mgOC^{-1}$ was between 6.8 and 15.5% for individual AA and less than 13% for Mur. Individual AA concentrations measured in all sediment samples are available in the Supplementary material file (Tables S1 and S2).

The relative abundance of individual AA was used to calculate three different degradation indices. The first one is the degradation index (DI) based on this equation presented in Dauwe et al. (1999):

$$DI = \sum_i \left[\frac{var_i - AVGvar_i}{STDvar_i}\right] \times fac.coef._i \quad (1)$$

where var_i is the molar % of AA *i* in the sediment sample. $Fac.coef._i$, $AVGvar_i$ and $STDvar_i$ are the principal component analysis factor coefficient, mean molar %, and standard deviation of AA *i* in the sediment dataset of Dauwe et al. (1999). The second index was the reactivity index (RI) developed by Jennerjahn and Ittekkot (1997):

$$RI = \frac{Tyr + Phe}{BAla + GAba} \quad (2)$$

where Tyr and Phe are the molar % of two aromatic AA, tyrosine and phenylalanine, and B-Ala + G-Aba are the molar % of two non-protein AA, beta-alanine and gamma-aminobutyric acid. Tyr and Phe are enriched in cell plasma and are rapidly degraded (Hecky et al., 1973). In contrast, B-Ala and G-Aba are degradation products of biomass AA and thus their proportion increases during diagenesis (Cowie and Hedges, 1992, 1994). The third index is the redox index (or Ox/Anox) developed by Menzel et al. (2013):

$$\text{Redox Index} = \frac{Asp + Glu + BAla + GAba + Lys}{Ser + Met + Ile + Leu + Tyr + Phe} \quad (3)$$

This index uses the molar % of aspartic acid (Asp), glutamic acid (Glu), B-Ala, G-Aba, lysine (Lys), serine (Ser), methionine (Met), isoleucine (Ile), leucine (Leu), Tyr, and Phe. These AA are degraded at different rates in oxic and anoxic (or less oxic) conditions, and these differences in compositions seem to be preserved in sediments (Cowie et al., 1995; Menzel et al., 2013, 2015). Generally, values greater than 1.4 are indicative of oxic conditions while values below 1 are indicative of anoxic conditions (Menzel et al., 2013).

3. Results

3.1. Bulk carbon and nitrogen

The %OC decreased with depth in the sediments, from 1.13% to 0.30% in the LSLE station and from 2.32% to 0.73% in the GSL station (Table 1 and Fig. 1). %OC in sediments of the GSL were about two times higher than those measured in the LSLE at the same depth or deposition period. The inorganic carbon (or carbonate = total C − OC) content of the sediments were generally below 0.1% and showed no significant trend with depth (not shown).

The %N also decreased with depth, from 0.11% to 0.030% in the LSLE and from 0.31% to 0.078% in the GSL (Table 1). The sediments of the GSL contained about three times more nitrogen than those of the LSLE at the same depth or deposition period. Thus, the atomic C/N ratios were significantly lower in the GSL (*t*-test, $p = 0.0001$) (Table 1 and Fig. 1). At the LSLE station, C/N ratios fluctuated between 10.5 and 12.8 in the top 500 cm of the sediments, but were lower (8.9 and 10.0, p=0.039) under 547 cm in the glaciomarine sediments from the Goldthwait Sea. At the GSL station, the C/N ratios fluctuated between 7.3 and 9.5, except for the deepest glaciomarine sample (755 cm) that had a C/N of 11.4 because of its relatively low nitrogen content.

Values of %OC and C/N ratios measured by Bourgoin and Tremblay (2010) in filtered particles from the water column and in surface sediments of the LSLE (48°18′2″N; 69°10′5″W) and of a northwestern location in the GSL (49°25′0″N; 64°45′0″W) are shown in Fig. 1 for comparison. The particles from the deep water layer contained 4.5 to 7.5 times more OC and N than the sediments located a few tens of meters below. The C/N ratios clearly increased with depth in the water column, but then decreased after deposition on the sediments (Fig. 1). It should be noted that for the GSL, the location of the water samples (Bourgoin and Tremblay, 2010) was very different from the location of the sediment core (this study).

Table 1
Age, organic carbon and nitrogen contents (%OC, %N), C/N ratios, total hydrolysable amino acid (THAA) concentrations, yields of total amino acids ($\%C_{AA}$, $\%N_{AA}$) and molar proportion of D-amino acid enantiomers (vs. THAA) of the sediments of the two cores.

Depth (cm)	Age (cal BP)	%OC (wt.%)[a]	%N (wt.%)[a]	C/N (atom)[b]	THAA (μmol g-1)[c]	$\%C_{AA}$[d]	$\%N_{AA}$[d]	Mol % D-AA
St. Lawrence Estuary								
1.5	15	1.13	0.110	11.7	19.0	8.16	28.4	1.25
10	100	0.94	0.086	12.8	14.2	7.47	28.3	1.55
20	201	0.95	0.090	12.3	15.7	7.99	29.8	1.51
30	302	0.85	0.090	11.4	15.0	8.57	29.5	1.51
50	503	0.89	0.084	12.3	13.7	7.53	27.8	1.64
70	706	0.73	0.081	10.5	12.5	8.41	26.8	1.38
100	1008	0.98	0.091	12.5	14.7	7.37	28.2	1.81
140	1623	0.74	0.070	12.3	10.2	6.53	24.8	2.41
150	1905	0.77	0.066	13.6	11.5	7.30	30.2	2.40
180	2688	0.76	0.074	12.0	9.95	6.46	23.7	2.50
220	3510	0.66	0.058	13.3	8.52	6.45	26.2	2.95
260	4120	0.59	0.055	12.6	7.95	6.59	25.4	3.07
320	5792	0.66	0.067	11.5	8.15	6.11	21.4	3.20
380	6955	0.53	0.051	12.2	5.80	5.40	19.5	4.06
440	7706	0.33	0.037	10.6	3.18	4.79	14.8	3.88
500[e]	**8577**	**0.31**	**0.033**	**11.0**	**2.39**	**3.91**	**12.4**	**4.04**
547	**8730**	**0.30**	**0.030**	**11.6**	**2.07**	**3.55**	**11.9**	**4.12**
590	**8865**	**0.37**	**0.043**	**10.0**	**2.09**	**2.91**	**8.34**	**3.30**
710	**9267**	**0.34**	**0.045**	**8.9**	**2.01**	**2.93**	**7.61**	**4.10**
Gulf of St. Lawrence								
1.5	16	2.32	0.30	9.1	51.4	10.8	31.7	2.20
5	55	2.22	0.31	8.3	47.9	10.7	28.6	2.01
15	166	2.14	0.29	8.6	44.5	10.2	28.6	2.09
20	224	2.03	0.29	8.3	48.2	11.6	31.2	2.46
25	282	1.80	0.29	7.3	50.1	12.0	28.5	2.02
40	450	2.02	0.26	9.2	41.2	9.93	29.4	2.37
70	835	2.02	0.25	9.4	38.8	9.42	28.8	2.76
110	1532	1.90	0.24	9.1	41.5	10.1	29.4	3.01
130	1890	1.87	0.23	9.5	41.3	10.1	30.6	3.04
150	2241	1.42	0.22	7.4	45.5	11.1	26.5	3.22
170	2524	1.60	0.21	8.9	29.4	9.17	26.2	3.13
190	2823	1.47	0.18	9.3	24.5	8.26	24.8	3.34
230	3435	1.39	0.18	9.2	23.8	8.36	25.1	3.24
290	4310	1.40	0.17	9.5	24.3	8.69	27.2	3.14
350	5178	1.15	0.16	8.2	20.4	8.93	23.4	3.33
410	6134	1.17	0.16	8.4	18.2	7.80	20.7	3.36
470	7231	0.93	0.12	8.7	12.2	6.52	18.2	3.60
530	7998	0.87	0.12	8.6	10.3	5.89	16.3	3.39
550	8223	0.81	0.11	8.9	10.4	6.54	18.5	3.67
570	8470	0.79	0.11	8.4	10.1	6.45	17.1	3.57
600	**8792**	**0.85**	**0.11**	**9.3**	**11.1**	**6.71**	**19.9**	**3.50**
650	**9325**	**0.74**	**0.11**	**7.6**	**11.6**	**7.95**	**19.0**	**3.17**
700	**9848**	**0.73**	**0.10**	**8.6**	**9.50**	**6.64**	**18.1**	**3.38**
755	**10,399**	**0.76**	**0.078**	**11.4**	**7.95**	**5.27**	**18.8**	**3.49**

[a] % of dry weight.
[b] Atomic organic carbon to nitrogen ratio.
[c] Total hydrolysable amino acids in 1 g of dry sediment.
[d] % of bulk organic carbon and nitrogen coming from amino acids.
[e] Values in bold are results from the glaciomarine sediments from the Goldthwait Sea.

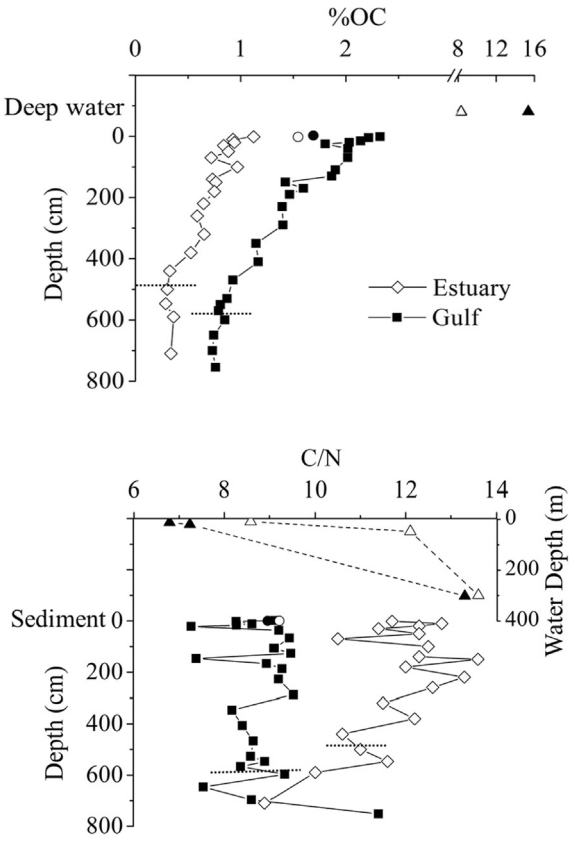

Fig. 1. Organic carbon contents (%OC) and C/N ratios of particles as a function of depth in the water column and in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. The values in the water column and in surface sediments (triangles and circles) are from Bourgoin and Tremblay (2010) at a similar location in the estuary, but about 400 km north-west of the core location in the gulf. Results below the dotted horizontal line are from the glaciomarine sediments from the Goldthwait Sea.

3.2. Amino acid contents and markers

The total hydrolysable AA (THAA) contents of the sediments sharply decreased with depth (i.e, surface sediments to the bottom of the core), from 19.0 to 2.01 μmol g^{-1} in the LSLE and from 51.4 to 7.95 μmol g^{-1} in the GSL (Table 1). Because this decrease was more pronounced than that of %OC, the contribution of THAA in bulk OC ($\%C_{AA}$) and N ($\%N_{AA}$) steadily decreased with depth (Table 1, Fig. 2). $\%C_{AA}$ decreased from 8.57% to 2.91% in the LSLE and from 12.0% to 5.27% in the GSL. $\%N_{AA}$ decreased from 30.3% to 7.61% in the LSLE and from 31.7% to 16.3% in the GSL. However, compared to filtered particles from the deep water layer (Bourgoin and Tremblay, 2010), SOM was richer in THAA (i.e, higher $\%C_{AA}$ and $\%N_{AA}$) (Fig. 2), which is consistent with lower C/N ratio in SOM versus deep-water particles.

In spite of the similar trends with depth at both stations, the THAA content and $\%C_{AA}$ in the sediments of the LSLE were significantly lower than in the GSL (*t*-test, $p = 0.0003$, 0.0001, respectively). In contrast, similar values of $\%N_{AA}$ were observed in the surface sediments of the two stations.

Several D-AA were detected and quantified in the studied sediments: D-aspartic acid and D-asparagine (D-Asx), D-glutamic acid and D-glutamine (D-Glx), D-alanine (D-Ala), D-serine (D-Ser), D-leucine (D-Leu), and D-valine (D-Val). In both stations, mol % D-AA (sum of all D-AA vs. THAA) increased with depth; from 1.25% to 4.12% in the LSLE and from 2.01% to 3.67% in the GSL (Table 1 and Fig. 3). These values were generally higher than those of filtered particles from the bottom waters (i.e., <1.3%, Bourgoin and Tremblay, 2010; presented in Fig. 3). The surface sediment of the LSLE showed the lowest mol% D-AA, but then values increased more rapidly than in the GSL.

The mol % of the two non-protein AA, G-Aba and B-Ala, increase with depth at both stations, except in the sediments from the Goldthwait Sea in the GSL (Fig. 4). Once again, values were lower in the surface sediment of the LSLE.

Fig. 5 shows that DI was already low in surface sediments, about −0.7 and −1 in the LSLE and GSL, respectively, indicative of relatively altered SOM (Dauwe et al., 1999). In addition, the DI values in the SOM were much lower than those measured in

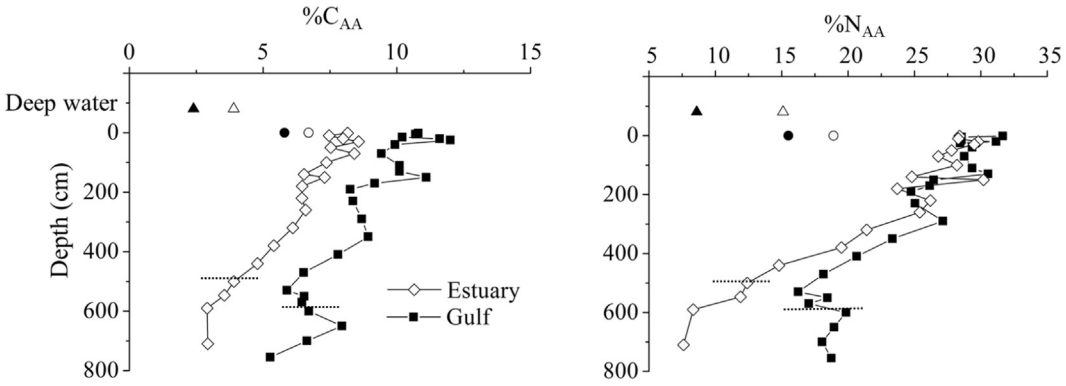

Fig. 2. Yields of total amino acids (%C_{AA}, %N_{AA}) in filtered particles from the deep water layers and in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. The values in the deep water layers and in surface sediments (triangles and circles) are from Bourgoin and Tremblay (2010) at a similar location in the estuary, but about 400 km north-west of the core location in the gulf. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

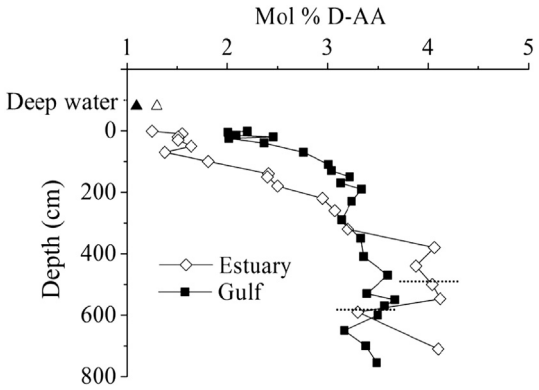

Fig. 3. Molar proportion of the sum of all D-amino acid enantiomers (vs. THAA) in filtered particles from the deep water layers of Bourgoin and Tremblay (2010) (triangles) and in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

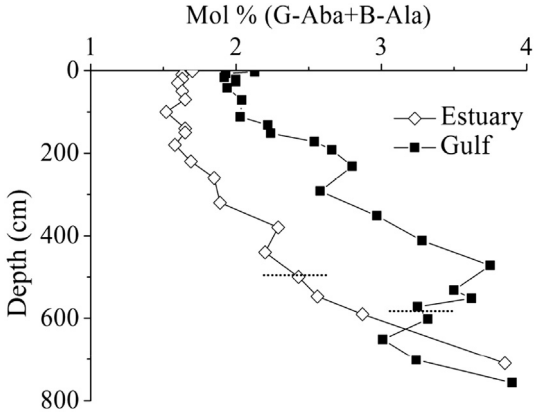

Fig. 4. Molar proportion of the non-protein amino acids G-Aba and B-Ala in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

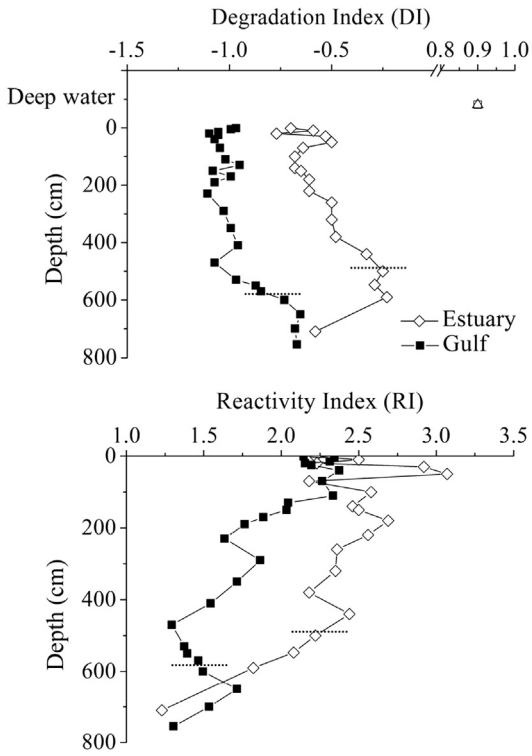

Fig. 5. Degradation index (DI, Dauwe et al., 1999) and reactivity index (RI, Jennerjahn and Ittekkot, 1997) in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. The DI of the particulate organic matter in the deep water layers of the estuary and the gulf (Bourgoin and Tremblay, 2010) are also presented. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

filtered particles from the deep water layer (~0.9, Bourgoin and Tremblay, 2010) (Fig. 5), indicating that the zone near the water-sediment interface is responsible for large variations in AA composition. Surprisingly, DI did not decrease with depth in the sediments. In contrast, the sediment layers near 600 cm had slightly greater DI than those of the surfaces layers (t-test, $p < 0.05$). This is in contradiction with all the other markers presented (Figs. 2–4) and with the RI shown in Fig. 5. RI values were generally higher in the LSLE than in the GSL at the same depth, suggesting that the SOM in the LSLE was more reactive or less degraded.

The redox index in the LSLE was generally lower than in the GSL at the same depth or deposition date (t-test, p=0.0001) (Fig. 6). A close look revealed a slight decrease of redox values in the last century (Fig. 6 right panel), consistent with the recent hypoxia, although no statistical test was done to confirm this trend. However, the lowest values were found at 50 cm and 440 cm in the LSLE suggesting other hypoxia episodes about 500 and 7700 cal BP,

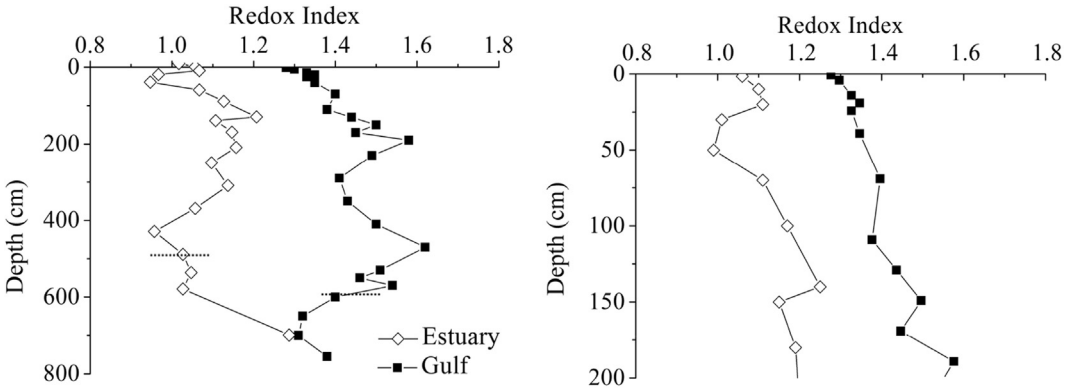

Fig. 6. Redox index in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. The right panel is a zoom-in view of the first 200 cm. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

respectively. This index also suggested that the O_2 concentrations gradually decreased since ~2900 years (i.e., 190 cm up to 0 cm). Similar trends of the redox index with time were observed at both stations except for a period that almost perfectly matches in both stations that is before 5500 cal BP (i.e., below 310 cm in the LSLE and below 375 in the GSL).

3.3. Muramic acid contents and markers

Mur was quantified in the sediments (present study) and in the filtered particles of the bottom water layer of the LSLE and GSL (Bourgoin and Tremblay, 2010) (Fig. 7). The SOM in surface sediments was much richer in Mur than the POM in the bottom waters. Furthermore, the SOM in surface sediments from the LSLE was about three times richer in Mur than the SOM from the GSL (i.e., 4.85 vs. 1.46 nmol $mgOC^{-1}$). This significant difference in the first sediment layers (*t*-test, $p < 0.05$) was also observed by Bourgoin and Tremblay (2010) even though the location of their GLS station were quite different from the present study (Fig. 7). Mur yields decreased by a factor of ~17 with depth in the sediments of the LSLE. However, this trend was not observed in the GSL, in part because Mur yields were already low in the GSL surface sediment.

Since Mur and D-AA are mostly from bacteria and that Mur is more labile than D-AA (Tremblay and Benner, 2006), D-Ala/Mur and D-Glx/Mur ratios can be used to evaluate the diagenetic state of bacterial SOM. In the LSLE, the D-Ala/Mur and D-Glx/Mur ratios were 1.18 in surface sediments, which is close to the value measured in living bacteria (~2) and in peptidoglycan (~1) (Kaiser and Benner, 2008) (Fig. 8). These low values were caused by high Mur yields. These ratios then gradually increased with depth in the LSLE. In the GSL, these ratios were already high in surface sediments (i.e., 11.5 and 5.0, respectively). D-Ala/Mur and D-Glx/Mur ratios increased with depth from 0 to 150 cm, but then decreased to values slightly lower than in surface SOM.

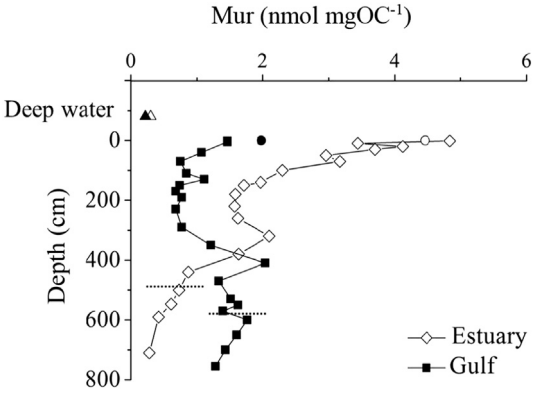

Fig. 7. Carbon-normalized muramic acid (Mur) yields in filtered particles from the deep water layers and in the sediments of the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. The values in the deep water layers and in surface sediments (triangles and circles) are from Bourgoin and Tremblay (2010) at a similar location in the estuary, but about 400 km north-west of the core location in the gulf. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

3.4. Total iron content

To examine the possible link between SOM and the mineral matrix containing Fe, total Fe content and the ratios between OC and total Fe contents (OC/Fe) were calculated. In the LSLE, Fe represented 3.6%–5.5% of the sediment dry weight, with the highest values measured in the sediments below 550 cm. In the GSL, Fe represented 4.8%–5.3% of the sediment dry weight, with no trend with depth. The OC/Fe ratios in the surface sediments were approximately 0.25 in the LSLE and 0.45 in the GSL. The greater ratios in the GSL and the decreasing trend with depth were caused by variations in OC contents.

4. Discussion

4.1. Origin of sedimentary organic matter

Values of C/N ratios and $\%C_{AA}$ presented here are consistent with previous studies which have shown that the SOM in the GSL has a marine origin while the SOM in the LSLE is in part terrigenous (e.g., Colombo et al., 1996; St-Onge and Hillaire-Marcel, 2001; Tremblay and Gagné, 2007; Bourgoin and Tremblay, 2010; Alkhatib et al., 2012). Vascular plants and terrigenous OM are poor in nitrogen and in AA (Cowie and Hedges, 1992; Hedges and Oades, 1997).

In the LSLE, bacterial biomass (living or intact cells) appears to be important in surface sediments, as indicated by high Mur yields and low D-AA/Mur ratios. In contrast, in the GSL, low Mur yields and high D-AA/Mur ratios suggested that bacterial SOM was already altered in surface sediments. However, Mur yields in the deep sediments of the GSL were slightly higher than in surface layers. Different hypotheses for this trend in the GSL can be set out. The first one is a significant and relatively recent production of bacterial biomass in deeper sediments (e.g., under 300 cm in situ or during storage at 4 °C). It is also possible that Mur in deep sediments comes from an important bacterial biomass deposited on the GSL surface sediments thousands of years ago. Finally, Mur might

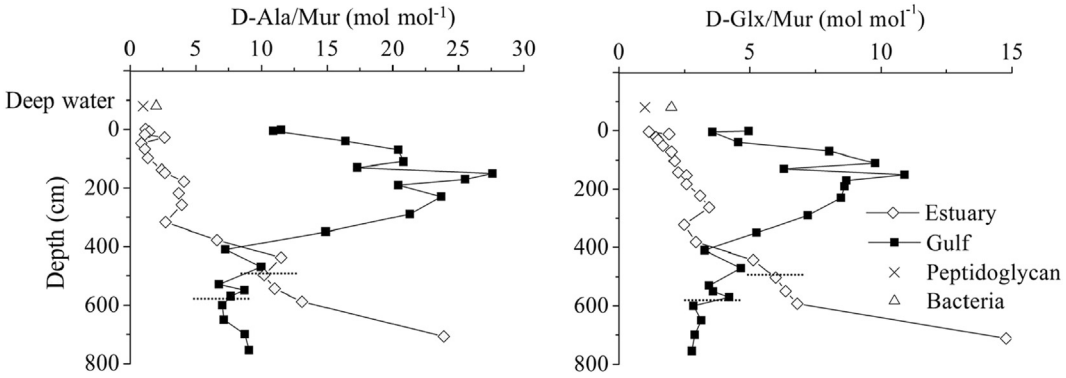

Fig. 8. Molar ratio of bacterial biomarkers (D-Ala/Mur and D-Glx/Mur) in peptidoglycan (Schleifer and Kandler, 1972), in bacteria (Kaiser and Benner, 2008) and in the sedimentary organic matter from the Lower St. Lawrence Estuary and the Gulf of St. Lawrence. Results below the dotted line are from the glaciomarine sediments from the Goldthwait Sea.

be selectively protected from degradation in the sediment of the GSL. However, considering that Mur is labile and rapidly degraded in sediment (e.g., Moriarty, 1977; Tremblay and Benner, 2006) and that a possible preservation mechanism of Mur was not observed in the LSLE, the last two hypotheses seem less plausible.

Previous studies have used D-AA and Mur yields to quantify the proportion of POM and SOM coming from bacterial biomass and debris (e.g., Tremblay and Benner, 2006, 2009; Kaiser and Benner, 2008; Bourgoin and Tremblay, 2010). The same approach was used in the present study, but estimates of bacterial contribution were highly variable and not always consistent. Estimates based on Mur fluctuated between 23 and 1.4%, while estimates based on D-Asx were between 84 and 573% (Mai-Thi, 2016; not shown here). Mur and D-Asx have a greater reactivity than bulk bacterial SOM or than most of the other bacterial molecules (Tremblay and Benner, 2006, 2009). Estimates based on D-Ala and D-Glx were more consistent and suggested that about 20% of C (range = 8–40%) and 40% of N (range = 15–52%) in the SOM from both stations were of bacterial origin. These mean values are similar to those found in POM from other aquatic environments reported by Kaiser and Benner (2008) and Tremblay and Benner (2009). However, the discrepancy in the estimates obtained with the different biomarkers indicates that the relative proportion of these biomarkers in the bacteria living in the studied sediments is variable and different from the bacterial cultures used as reference in this quantitative approach (Tremblay and Benner, 2006, 2009).

4.2. Diagenesis and its impact on dissolved oxygen

Globally, diagenesis in surface sediments leads to the oxidation of about 90% of the SOM that reaches the seafloor (Emerson and Hedges, 2003). The depletion of %OC with depth and the different markers of SOM alteration state clearly indicated the process of SOM degradation with time in both the LSLE and the GSL sediments.

Temporal changes in the nature of the POM produced and in the composition of the SOM deposited since the last deglaciation could be another cause of the downcore changes in SOM composition. However, there are no data indicating gradual or episodic changes in the nature of the POM in the studied areas over this period. Changes in the proportion of terrigenous SOM since human settlement (300–400 years ago) have been reported in the LSLE (Thibodeau et al., 2006), but in the GSL there is no evidence, including geochemical, isotopic and dinoflagellate cyst assemblage data, for a significant input of terrestrial OM in the last few hundred years (Muzuka and Hillaire-Marcel, 1999; Genovesi et al., 2011). Moreover, no data indicate a gradual change in the planktonic community over the Holocene (Lapointe, 2000; de Vernal et al., 1993). The Holocene was characterized by sea-surface conditions similar to present throughout the GSL (de Vernal et al., 1993). Thus, diagenesis appears as the most probable cause of the gradual downcore trends observed here in both the LSLE and GSL.

The steady decrease in $\%C_{AA}$ and $\%N_{AA}$ with depth confirmed the preferential degradation of AA compared to the rest of SOM (Burdige and Martens, 1988; Cowie and Hedges, 1994; Wakeham and Lee, 1993; Harvey et al., 1995). Among the diagenetic markers, the DI using the reference values of Dauwe et al. (1999) was the only one not showing an increase in SOM alteration state with depth. Although DI provided consistent result in the surface sediment of the St. Lawrence (Alkhatib et al., 2012), it appears that this approach is not applicable in long sediment cores, at least in the LSLE and the GSL. Möbius et al. (2011) arrived at the same conclusion in their study of Arabian Sea sediments. Menzel et al. (2013) estimated that terrigenous OM contribution and changes in redox conditions can interfere with the DI. In contrast, RI seemed to be a better diagenetic marker in these conditions and in long sediment cores.

The diagenetic markers (e.g., $\%N_{AA}$, mol% D-AA) also indicated that the SOM in the LSLE is more rapidly and intensely degraded than the SOM from the GSL. This is consistent with the study from Alkhatib et al. (2012) showing that the SOM in the LSLE was more reactive than the SOM in the GSL. This difference appears to be mostly caused by the fact that the SOM in the GSL is already altered in surface sediments. Thus, an important degradation of POM occurs in the water column of the GSL, while it takes place mostly in the sediment in the LSLE. A recent study has shown that the POM and dissolved OM just above the sediment in the LSLE was on average less altered than in the rest of the water column or in the GSL (Hébert and Tremblay, 2017). The presence of heterogeneous OM (i.e., marine plus terrigenous) and hypoxic conditions in the LSLE deep waters could reduce OM degradation rate in the water column. Arnosti (2015) showed that water-column bacteria are more effective at degrading homogeneous POM, such as the marine POM found in the GSL, than heterogeneous POM like the one found in the LSLE. In contrast, benthic bacteria are more adapted for degrading heterogeneous SOM (Arnosti, 2015) which might explain why the OM in the LSLE is mostly degraded in the sediments. In addition, the marine OM produced in the surface waters of the GSL is enriched in nitrogen, including THAA, and is therefore of higher nutritional value and labile than the terrigenous OM of the LSLE (Hunt et al., 2000). Moreover, the higher O_2 concentration in the bottom layer, the lower sedimentation rate, and the deeper water column in the GSL (see section 2.1 and Table 1) increase exposure time to O_2 and thus promote the degradation of POM (Hartnett

et al., 1998; Niggemann et al., 2007). All these findings explain why the degradation process occurs mostly in the sediment in the LSLE, while it starts much earlier in the water column in the GLS.

In most studies, the proportion of THAA in POM ($\%C_{AA}$) decreases in the water column and continues to decrease after deposition and burial in sediments (Cowie and Hedges, 1992; Wakeham et al., 1997; Lee et al., 2000; Carstens and Schubert, 2012). In the present study, we found that $\%C_{AA}$ and THAA concentration in surface sediments were much higher than those in filtered particles from the bottom waters (Bourgoin and Tremblay, 2010). The same trend was observed in Bourgoin and Tremblay (2010) and in this case the sediment samples were taken at the same locations as the water samples. To our knowledge, the only other area where THAA enrichment in POM has been reported near the sediment-water interface was in the equatorial Pacific (Lee et al., 2000). Lee et al. (2000) attributed the enrichment in THAA at only one of their study sites to the presence of carbonate-rich sediments that can protect THAA from microbial degradation and hydrolysis. Hébert and Tremblay (2017) observed an accumulation of THAA, including bacterial D-AA, in the nepheloid layer of the LSLE, but not in the GSL. It thus appears that the accumulation of THAA, leading to high $\%C_{AA}$ and THAA concentration in surface sediments, occurs in the nepheloid layer and near the water-sediment interface in the LSLE. In the GSL this enrichment in THAA occurs only in the surface sediment. Although the depth of the most active zone of degradation may change according to locations, the water-sediment interface was a zone of intense recycling of relatively altered materials into AA-rich biomass.

Differences in the main location of the OM degradation process between the LSLE and the GSL have implications on O_2 consumption and concentrations in these waters. The intense degradation of POM in the water column of the GSL is probably an important factor contributing to the depletion of dissolved O_2 concentration of bottom waters as they move upstream from the GSL to the LSLE. Lehmann et al. (2009) and Tremblay and Gagné (2009) reported that pelagic respiration may account for an important (up to 40%) part of the O_2 consumption in the deep water of the Laurentian Channel. The results of the present study, focusing on the molecular composition of the substrate, suggest that respiration in deep-water is more important in the GSL than in the LSLE. In the LSLE, the most important O_2 sink are probably the surface sediment (Benoît et al., 2006), which contributes to deep-water hypoxia. As previously mentioned, the current conditions in LSLE deep-waters are likely not favorable for OM degradation and thus pelagic degradation in the LSLE may occur mainly in surface and intermediate water layers (Tremblay and Gagné, 2009).

The hypoxia in the deep-water of the LSLE reduces OM degradation rates (Hartnett et al., 1998; Hébert and Tremblay, 2017) and the resulting reduction of O_2 consumption represents a negative feedback to hypoxia. However, the role of oxygen in OM degradation could be more complex. When O_2 concentrations decrease, the sediment becomes more reducing, promoting the dissolution of iron oxides. Considering that a part of SOM is associated with iron oxides (Lalonde et al., 2012), their dissolution may release OM in pore waters where it can be more easily degraded, via respiration, than SOM bound to iron oxides. However, the fact that labile compounds, such as AA, persist in the deep-water layer of the LSLE (Hébert and Tremblay, 2017), suggests that this positive feedback mechanism to hypoxia is less important.

The OC/Fe ratios in the surface sediment of this study were approximately 8–16 times lower than those reported by Lalonde et al. (2012) (i.e., ~4) because only reactive Fe (e.g., ferrihydrite, lepidocrocite, goethite), extracted with sodium dithionite, were quantified in their study. This difference indicates that most of total Fe in these sediments is not reactive. In addition, the opposite trend with depth observed between %OC and % total Fe support the idea of Lalonde et al. (2012) that SOM-Fe interactions are mostly with reactive Fe and not with the less reactive forms of Fe (e.g., pyrite and silicate Fe).

The present study calculated the redox index (or Ox/Anox) developed by Menzel et al. (2013). Although this fairly new index has not been tested in many environments, Menzel et al. (2015) obtained reliable results in lake sediments. The findings of higher values in the sediments of the GSL, versus those of the LSLE, and of decreasing values since the appearance of hypoxia in the LSLE (Gilbert et al., 2005; Thibodeau et al., 2006), provide more support to the robustness of this index. According to this index, the bottom waters of the LSLE and GSL began to be less oxic approximately 2900 cal BP. Values also suggested that other hypoxic events occurred about 500 and 7700 cal BP in the LSLE. Thibodeau et al. (2013) observed in the Esquiman Channel of the GSL that benthic foraminifera striving in warm waters with low dissolved O_2 concentration (e.g., *Brizalina subaenariensis* and *Oridorsalis umbonatus*), have become more abundant about 4000–6000 cal BP. In the present study, this period of apparent hypoxia in the LSLE coincides with highly oxic conditions in the Cabot Strait of the GSL. These opposite trends in the redox index at these two locations might be caused by drastic variations in relative sea level and detrital sediment sources during this period (Casse et al., 2017). These changes might have affected the redox index differently in the LSLE and the GSL.

5. Conclusions

This study examined for the first time the molecular compositions and transformations of the SOM accumulated in the LSLE and the GSL since the last deglaciation. The most important finding of this work is the important differences in the nature and transformation processes of SOM observed between the two stations. The surface sediments of the GSL possess altered SOM, including altered bacterial detritus. The marine and labile nature of the POM in the GSL likely promotes its degradation in the water column. Water-column O_2 consumption in this area is probably an important factor contributing to hypoxia in the upstream locations of the LSLE. In contrast, the surface sediments of the LSLE contain less altered SOM and bacterial biomolecules. The heterogeneous nature of the POM and the lower dissolved O_2 concentrations in the bottom waters of the LSLE likely allow for the deposition of less altered SOM. However, after the deposition of this SOM, heterotrophic organisms (e.g., bacteria) near the water-sediment interface of the LSLE appear to actively recycle this SOM into biomass and detritus. The reworking of relatively altered material seems to occur deeper in the sediments of the GSL. This study highlights the importance of ambient conditions in the fate of SOM. This supports the emerging view that the terms “recalcitrant” and “labile” depend on the ambient environment (Bianchi, 2011).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ecss.2017.08.044.

References

Alkhatib, M., Schubert, C.J., Del Giorgio, P.A., Gélinas, Y., Lehmann, M.F., 2012. Organic matter reactivity indicators in sediments of the St. Lawrence estuary. Estuar. Coast. Shelf Sci. 102–103, 36–47.

Arnosti, C., 2015. Contrasting patterns of peptidase activities in seawater and sediments: an example from Arctic fjords of Svalbard. Mar. Chem. 168, 151–156.

Barletta, F., St-Onge, G., Stoner, J.S., Lajeunesse, P., Locat, J., 2010. A high-resolution Holocene paleomagnetic secular variation and relative paleointensity stack from eastern Canada. Earth Planet. Sci. Lett. 298, 162–174.

Benoît, P., Gratton, Y., Mucci, A., 2006. Modeling of dissolved oxygen levels in the bottom waters of the Lower St, Lawrence estuary: coupling of benthic and pelagic processes. Mar. Chem. 102, 13–32.

Bianchi, T.S., 2011. The role of terrestrially derived organic carbon in the coastal ocean: a changing paradigm and the priming effect. Proc. Natl. Acad. Sci. U. S. A. 108 (49), 19473–19481.

Bourgault, D., Cyr, F., Galbraith, P.S., Pelletier, E., 2012. Relative importance of pelagic and sediment respiration in causing hypoxia in a deep estuary. J. Geophys. Res. 117, C08033. http://dx.doi.org/10.1029/2012JC007902.

Bourgoin, L.-H., Tremblay, L., 2010. Bacterial reworking of terrigenous and marine organic matter in estuarine water columns and sediments. Geochim. Cosmochim. Acta 74, 5593–5609.

Burdige, D.J., Martens, C.S., 1988. Biogeochemical cycling in an organic-rich coastal marine basin: 10. The role of amino acids in sedimentary carbon and nitrogen cycling. Geochim. Cosmochim. Acta 52 (6), 1571–1584.

Burdige, D.J., 2007. Preservation of organic matter in marine sediments: controls, mechanisms and an imbalance in sediment organic carbon budgets. Chem. Rev. 107, 467–485.

Carstens, D., Schubert, C.J., 2012. Amino acid and amino sugar transformation during sedimentation in lacustrine systems. Org. Geochem. 50, 26–35.

Casse, M., Montero-Serrano, J.-C., St-Onge, G., 2017. Influence of the Laurentide Ice Sheet and relative sea-level changes on sediment dynamics in the Estuary and Gulf of St. Lawrence since the last deglaciation. Boreas 46, 541–561.

Colombo, J.C., Silverberg, N., Gearing, J.N., 1996. Biogeochemistry of organic matter in the Laurentian Trough, II. Bulk composition of the sediments and relative reactivity of major components during early diagenesis. Mar. Chem. 51, 295–314.

Conley, D.J., Carstensen, J., Aigars, J., Axe, P., Bonsdorff, E., Eremina, T., Haahti, B.-M., Humborg, C., Jonsson, P., Kotta, J., Lännegren, C., Larsson, U., Maximov, A., Rodriguez Medina, M., Lysiak-Pastuszak, E., Remeikaitė-Nikienė, N., Walve, J., Wilhelms, S., Zillén, L., 2011. Hypoxia is increasing in the coastal zone of the Baltic Sea. Environ. Sci. Technol. 45, 6777–6783.

Cowie, G.L., Hedges, J.I., 1992. Sources and reactivities of amino acids in a coastal marine environment. Limnol. Oceanogr. 37, 703–724.

Cowie, G.L., Hedges, J.I., 1994. Biochemical indicators of diagenetic alteration in natural organic matter mixtures. Nature 369, 304–307.

Cowie, G.L., Hedges, J.I., Prahl, F.G., de Lange, G.J., 1995. Elemental and major biochemical changes across an oxidation front in a relict turbidite: an oxygen effect. Geochim. Cosmochim. Acta 59, 33–46.

Dauwe, B., Middelburg, J.J., Herman, P.M.J., Heip, C.H.R., 1999. Linking diagenetic alteration of amino acids and bulk organic matter reactivity. Limnol. Oceanogr. 44, 1809–1814.

de Vernal, A., Guiot, J., Turon, J.-L., 1993. Late and postglacial paleoenvironments of the Gulf of St. Lawrance: marine and terrestrial palynological evidence. Géochraphie Phys. Quaternaire 47, 167–180.

El-Sabh, M.I., Silverberg, N., 1990. Oceanography of a Large-scale Estuarine System : the St. Lawrence. Springer-Verlag, New York.

Emerson, S., Hedges, J., 2003. Sediment diagenesis and benthic flux. In: Elderfield, H. (Ed.), The Oceans and Marine Geochemistry. Elsevier-Pergamon, Oxford, pp. 293–320.

Genovesi, L., de Vernal, A., Thibodeau, B., Hillaire-Marcel, C., Mucci, A., Gilbert, D., 2011. Recent changes in bottom water oxygenation and temperature in the Gulf of St, Lawrence. Micropaleontological and geochemical evidence. Limnol. Oceanogr. 56 (4), 1319–1329.

Gilbert, D., Sundby, B., Gobeil, C., Mucci, A., Tremblay, G.H., 2005. A seventy-year record of diminishing deep-water oxygen levels in the St, Lawrence estuary–the northwest Atlantic connection. Limnol. Oceanogr. 50, 1654–1666.

Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391, 572.

Harvey, R.H., Tuttle, J.H., Bell, T.J., 1995. Kinetics of phytoplankton decay during simulated sedimentation: changes in biochemical composition and microbial activity under oxic and anoxic conditions. Geochim. Cosmochim. Acta 59, 3367–3377.

Hébert, M., Tremblay, L., 2017. Production and persistence of bacterial organic matter at the hypoxic water-sediment interface of the St. Lawrence estuary. Limnol. Oceanogr. http://dx.doi.org/10.1002/lno.10556.

Hecky, R.E., Mopper, K., Kilham, P., Degens, E.T., 1973. The amino acid and sugar composition of diatom cell-walls. Mar. Biol. 19, 323–331.

Hedges, J.I., Oades, J.M., 1997. Comparative organic geochemistries of soils and marine sediments. Org. Geochem. 27 (7–8), 319–361.

Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr. 29 (3), 657–663.

Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. 49, 81–115.

Hedges, J.I., Keil, R.G., 1999. Organic geochemical perspectives on estuarine processes: sorption reactions and consequences. Mar. Chem. 65, 55–65.

Hunt, A.P., Parry, J.D., Hamilton-Taylor, J., 2000. Further evidence of elemental composition as an indicator of the bioavailability of humic substances to bacteria. Limnol. Oceanogr. 45 (1), 237–241.

Jennerjahn, T.C., Ittekkot, V., 1997. Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil: 1. Amino acids and hexosamines. Oceanol. Acta 20, 359–369.

Kaiser, K., Benner, R., 2005. Hydrolysis-induced racemization of amino acids. Limnol. Oceanogr. Methods 3, 318–325.

Kaiser, K., Benner, R., 2008. Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen. Limnol. Oceanogr. 53, 99–112.

Lalonde, K., Mucci, A., Ouellet, A., Gélinas, Y., 2012. Preservation of organic matter in sediments promoted by iron. Nature 483 (7388), 198–200.

Lapointe, M., 2000. Modern diatom assemblages in surfaces sediments from the maritime estuary and the Gulf of St. Lawrence, Québec (Canada). Mar. Micropaleontol. 40, 43–65.

Lee, C., Wakeham, S.G., Hedges, J.I., 2000. Composition and flux of particulate amino acids and chloropigments in equatorial Pacific seawater and sediments. Deep-Sea Res. 47, 1535–1568.

Lehmann, M.F., Barnett, B., Gélinas, Y., Gilbert, D., Maranger, R., Mucci, A., Sundby, B., Thibodeau, B., 2009. Aerobic respiration and hypoxia in the lower St. Lawrence Estuary: stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning. Limnol. Oceanogr. 54, 2157–2169.

Lucotte, M., Hillaire-Marcel, C., Louchouarn, P., 1991. First-order organic-carbon budget in the St-Lawrence lower estuary from C-13 data. Estuar. Coast. Shelf Sci. 32, 297–312.

Madigan, M.T., Martinko, J.M., 2006. Brock Biology of Microorganisms. Pearson Prentice Hall, London, p. 992.

Mai-Thi, N.N., 2016. Transformations de la matière organique au cours des 13 000 dernières années dans les sédiments de l'Estuaire et du Golfe du Saint-Laurent. M.Sc. Thesis. Department of Chemistry and Biochemistry, Université de Moncton, Moncton, NB, Canada.

Menzel, P., Gaye, B., Wiesner, M.G., Prasad, S., Stebich, M., Das, B.K., Anoop, A., Riedel, N., Basavaiah, N., 2013. Influence of bottom water anoxia on nitrogen isotopic ratios and amino acid contributions of recent sediments from small eutrophic Lonar Lake, central India. Limnol. Oceanogr. 58, 1061–1074.

Menzel, P., Anupama, K., Basavaiah, N., Das Brijraj, K., Gaye, B., Herrmann, N., Prasad, S., 2015. The use of amino acid analyses in palaeo-limnological investigations: a comparative study of four Indian lakes in different climate regimes. Geochim. Cosmochim. Acta 160, 25–37.

Möbius, J., Gaye, B., Lahajnar, N., Bahlmann, E., Emeis, K.C., 2011. Influence of diagenesis on sedimentary $\delta^{15}N$ in the Arabian Sea over the last 130 kyr. Mar. Geol. 284 (1–4), 127–138.

Moriarty, D.J.W., 1977. Improved method using muramic acid to estimate biomass of bacteria in sediments. Oecologica 26, 317–323.

Muller-Karger, F.E., Varela, R., Thunell, R., Luerssen, R., Hu, C., Walsh, J.J., 2005. The importance of continental margins in the global carbon cycle. Geophys. Res. Lett. 32, L01602.

Muzuka, A.N.N., Hillaire-Marcel, C., 1999. Burial rates of organic matter along the eastern Canadian margin and stable isotope constraints on its origin and diagenetic evolution. Mar. Geol. 160, 251–270.

Nagata, T., Meon, B., Kirchman, D.L., 2003. Microbial degradation of peptidoglycan in seawater. Limnol. Oceanogr. 48, 745–754.

Niggemann, J., Ferdelman, T.G., Lomstein, B.A., Kallmeyer, J., Schubert, C.J., 2007. How depositional conditions control input, composition, and degradation of organic matter in sediments from the Chilean coastal upwelling region. Geochim. Cosmochim. Acta 71, 1513–1527.

Petrie, B., Drinkwater, K., Sandstrom, A., Pettipas, R., Gregory, D., Gilbert, D., Sekhon, R., 1996. Temperature, salinity and sigma-t atlas for the Gulf of St. Lawrence. Can. Tech. Rep. Hydrogr. Ocean Sci. 178, 256.

Saucier, F.J., Roy, F., Gilbert, D., Pellerin, P., Ritchie, H., 2003. Modeling the formation and circulation processes of water masses and sea ice in the Gulf of St. Lawrence, Canada. J. Geophys. Res. 108, 3269. http://dx.doi.org/10.1029/2000JC000686.

Schleifer, K.H., Kandler, O., 1972. Peptidoglycan types of bacterial cell walls and their taxonomic implications. Bact. Rev. 36 (4), 407–477.

Schmidt, M.W., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D.A., Nannipieri, P., Rasse, D.P., Weiner, S., Susan, E.T., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478, 49–56.

Steven, D.M., 1974. Primary and Secondary Production in the Gulf of St. Lawrence, vol. 26. McGill Univ., Mar. Sci. Centre, M.S. Rep., 116–116.

St-Onge, G., Hillaire-Marcel, C., 2001. Isotopic constraints of sedimentary inputs and organic carbon burial rates in the Saguenay Fjord, Québec. Mar. Geol. 176, 1–22.

St-Onge, G., Lajeunesse, P., Duchesne, M.J., Gagné, H., 2008. Identification and dating of a key late pleistocene stratigraphic unit in the St. Lawrence estuary and Gulf (eastern Canada). Quat. Sci. Rev. 27, 2390–2400.

Therriault, J.C., Levasseur, M., 1985. Control of phytoplankton production in the lower St. Lawrence Estuary: Light and freshwater runoff. Nat. Can. 112, 77–96.
Thibodeau, B., de Vernal, A., Mucci, A., 2006. Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St, Lawrence Estuary: enhanced primary productivity, organic carbon fluxes and the development of hypoxic bottom waters in the Lower St, Lawrence Estuary, Eastern Canada: micropaleontological and geochemical evidence. Mar. Geol. 231, 37–50.
Thibodeau, B., de Vernal, A., Limoges, A., 2013. Low oxygen events in the Laurentian Channel during the Holocene. Mar. Geol. 346, 183–191.
Tremblay, L., Benner, R., 2006. Microbial contributions to N-immobilization and organic matter preservation in decaying plant detritus. Geochim. Cosmochim. Acta 70 (1), 133–146.
Tremblay, L., Benner, R., 2009. Organic matter diagenesis and bacterial contributions to detrital carbon and nitrogen in the Amazon River system. Limnol. Oceanogr. 54, 681–691.
Tremblay, L., Gagné, J.-P., 2009. Organic matter distribution and reactivity in the waters of a large estuarine system. Mar. Chem. 116, 1–12.
Tremblay, L., Gagné, J.-P., 2002. Fast quantification of humic substances and organic matter by direct analysis of sediments using DRIFT spectroscopy. Anal. Chem. 74, 2985–2993.
Tremblay, L., Gagné, J.-P., 2007. Distribution and biogeochemistry of sedimentary humic substances in the St, Lawrence estuary and the Saguenay Fjord, Québec. Org. Geochem. 38, 682–699.
Wakeham, S.G., Lee, C., 1993. Production, transport, and alteration of particulate organic matter in the marine water column. In: Engel, M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum Press, Springer US, pp. 145–169.
Wakeham, S.G., Lee, C., Hedges, J.I., Hernes, P.J., Peterson, M.L., 1997. Molecular indicators of diagenetic status in marine organic matter. Geochim. Cosmochim. Acta 61 (24), 5363–5369.
Yeats, P.A., 1988. Nutrients. In: Strain, P.M. (Ed.), Chemical Oceanography in the Gulf of St. Lawrence, vol. 3. Dept. of Fisheries and Oceans, Canada, pp. 29–48.