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Benthic fluxes of dissolved organic nitrogen in the Lower St. Lawrence Estuary and implications for selective organic matter degradation

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Abstract

The distribution of dissolved organic nitrogen (DON) and carbon (DOC) in sediment pore waters was determined at nine locations along the St. Lawrence Estuary and in the Gulf of St. Lawrence. The study area is characterized by gradients in the sedimentary particulate organic matter (POM) reactivity, bottom water oxygen concentrations, as well as benthic respiration rates. Based on pore water profiles we estimated the benthic diffusive fluxes of DON and DOC. Our results show that DON fluxed out of the sediments at significant rates (110 to 430 $\mu mol\,m^{-2}\,d^{-1}$). DON fluxes were positively correlated with sedimentary POM reactivity and sediment oxygen exposure time (OET), suggesting direct links between POM quality, aerobic remineralization and the release of DON to the water column. DON fluxes were on the order of 30 % to 64 % of the total benthic inorganic fixed N loss due to denitrification, and often exceeded the diffusive nitrate fluxes into the sediments. Hence they represented a large fraction of the total benthic N exchange. This result is particularly important in light of the fact that DON fluxes are usually not accounted for in estuarine and coastal zone nutrient budgets. The ratio of the DON to nitrate flux increased from 0.6 in the Lower Estuary to 1.5 in the Gulf. In contrast to DON, DOC fluxes did not show any significant spatial variation along the Laurentian Channel (LC) between the Estuary and the Gulf ($2100 \pm 100\,\mu mol\,m^{-2}\,d^{-1}$), suggesting that production and consumption of labile DOC components proceed at similar rates, irrespective of the overall benthic characteristics and the reactivity of POM. As a consequence, the molar C/N ratio of dissolved organic matter (DOM) in pore water and the overlying bottom water varied significantly along the transect, with lowest C/N in the Lower Estuary (5–6) and highest C/N (> 10) in the Gulf. We observed large differences between the C/N of pore water DOM with respect to POM, and the degree of the C– versus –N element partitioning seems to be linked to POM reactivity and/or redox conditions in the sediment pore waters. Our results thus highlight the variable effects selective OM degradation and preservation can have on bulk sedimentary C/N ratios, decoupling the primary source C/N signatures from those

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in sedimentary archives. Our study further underscores that the role of estuarine sediments as efficient sinks of bioavailable nitrogen is strongly influenced by the release of DON during early diagenetic reactions, and that DON fluxes from continental margin sediments represent an important internal source of N to the ocean.

1 Introduction

Coastal marine systems are areas under particularly high environmental stress due to increased inputs of nutrients and organic matter (OM) from different land sources, which strongly influence both water quality and the biota (Gilbert et al., 2005; Thibodeau et al., 2006). Marine and estuarine systems are biogeochemically responsive to fixed nitrogen (N), exhibiting rapid uptake of dissolved inorganic N (DIN) and dissolved organic N (DON) (Seitzinger et al., 2002; Seitzinger and Sanders, 1999). However, in estuaries, DIN accounts for only a portion of the total N inputs, while DON is often a much more important (30–80 %) component of the dissolved N pool (Berman and Bronk, 2003; Lønborg et al., 2009). In marine sediments, during early sedimentary diagenesis, a large portion of particulate organic matter (POM) is recycled by bacterial hydrolysis to DON and dissolved organic carbon (DOC) directly in the sediment pore water. Subsequently, DOC and DON are partitioned between several processes, namely the bacterially-mediated remineralization of dissolved organic matter (DOM) to CO_2 and nutrients, diffusion to the overlying bottom water, where it can ultimately be assimilated by phytoplankton and bacteria in the water column, and/or stabilization and burial in sediments due to abiotic adsorption on mineral surfaces and complexation by metal hydroxide nanoparticles and geo-polymerization (Alperin et al., 1999; Burdige, 2001; Lalonde et al., 2012). DOC and DON dynamics in sediments and their release to the water column are important in the context of the productivity of these aquatic environments, and the exchange of climate relevant gases with the atmosphere.

DON has seldom been considered in N budgets of estuaries and the ocean, in part because it is generally assumed to be mostly recalcitrant (e.g.,

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Berman and Bronk, 2003; Knapp et al., 2005; Bourbonnais et al., 2009). However, some algae and bacteria have the capacity to use DON as a source of N for biosynthesis (Seitzinger et al., 2002; Seitzinger and Sanders, 1999). Therefore, N budgets for aquatic ecosystems based only on DIN sources and sinks may underestimate the pool of bioavailable N (Seitzinger et al., 2002). Likewise, most benthic studies have mainly focused on net DIN fluxes when assessing total denitrification rates and the N elimination capacity of the estuarine bottom sediments, neglecting the reflux of remineralized N as DON. For example, Thibodeau et al. (2010) have shown that sediments of the Laurentian Channel (LC) function as an efficient sink for nitrate, especially in the Lower St. Lawrence Estuary section, but the role of sediments as a potential source of DON and its biogeochemical role of benthic DON fluxes have not been investigated yet.

Another aspect that has not been well explored to date is the connection between DON and DOC dynamics in estuarine sediments, which can provide insight into element fractionation during benthic remineralization of sedimentary POM. For example, the bioavailability of DOC from sediments with respect to DON, and its role with regards to ecosystem respiration and the generation of basin-scale oxygen deficits (e.g., hypoxia) has been a matter of unresolved debate (Faganeli et al., 1991; Lahajnar et al., 2005; Lønborg et al., 2009). Therefore, the identification of key reaction and transport processes that affect pore water DOC and DON distributions is critical to assessing the significance of benthic metabolism during early sedimentary diagenesis and the associated alteration of the bulk sedimentary organic matter pool.

It is generally accepted that refractory POM in sediments has a higher carbon-to-nitrogen (C/N) atomic ratio and a lower potential for further remineralization than for bioavailable POM in the water column (Meyers and Eadie, 1993). Hence, it is reasonable to assume that general sediment characteristics (i.e., amount, composition and reactivity/age of the POM) and redox conditions in estuarine and coastal-area sediments may influence not only the overall rates of benthic inorganic and organic solute exchange (Alkhatib et al., 2012a; Thibodeau et al., 2010), but also the element parti-

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tioning during remineralization. However, the effect of POM reactivity on the fluxes and fate of remineralized DOM remains uncertain.

Here we provide a detailed assessment of the distribution of DON and DOC in sediments and in near-bottom waters along a transect from the St. Lawrence River estuary to the Gulf of St. Lawrence, which is characterized by systematic changes in sediment OM reactivity and bottom water oxygenation (Lehmann et al., 2009; Alkhatib et al., 2012a, b). We first tested the suitability of different pore water extraction techniques for DOM. We then used the pore water DON and DOC profiles to estimate benthic diffusive fluxes of DON and DOC in the estuary, and in the Gulf. The main goals of this study were (1) to quantify the spatial heterogeneity in DON and DOC fluxes in the St. Lawrence Estuary, (2) to establish the connection between the DON and DOC fluxes, and between these fluxes and the reactivity of the sedimentary POM, particularly in terms of potential elemental discrimination during hydrolysis and bacterial degradation, and (3) to assess the potential contribution of benthic DON fluxes to the net dissolved N exchange rates at the sediment-water interface (SWI) along the estuary.

2 Materials and methods

2.1 Study area

The bathymetry of the St. Lawrence River Estuary is dominated by the Laurentian Channel (LC), a 250–500 m deep submarine valley that extends landward 1240 km from the edge of the Atlantic continental shelf (Fig. 1). The Gulf of St. Lawrence, a large (250 000 km^2) and roughly triangular inland sea, is connected to the Atlantic by the Strait of Belle Isle and Cabot Strait at the northeast and southeast corners, respectively. Water mass movement in the St. Lawrence system is characterized by an estuarine circulation: less saline water flows seaward in the surface mixed layer, overlying more saline water mass that formed in the northwest Atlantic and flows landward. The water in the deeper layer is isolated from the atmosphere by a permanent pycnocline at

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100–150 m depth and the water residence time is approximately 3–4 yr (Gilbert et al., 2005). As the deep-water mass flows landward, it gradually loses oxygen through aerobic microbial respiration. Sedimentary respiration was plausibly pointed out as the most important sink of oxygen in the St. Lawrence estuarine system (Lehmann et al., 2009), yet the relative importance of benthic versus pelagic oxygen demand in the St. Lawrence Estuary is an ongoing debate (Bourgault et al., 2012). In previous work, we have shown that POM source, oxygen concentration, benthic nutrient and DO fluxes, as well as POM reactivity, vary along the Laurentian Channel (Thibodeau et al., 2010; Alkhatib et al., 2012a). Chlorin- and amino acid-based degradation indices show that sedimentary OM in the Lower Estuary is more reactive than in the Gulf (see Table 1). Carbon isotope measurements and C/N ratios indicate that sedimentary POM along the Lower Estuary and the Gulf is mainly of marine origin. The terrestrial content of the sedimentary OM pool decreases with distance from the head of the Lower Estuary, as does sediment reactivity (Alkhatib et al., 2012a; Table 1).

2.2 Sampling

Sediment multicores and box cores were recovered at multiple stations along the LC (Sta. 16–25) and at one station at the head of the Anticosti Channel in the Gulf during two cruises in June and August 2006 (Fig. 1). Stations were chosen to represent the spatial heterogeneity in sedimentary OM characteristics (see above), and hydrochemical parameters (e.g., dissolved oxygen (DO), salinity) in the overlying water. Sediment pore waters were extracted immediately after core recovery using the whole core squeezing (WCS) method (Jahnke, 1988; Bender et al., 1987). During pore water extraction, the multicores were kept at in situ temperatures by wrapping the core tubes with ice bags. Extracting pore water from the upper 1.5 to 2 cm generally took about 20–30 min. The WCS is a pore water sampling technique that yields millimeter depth resolution near the sediment-water interface. Water samples were collected with syringes equipped with Teflon coated pistons. For collecting pore water from greater depths than allowed by WCS, but also as a quality control of WCS data and for sampling method

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comparison, pore water was extracted using Rhizon membrane samplers (Seeberg-Elverfeldt et al., 2005). The sediments processed with the Rhizon membrane samplers were obtained from box cores using push-core liners with holes (0.5 mm diameter) at 1 cm intervals. DON blank contribution of the Rhizon sampler was negligible. Using the Rhizon sampling technique, pore water can be sampled with minimum disturbance to the sediment structure, while the WCS method applies high pressures to the sediments, which can lead to rupturing of benthic organisms and the lysis of bacterial or algal cells.

Water samples collected for nutrient and total dissolved N (TDN, the sum of NO_3^-, NO_2^-, NH_4^+ and DON) analyses were filtered through 0.45 µm Teflon syringe filters. For DOC water samples, PTFE syringe filters were used. Nutrient samples were stored frozen in pre-washed plastic vials until analysis in the lab. Pore water samples for DOC analyses were kept acidified with HCl (pH < 2) in glass vials (combusted, 500 °C, 3 h) and stored in the dark prior to analysis.

2.3 Laboratory analyses

The concentration of TDN for water samples was measured using the persulfate oxidation method following Solorzano and Sharp (1980). Persulfate was re-crystallized three times prior to oxidation to reduce N blanks (Bronk et al., 2000). Briefly, for TDN determination, 0.5 mL of alkaline persulfate oxidizing reagent was added to 3 mL of sample in a borosilicate glass test tube. Samples and three test tubes with the persulfate oxidation reagent only (blank) were then autoclaved for 45 min to quantitatively convert TDN to NO_3^-. TDN-derived nitrate was then quantified using an Antek 7020 Nitric Oxide Analyzer: Nitrate was reduced to nitric oxide (NO) in an acidic heated (90 °C) vanadium (III) solution (Braman and Hendrix, 1989), and the NO was measured by chemiluminescence detection. Reproducibility for replicate analyses was better than 2 % or ±0.2 µmol L^{-1}. The total procedural blank never exceeded 3 µmol L^{-1} and was on average 2 µmol L^{-1}. TDN concentrations were corrected for blank contribution. Sample nitrate + nitrite concentrations were also measured using the vanadium

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method. DON was determined by subtracting total dissolved inorganic nitrogen (DIN; nitrate, nitrite, and ammonia) from TDN, where NH_4^+ concentrations were measured using standard colorimetric autoanalysis (Hansen and Koroleff, 1999). DOC concentrations were measured by high-temperature catalytic oxidation (HTCO) using a Shimadzu TOC 5000 analyzer. The samples were filtered and acidified onboard directly after collection. Once in the laboratory, samples were purged with oxygen to remove inorganic carbon. A sample aliquot of 100 µL was then injected into the combustion column packed with platinum-coated alumina beads held at 680 °C. Organic carbon compounds were combusted and quantitatively converted to CO_2, which was quantified by a non-dispersive infrared detector.

2.4 DOC and DON benthic fluxes

DOM fluxes (F) across the SWI were estimated based on pore water concentration gradients (WCS or Rhizon) using Fick's first law of diffusion (Berner, 1980; Boudreau, 1996):

$$F = D_{\text{sed}} \Delta C / \Delta z \quad (1)$$

where D_{sed} is the temperature-dependent free diffusion coefficient for DOM ($D°$, in $\text{cm}^2\,\text{s}^{-1}$), corrected for sediment porosity (Boudreau, 1996), and $\Delta C/\Delta z$ is the solute (i.e., DON or DOC) concentration gradient with depth z in the sediment. $\Delta C/\Delta z$ was calculated from the first derivative of best-fit curves of the WCS-derived DOC or DON concentration profiles just below the sediment–water interface. To calculate F from Rhizon membrane profiles, $\Delta C/\Delta z$ was calculated as the concentration difference between the overlying water and the first sample below the SWI, in all cases at depths of less than 2 cm. A similar approach was used in previous work (Martin and McCorkle, 1993; Lahajnar et al., 2005; Hall et al., 2007). Bottom water temperatures ranged from 3 to 5 °C, and the porosity of the surface sediments generally decreased from 95 % to 75 % within the top 5 cm. To determine $D°$ for DOC and DON in seawater, we used

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the empirical relationship between molecular diffusion and molecular weight (MW; at 25 °C in distilled water) reported by Burdige et al. (1992), assuming a fixed average MW of 2500 daltons for both DON and DOC. This MW represents an intermediate value of previous estimates for pore water DOM. Alperin et al. (1999) proposed an average MW of 5000 daltons, while other studies show that the vast majority (> 80 %) of the DOC and DON in sediment pore waters has a molecular weight of less than 3000 daltons. Uncertainty in the molecular weight has relatively little impact on the calculated fluxes because of the inverse cube–root relationship between D° and MW (Burdige et al., 1992). *In situ* salinity and temperature were taken into consideration using the Stokes–Einstein formula (Boudreau, 1996) and the corrected value for D° was $1.56 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, translating into a D_{sed} value of $1.5 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ after correction for sediment porosity.

3 Results

3.1 DON and DOC in sediment pore waters

Sediment profiles of DON and DOC are shown in Figs. 2 and 3, respectively. In most cores, the porewater DON concentrations sharply increased below the SWI and reached a plateau of 40–200 µM at a depth of about 5 cm. At all sites, average pore water DON concentrations in the uppermost cm of the sediment column were at least two-fold higher than in the overlying water column, suggesting a substantial flux of DON out of the sediments (see below). The agreement between WCS and Rhizon-sampler-derived DON profiles was good in the upper 1–2 cm, but there were large differences between the two methods below that depth at several stations. In these deeper samples, WCS-derived DON concentrations were often several fold higher (Fig. 2), suggesting artifacts that probably result from the pressure applied during the core squeezing (see discussion), which may lead to the release of intracellular DON. In general, average pore water DON concentrations in the uppermost centimeter of the sediment

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decreased eastward along the LC (Fig. 4a), with the highest subsurface DON concentrations measured landward at the Lower Estuary stations and the Anticosti Channel (~ 21 µM), and the lowest ones in the Gulf (8–18 µM).

Porewater DOC concentration profiles suggest a distribution qualitatively similar to that of DON. DOC concentrations in the uppermost centimeter of the sediment column did not show a clear spatial trend along the Lower Estuary (Fig. 4a), with average concentrations ranging between 97 and 141 µM. The highest DOC concentration was measured in sediment pore water at Sta. Anticosti Channel (~ 274 µM). The pore water molar ratio of DOC-to-DON (C/N_{DOM}) in the uppermost centimeter in the sediment column varied between 5.2 at Sta. 25 in the Lower Estuary and 11 at Sta. 16, with a maximum of 13.3 at the Anticosti Channel station (Fig. 5).

3.2 Benthic DON and DOC fluxes

Benthic diffusive DON fluxes at the SWI based on Rhizon sample measurements were in general agreement with those determined using the WCS concentration gradients. DON Rhizon-based fluxes were slightly lower than the WCS ones only at Sta.18 and Sta. 20 in the Gulf (Table 2). The highest DON fluxes (average of both WCS- and Rhizon-based calculations) were observed at the head of the LC (~ 440 µmol m^{-2} d^{-1} at Sta. 25) with fluxes decreasing seaward, and the lowest flux (~ 110 µmol m^{-2} d^{-1}) measured at Sta. 16. Diffusive DOC fluxes (0 to ~ 2 cm depth profiles; WCS-based only) averaged ~ 2100 µmol m^{-2} d^{-1} and did not display any consistent trend along the Lower Estuary seaward up to Sta. 19 in the Gulf; however, much lower DOC fluxes (~ 1400 and ~ 1300 µmol m^{-2} d^{-1}) were observed at Sta.18 and at Sta. 16, respectively (Table 2). The highest DOC flux (~ 3850 µmol m^{-2} d^{-1}) was observed at Sta. Anticosti (Table 2), consistent with the high pore water DOC and DON concentrations. The C/N ratio of the DOM efflux from the sediments was lowest in the Lower Estuary (average C/N of ~ 5), intermediate between Sta. 22 and Sta. 20 (average C/N of ~ 7), and it was highest at Sta. 16 and Anticosti in the Gulf (average C/N of ~ 13) (Fig. 5).

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3.3 DON and DOC in the bottom water

The DON concentrations in the bottom waters overlying the sediments were highest at the head of the LC at Sta. 25 and 23 (~ 10 µM) and were comparatively low in the Gulf of St Lawrence, with lowest concentrations at Sta. 20 (6.3 µM) (Fig. 4b). This pattern agrees well with the spatial trends in DON fluxes that we described above. In contrast, DOC concentrations were slightly higher in the Gulf (~ 60 µM) than in the Lower Estuary (~ 50 µM). The highest DOC concentration was observed at the Anticosti station (82 µM). The observed patterns in bottom water DOC and DON concentrations resulted in a clear increasing trend in the bottom water DOM C/N ratios, from 5 in the Lower Estuary to ~ 9 in the Gulf at Sta. 16 (Fig. 5).

4 Discussion

4.1 Suitability of whole core squeezing for DOM extraction

Previous studies on the applicability of WCS in determining DOC in sediment pore waters have shown that this pore water extraction technique tends to overestimate DOC concentrations in deeper layers of the sediments, most likely due to the lysis of bacterial cells (Bolliger et al., 1992; Martin and McCorkle, 1993). This bias is likely to increase with depth, as the pressure that has to be applied to the sediment core increases with the depth of the sediment layer from which pore water is extracted (Martin and McCorcle, 1993). Indeed, at several stations and at depths greater than 2–3 cm, the average DON concentration measured by WCS was several-fold higher than that obtained for the Rhizon samples (Fig. 2), suggesting that intracellular metabolites from only partially lysed or living sediment microorganisms may have been released into the aqueous extract at high pressures (Bolliger et al., 1992; Martin and McCorkle, 1993). Thus, the observed differences were most probably due to the liberation of benthic N immobilized in bacteria and other benthic organisms (Benner, 2002; Tremblay and Benner, 2006)

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during the WCS processing. In the first two cm of the sediment column, however, the agreement between WCS and the Rhizon sampler was good for DON concentrations (see Fig. 2), demonstrating that possible pressure effects are negligible in the upper sediment layer below the SWI. Hence, we show evidence that (at least in the St. Lawrence sediments) WCS can be used to sample pore water for benthic flux determination, as the gradient down to ∼ 2 cm below SWI does not seem to be affected by WCS artifacts.

A large fraction of the total sedimentary organic matter is associated with mineral particles. Metal oxides that accumulate near the SWI at the oxic–anoxic interface can possibly act as DOM filters (Skoog et al., 1996; Arnarson and Keil 2000; Skoog and Arias-Esquivel 2009). Hence redox conditions, i.e. the distribution of redox-sensitive metals within the sediments, for example, may exert a strong control on the fluxes of DOM out of the sediments (Skoog et al., 1996). Mineral matrix–DOM interactions can potentially bias pore water DOM measurements. As pore water is slowly forced through the interstices of the sediment during core squeezing, pore waters from deeper sediment layers come into contact with surface-reactive oxic sediments that were in equilibrium with waters with different DOM concentrations. DOM may equilibrate with the ambient mineral phase through adsorption/desorption reactions that occur on a sub-minute time scale (Alperin et al., 1999; Arnarson and Keil, 2000), and therefore, it is possible that DOC and DON concentration of WCS samples and the DOM composition is modified by solid–solution partitioning. Moreover, the high pressures associated with the WCS extraction of DOM from the deeper layers of the sediment also modify partitioning of DOM, with higher pressures favoring the release of a greater fraction of exchangeable, sorbed OM into the liquid phase (leading to higher measured DOC and DON concentrations in the deeper layers where WCS and Rhizons results diverge).

Predicting the combined effects of cell lysis, sorption/desorption of deep DOM diffusing through shallower sediment layers, and pressure-driven changes in solid–liquid partitioning, and how these effects may change with depth is not straightforward. Even though the concentration of highly reactive nanophase ferrihydrite is highest near the

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SWI (Lalonde et al., 2012), the low pressure applied to the system during the extraction and short diffusion path would minimize these effects, which might explain why there was a very good agreement between the two extraction approaches for the first 2 cm. Below 2 cm, the high pressures applied to the core during squeezing and the fact that DOM has to diffuse through a mineral matrix of varying iron hydroxide concentrations makes it more susceptible to biases (Martin and McCorkle, 1993; Lalonde et al., 2012). We thus believe that the combination of the high-resolution WCS data between 0–2 cm and lower-resolution but more reliable Rhizon data below 2 cm provides the best pore water DON and DOC profiles.

4.2 DOC and DON fluxes

At all sites, DON and DOC concentrations were systematically higher in pore waters compared to the water column bottom water (Fig. 4). The higher concentrations in pore waters imply a net production of DOM within the sediments, and a net upward flux of DON and DOC across the SWI. Numerous studies from a wide variety of marine environments have shown that DOC and DON concentrations in sediment pore water may be several fold higher than in the overlying water (e.g., Martin and McCorkle, 1993; Blackburn et al., 1996; Burdige and Zheng, 1998; Alperin et al., 1999; Holcombe et al., 2001). We have summarized the published sedimentary fluxes of DON and DOC from different marine systems in Table 3. Our calculated sediment DON fluxes were much higher than reported fluxes from deep-sea sediments (Brunnegård et al., 2004), within the lower limits of fluxes calculated for the Chesapeake Estuary (Burdige and Zheng, 1998) and in the Svalbard, Norway (Blackburn et al., 1996), much lower than DON fluxes calculated from a shallow coastal area (Knebel Vig) in Denmark (Lomstein et al., 1998), but generally within the range reported for other estuarine and continental shelf sites (reviewed by Bronk and Steinberg, 2008). DOC fluxes (1300 to 3900 $\mu mol\,m^{-2}\,d^{-1}$) are within the range of values reported previously by Colombo et al. (1996) at two locations in the LC ($\sim 1700\,\mu mol\,m^{-2}\,d^{-1}$), and similar to estimates reported by Burdige and Homstead (1994) from Chesapeake Bay sediments (1400

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to 2900 µmol m^{-2} d^{-1}), but significantly higher, for example, than fluxes determined by Holcombe et al. (2001) for Mexican margin sediments (400 µmol m^{-2} d^{-1}).

We found the highest DON fluxes in sediments of the Lower Estuary and the lowest ones in the Gulf (Table 2). We attribute these variations to patterns in POM reactivity across the sites as the fluxes strongly correlated with OM reactivity (chlorin index (CI), r^2 = 0.83, n = 9; degradation index (DI), r^2 = 0.74, n = 9; Fig. 6a, b). In addition, there was an inverse correlation between DON fluxes and dissolved oxygen concentrations in the bottom waters (r^2 = 0.83, n = 9; Fig. 6c). Moreover, DON fluxes correlated linearly with the oxygen exposure time (OET), which defines the average time that sediment OM is exposed to "oxic" conditions during burial in the sediments (Hartnett et al., 1998; Hedges et al., 1999; r^2 = 0.9, n = 5; Fig. 6d). The higher DON fluxes measured in the Lower Estuary compared to the Gulf would thus appear to be linked to an increased supply of more reactive POM, higher overall sediment POM reactivity, and probably to the lower DO concentration in the overlying bottom water (see Table 1; Bourgoin and Tremblay 2010; Alkhatib et al., 2012a).

A number of studies have shown a positive correlation between POM delivery to the sediment and DON concentration in pore waters (e.g., Hansen and Blackburn, 1991; Sloth et al., 1995). The rate-determining step for both aerobic and anaerobic microbial degradation of POM and production of DOM is the hydrolysis by extracellular enzymes (Wilczek et al., 2005). Higher POM reactivity induces the production and activity of bacterial hydrolytic enzymes (Boetius and Lochte, 1994; Wilczek et al., 2005), and hydrolysis proceeds under both oxic and anoxic conditions, although not necessarily always at the same rates (Hansen and Blackburn 1991; Kristensen and Holmer 2001). In this regard, Thibodeau et al. (2010) recently reported that OM remineralization rates along the LC are highest in the Lower Estuary and decrease eastwards. Alkhatib et al. (2012a) also found a significant correlation between OM reactivity and OM remineralization rates along the LC reported by Thibodeau et al. (2010; r^2 = 0.76, n = 8). Therefore, it would appear that a high POM flux of relatively reactive POM is particularly conducive to high rates of OM hydrolysis in the Lower Estuary, resulting

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in both high pore water [DON] and high DON fluxes. Similarly, the inverse relationship between DON fluxes and dissolved O_2 concentrations in the bottom waters, as well as OET, confirms the close links between redox conditions, sediment POM degradation, and DON production in the sediments. In an earlier paper (Alkhatib et al., 2012a), we argued that the sedimentary diagenesis and the degradation rate are largely controlled by the reactivity of available organic substrates, as opposed to the relative supply of different electron acceptors. In vitro laboratory experiments have shown much slower and less efficient anoxic degradation of refractory POM and carbon-rich substrates, such as complex lipids (Kristensen and Holmer, 2001; Emerson and Hedges, 2003). In contrast, remineralization rates of more reactive OM appear to be controlled by the quality and the quantity of available organic matter, and are also largely independent of sediment redox conditions (Burdige, 2007 and references therein). The inverse correlations between dissolved O_2 concentrations and OET with DON fluxes suggest that oxygen-sensitive POM (i.e., POM requiring oxic conditions for degradation) is selectively concentrated with increasing POM maturity seaward along the LC.

The minor variations in DOC fluxes that we observed over this wide range of environmental conditions, in terms of vertical OM flux, dissolved O_2 concentration, and sediment POM reactivity, suggest a rather tight balance between production and consumption of labile DOC within the sediment, irrespective of the overall benthic activity in this system (Otto and Balzer, 1998). Because the bottom waters move inland along the LC, we would expect a continuous increase in DOC and DON concentrations owing to the cumulative flux of DOM across the SWI during transit. Figure 4b shows that, as the bottom water currents move inland along the LC, DOC concentrations in the bottom water slightly decreased from $> 60\,\mu mol\,L^{-1}$ at Sta. 20 to $< 50\,\mu mol\,L^{-1}$ at Sta. 25, while DON increased from $\sim 6\,\mu mol\,L^{-1}$ to $\sim 10\,\mu mol\,L^{-1}$ at the head of the LC (Fig. 5). While the concentration gradient between the sediment and the bottom water DOC pools predicts a flux of DOC out of the sediments at all stations (Table 2), the inland decline in bottom water DOC suggests that the benthic DOC fluxes were offset by water column

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respiration of the DOC, preventing the accumulation of dissolved organic matter as the bottom waters are slowly advected inland.

Alternatively, adsorption processes right at and just below the SWI can also modulate benthic DOC exchange. Adsorption of DOM to mineral and metal oxides/hydroxides surfaces can potentially remove significant amounts of DOC from the pore water before it actually fluxes into the water column (Boto et al., 1989; Skoog et al., 1996; Arnarson and Keil, 2000; Skoog and Arias-Esquivel, 2009). Adsorption on mineral surfaces and coprecipitation with metal hydroxides are processes that take place at all depths in the sediment but that are more pronounced near the SWI, where the highly surface-reactive nanophase ferrihydrite is enriched (Lalonde et al., 2012). This effect might partly cause the decrease in the porewater DOC concentration slopes between the SWI and a depth of 0.5 to 1.5 cm at most stations (Skoog et al., 1996; Arnarson and Keil, 2000; Skoog and Arias-Esquivel, 2009). The fact that no increase in bottom water DOC concentrations was observed, and that DOC fluxes varied little between stations despite large differences in porewater DOC concentrations, suggests that DOC-mineral interactions may have played a role in controlling DOC fluxes to the water column.

4.3 C versus N partitioning during DOM production and remineralization

The differences in molar C/N ratios between the pore water DOM and sedimentary POM along the estuarine transect suggest preferential hydrolysis of N-rich DOM during initial break-down of sediment POM (except at Sta. 16 and Anticosti Channel station; see Fig. 5). Initial hydrolysis of freshly deposited POM in surface sediments generally produces DOM with a C/N ratio that is lower than that of the deposited POM (Blackburn et al., 1996; Burdige and Zheng, 1998; Weston et al., 2006). We observed that the difference between C/N ratios of sediment POM and pore water DOM ($\Delta C/N = C/N_{POM} - C/N_{DOM}$) decreases along the LC from ~6 at the head of the LC to ~1 at Sta. 18, while the difference was negative (about −3) at Sta. 16, and in the Anticosti Channel sediments (Fig. 5). There was a strong correlation between sediment POM reactivity (as defined by CI and DI; for definition see caption of Fig. 7) and

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the ΔC/N (r^2 = 0.85, n = 8, excluding the Channel Anticosti from the regression as its location is not on the estuarine transect line; Fig. 7a). The ΔC/N also correlated with the oxygen exposure time (OET) (r^2 = 0.88, n = 8; Fig. 7b). These patterns are most likely related to the nature of the hydrolysed sediment POM (i.e. hydrolysable (reactive) vs. hydrolysis-resistant or oxygen-sensitive OM), and to the mode of hydrolysis, i.e. the initial depolymerisation step (or oxidative cleavage) of sedimentary POM to form dissolved intermediates, which is a function of the redox conditions (Emerson and Hedges, 2003; Burdige, 2007). While the hydrolysis of more labile POM is not limited by oxygen availability and takes place at comparable rates under both oxic and anoxic redox conditions (Hansen and Blackburn, 1991; Emerson and Hedges, 1988, 2003), effective degradation of the hydrolysis-resistant refractory POM requires molecular oxygen (Emerson and Hedges, 1988; Fenchel et al., 1998). Most of the strong oxidants such as peroxide (H_2O_2) and other reactive oxygen-containing enzymes are nonspecific, as they do not target specific compounds, chemical groups or types of bonds during the break-down of more refractory POM (Fenchel et al., 1998; Emerson and Hedges, 1988), thus minimizing element partitioning. Given that the CI and DI indexes reveal that sedimentary POM reactivity is highest in the Lower Estuary (Sta. 25, 23, 22, and 21) and becomes more refractory seaward along the LC, the fraction of hydrolysable POM likely decreases seaward, while that of hydrolysis-resistant POM increases.

Consistent with the observed increase in DOM C/N ratios (both in pore water and bottom water) seaward, we observed a decline in the C/N ratio of the sedimentary POM pool (Fig. 5). While the extent to which immobilized DOM in bacterial biomass contributes to the C/N signatures of the POM remains uncertain (Alkhatib et al., 2012b), it is clear that early diagenetic degradation of bulk OM, and the partitioning between the particulate and dissolved OM pools is associated with an elemental fractionation of C versus N, which appears to be sensitive to environmental conditions (i.e., bottom water O_2 concentration) and sediment characteristics (i.e., OM reactivity). The comparatively low difference in C/N ratios between pore water DOM, the DOM flux, and bottom water

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DOM in the St. Lawrence Estuary suggests post-hydrolytic bacterial DOM remineralization with little, if any, C versus N elemental fractionation.

4.4 Significance of benthic DON fluxes for estuarine N budgets

In the Lower Estuary and the Gulf, DON was the most important dissolved nitrogen component in pore water, comprising up to 85 % of the TDN at the sedimentary redox transition zone. Thibodeau et al. (2010) reported that nitrate and ammonium fluxes out of the sediments are zero or very low at the same stations. To place the DON fluxes in the context of the total benthic nitrogen budget of the St. Lawrence system, we compared the N loss rates by sediment denitrification reported by Thibodeau et al. (2010), to the benthic DON fluxes estimated in this study. Observed DON fluxes account for 30 % to 64 % of the total benthic denitrification (including nitrification–denitrification coupling), as estimated by Thibodeau et al. (2010) from porewater nitrate gradients (Table 1). The extrapolation of the DON fluxes presented here (average 310 $\mu mol\,m^{-2}\,d^{-1}$) to the total sediment surface area of the Laurentian Channel between Sta. 23 and 16 ($\sim 35\,700\,km^2$) suggests that between 40 and $60 \times 10^6\,kg\,N\,yr^{-1}$ of DON are liberated annually from the sediments to the water column of the St. Lawrence Estuary and Gulf.

The DON fluxes that we present here are within the range of DON fluxes reported for various coastal marine environments (Bronk and Steinberg, 2008 and references therein), and we assume that the DON fluxes from the St. Lawrence Estuary and Gulf sediments can be considered representative for other continental shelf regions. Given a global shelf area of $\sim 30 \times 10^6\,km^2$, (Milliman, 1993) and an average DON flux of $1.58 \times 10^6\,g\,N\,km^{-2}\,yr^{-1}$ (equivalent to 310 $\mu mol\,m^{-2}\,d^{-1}$), we calculate that the global benthic DON flux from shelf sediments may result in a flux of approximately $48\,Tg\,N\,yr^{-1}$. This estimate is ~ 1.5 times higher than the estimated riverine DON input to the ocean ($\sim 35\,Tg\,N\,yr^{-1}$), and about one third to half of the total oceanic biological N_2 fixation (100–150 $Tg\,N\,yr^{-1}$; Codispoti et al., 2001). Although these estimates are still uncertain, they suggests that benthic DON fluxes are a key source of reduced N to

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the marine environment, representing an important component of the internal marine N cycle, at the ecosystem scale (e.g., the St. Lawrence system) and globally.

5 Summary and concluding remarks

In this study, we measured the DON and DOC concentrations of sediment pore water along the Laurentian Channel of the St. Lawrence Estuary, and determined benthic DOC and DON fluxes in the Lower Estuary and the Gulf of St. Lawrence. Our results suggest that both the sediment POM reactivity and the oxygen exposure time of organic particles after sedimentation influence the C/N ratio of hydrolysed DOM. The degree of C versus N element partitioning between the particulate and dissolved OM pools was greatest when fresh, reactive OM is hydrolyzed under less oxygenated conditions in the Lower St. Lawrence Estuary. Hydrolysis of less reactive OM under aerobic conditions in the Gulf of St. Lawrence appears to be less specific with regards to C and N containing components. The general validity of these results need to be further tested in other environments, and we cannot be certain whether the C/N fractionation between POM and DOM is mostly due to the hydrolysis step of the OM degradation or whether it is the result of the elemental fractionation during subsequent DOM mineralization. Nonetheless, our results have implications for the interpretation of bulk OM C/N ratios in sedimentary archives, as they confirm that variable preservation conditions and sedimentation regimes can result in variable early diagenetic C/N shifts that can compromise the use of C/N ratios of sedimentary OM as basic OM source indicator.

Both in the Lower Estuary and in the Gulf, DON contributes significantly to the overall dissolved N exchange between the sediments and the water column. Assuming that DOM fluxes determined for the St. Lawrence estuarine environment are representative of coastal shelf environments in general, extrapolation of our results reveals that DON fluxes from continental shelf represent an important component of the global N cycle. The fate and reactivity of the DON escaping the sediments is uncertain. Several studies have reported on the dynamic nature of DON in the ocean water column and

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the susceptibility of DON to bacterial enzymatic remineralization (e.g. Bastviken et al., 2004; Van Engeland et al., 2010). Given the discrepancy between relatively large marine benthic DON fluxes (this study) and the low DON concentrations in the ocean (e.g. Knapp et al., 2005; Bourbonnais et al., 2009), it is likely that sediment-derived DON undergoes rapid oxidation and adds substantially to the reactive water column N pool (Bastviken et al., 2004; e.g. Burdige, 2007; Van Engeland et al., 2010). Benthic DON fluxes therefore represent an important component of the internal N cycle, eventually supporting a significant fraction of ecosystem productivity.

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Table 1. Biogeochemical parameters of sediments in the Estuary and Gulf of St. Lawrence.

Station	OET[(B),1]	OPD[(B),2]	O_2 flux[(A)]	%N[(B)]	$\%C_{org}^{(B)}$	C_{org} flux	Nitrate flux[(A)]	Tot. Nitrate reduction [(A)]	CI[3]	DI[4]
I.D.	(yr)	(cm)	($\mu mol\,m^{-2}\,d^{-1}$)	(dry weight sediment)		($mg\,C_{org}\,m^{-2}\,d^{-1}$)	($\mu mol\,m^{-2}\,d^{-1}$)			
25	1.2	0.64	−6410	0.13	1.31	N.D.	−450	−870	0.63	−0.40
23	1.7	0.92	−4300	0.17	1.62	471 to 932[(C)]	−580	−640	0.66	−0.41
22	N.D.	N.D.	N.D.	0.15	1.57	573[(D)]	N.D.	N.D.	0.69	−0.53
21	6.6	1.46	−3220	0.18	1.63	N.D.	−250	−510	0.65	−0.48
20	N.D.	N.D.	N.D.	0.18	1.56	~ 22[(E)]	N.D.	N.D.	0.7	−0.50
19	7.7	1.82	−3750	0.19	1.52	66 to 160[(F)]	N.D.	−540	0.74	−0.63
18	13.6	1.56	−4950	0.2	1.59	~ 19[(E)]	−130	−660	0.77	−0.68
Anticosti	N.D.	1.53	−4360	0.26	2.19	N.D.	N.D.	−630	0.71	−0.55
16	N.D.	N.D.	N.D.	0.25	1.85	~ 22[(E)]	N.D.	N.D.	0.82	−1.02

Data from: (A) Thibodeau et al. (2010), (B) Alkhatib et al. (2012a), (C) Silverberg et al. (1987), (D) Colombo et al. (1996), (E) Muzuka and Hillaire-Marcel (1999), (F) Silverberg et al. (2000).

[1] OET: Oxygen exposure time.

[2] OPD: Oxygen penetration depth.

[3] CI: Chlorin index indicates OM reactivity (Schubert et al., 2005). The CI scale ranges from 0.2 for pure chlorophyll to approximately 1 for highly degraded OM.

[4] DI: Degradation index indicates OM reactivity (Dauwe et al., 1999). DI scores for fresh phytoplankton and sediment trap material vary between 1 and 1.5, while coastal and ocean margin sediments have scores between –1 for extensively degraded materials and 1 for relatively reactive OM.

N.D.: not determined.

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Table 2. DOC and DON fluxes at several locations along the Laurentian and Anticosti Channels. DON flux was calculated from both WCS and Rhizon membrane pore water samples. The average DON flux is used for the calculation of flux ratios, as well as % DON flux relative to nitrate fluxes and the total denitrification rates (from Thibodeau et al., 2010).

Sta. ID	DOC flux (WCS)	DON flux (Rhizon)	DON flux (WCS)	Av. DON flux	DON flux/ NO_3^- flux	DON flux/ Tot. Nitrate reduction
	($\mu mol\, m^{-2}\, d^{-1}$)					
Sta. 25	2150	440	420	430	0.95	0.49
Sta. 23	2120	N.D.	350	350	0.60	0.55
Sta. 22	2230	260	340	300	N.D.	N.D.
Sta. 21	2270	320	330	330	1.30	0.64
Sta. 20	1950	160	260	210	N.D.	N.D.
Sta. 19	2080	300	260	280	N.D.	0.52
Sta. 18	1430	170	230	200	1.54	0.30
Sta. 16	1310	110	N.A.	110	N.D.	N.D.
Anticosti	3850	260	290	270	N.D.	0.43

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Table 3. Comparison of calculated benthic DON and DOC fluxes along the Laurentian Channel and Anticosti Channel with benthic DON and DOC fluxes from other estuarine and coastal environments. All fluxes (in $\mu mol\,m^{-2}\,d^{-1}$) are from the sediment to the water column.

Site	DON flux	DOC flux	Reference
Laurentian Channel, Canada	110–430	1300–2150	This study
Anticosti Channel, Canada	270	3850	This study
Chesapeake Bay, USA, Site M3	60–320	670–1650	Burdige and Zheng (1998)
Chesapeake Bay, USA, Site S3	40–550	200–850	Burdige and Zheng (1998)
Laholmm Bay, Sweden	100–400	–	Enoksson (1993)
Porcupine Abyssal Plain, NE Atlantic	100	–	Brunnegård et al. (2004)
Svalbard, Norway	950	–	Blackburn et al. (1996)
Temperate Australian Estuaries	–	up to ~ 50 000	Maher and Eyre (2010)
Knebel Vig, Denmark	3900	–	Lomstein et al. (1998)
Mexican Margin	–	250–400	Holcombe et al. (2001)
California continental margin	–	100–3100 ± 2700	Burdige et al. (1999)

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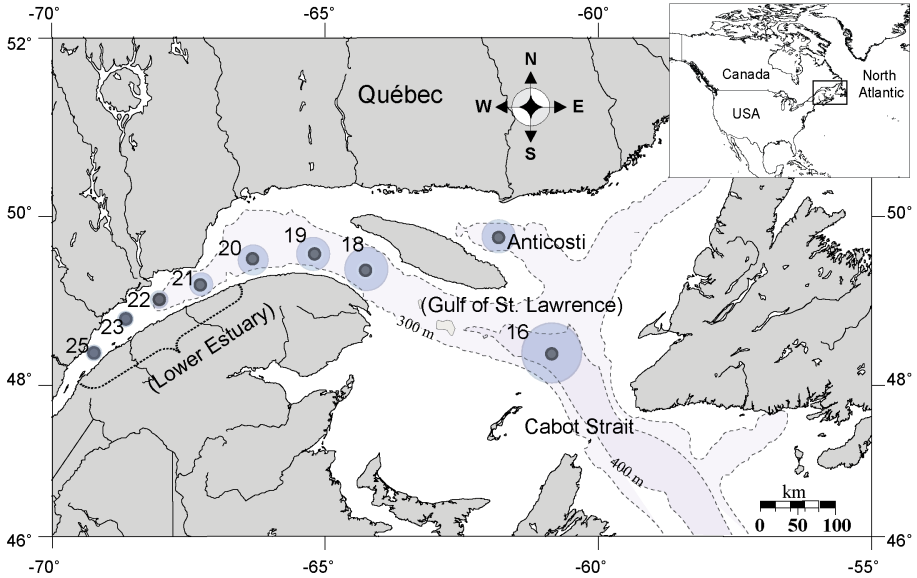

Fig. 1. Sampling locations in the St. Lawrence Estuary and Gulf. Bathymetric contours outline the Laurentian Channel along the 300 and 400 m isobaths. The size of shadowed circles around study sites denotes the relative dissolved O_2 concentrations (see Table 1 for absolute values).

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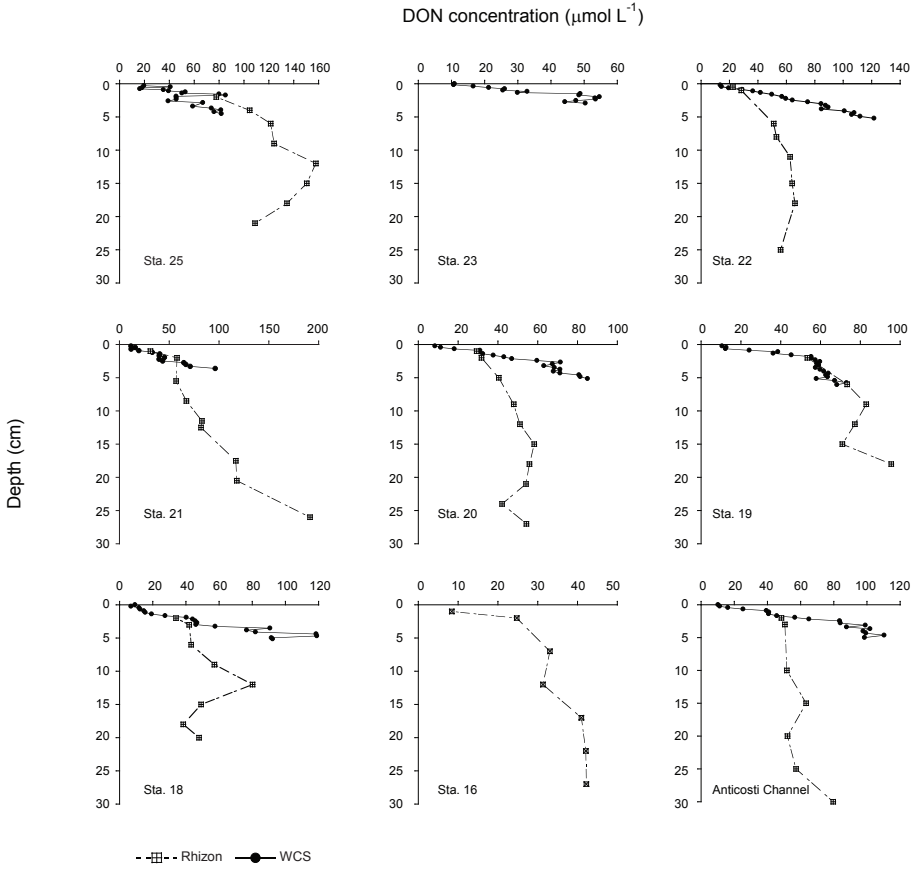

Fig. 2. Pore water profiles of dissolved organic nitrogen (DON) in the Lower Estuary and the Gulf of St. Lawrence. Data for both whole core squeezing (WCS) and the Rhizon membrane samples are shown.

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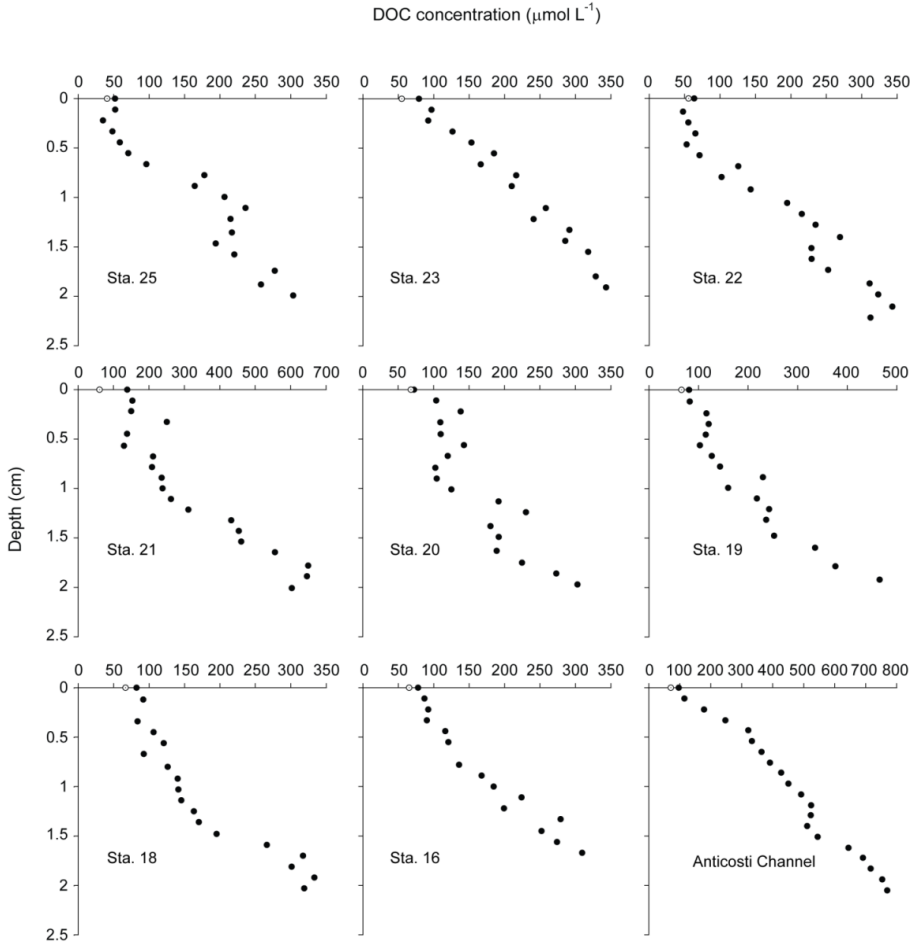

Fig. 3. Pore water profiles of dissolved organic carbon (DOC) in the Lower Estuary and the Gulf of St. Lawrence. Open circles on the upper x-axes represent bottom-water DOC concentrations.

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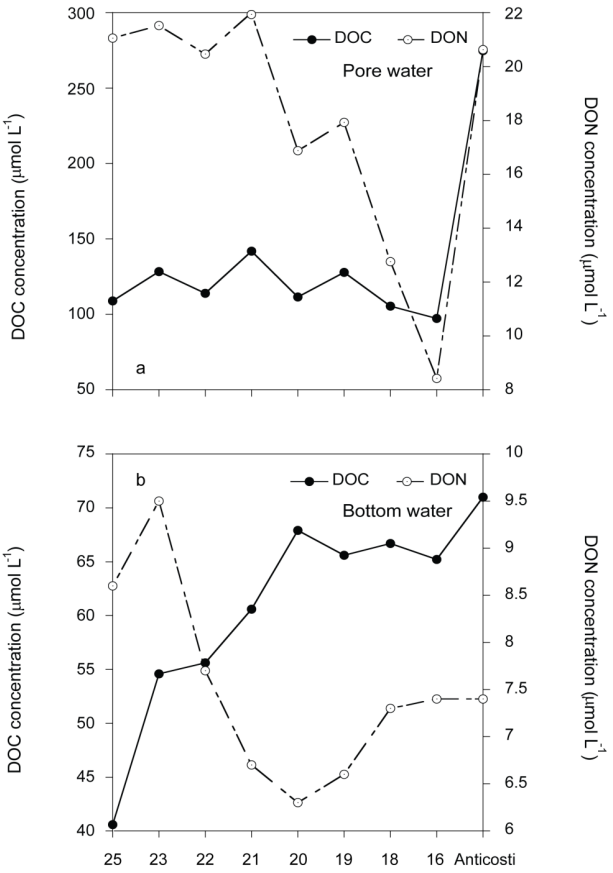

Fig. 4. Dissolved organic carbon (DOC) on the left y-axis and dissolved organic nitrogen (DON) on the right y-axis concentrations ($\mu mol\,L^{-1}$) in: **(a)** pore waters (average of the first cm), **(b)** overlying bottom water along the lower Estuary and Gulf of St. Lawrence.

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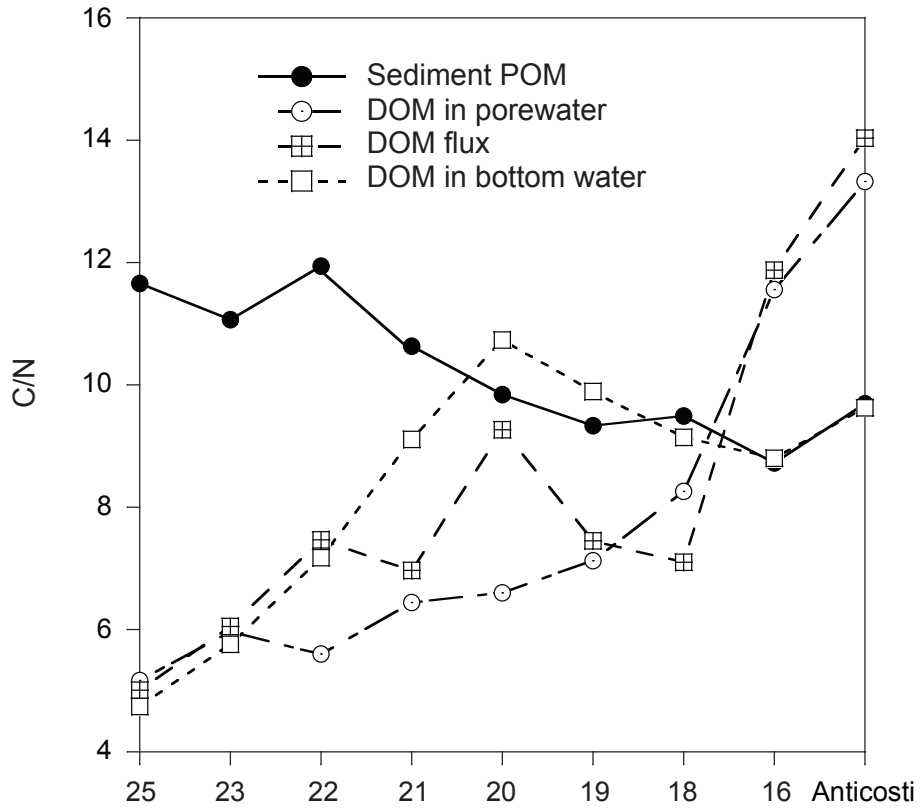

Fig. 5. Molar C/N ratios in sedimentary particulate organic matter (POM), pore water dissolved organic matter, and sediments overlying bottom water along the Lower Estuary and Gulf of St. Lawrence.

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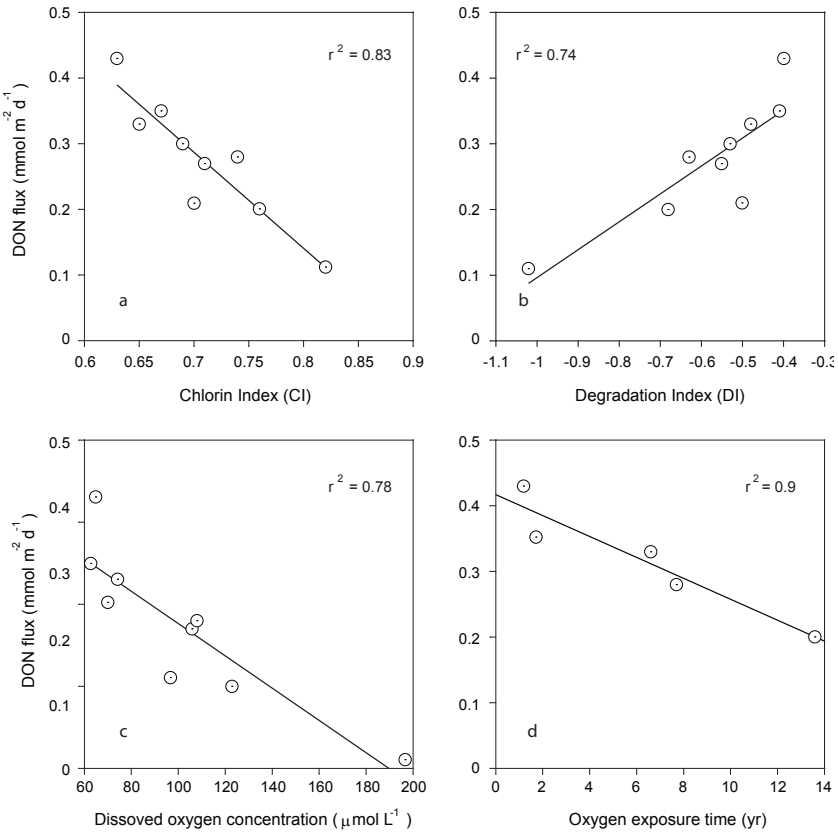

Fig. 6. Correlation between the dissolved organic nitrogen (DON) fluxes and reactivity indices: **(a)** the chlorin index (CI), **(b)** the degradation index (DI), as well as **(c)** dissolved oxygen, and **(d)** oxygen exposure time in sediments along the St. Lawrence Estuary and the Gulf of St. Lawrence. See caption of Table 1 for details on CI and DI.

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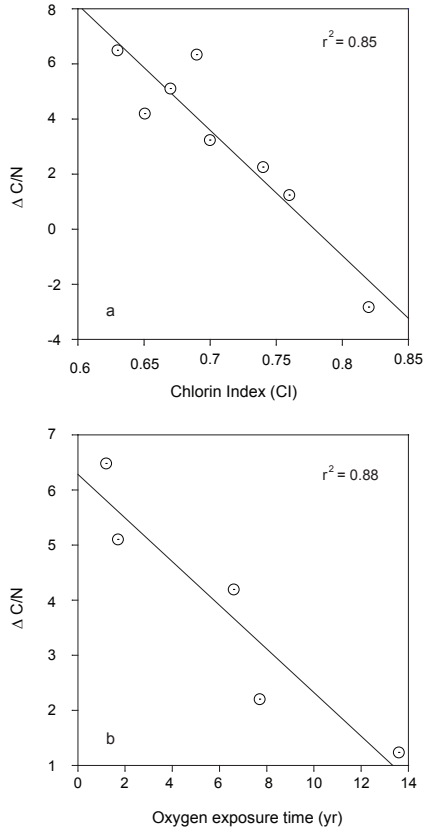

Fig. 7. Correlation between the differences between the molar C/N ratios in sedimentary particulate organic matter (POM) and pore water dissolved organic matter (ΔC/N) and **(a)** the chlorin index (CI) and **(b)** oxygen exposure time in sediments along the St. Lawrence Estuary and the Gulf of St. Lawrence. See caption of Table 1 for details on CI.

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