The Cycling of Organic Carbon in the St. Lawrence Estuary

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A Thesis in

The department of

Chemistry and Biochemistry

Presented in Partial Fulfillment of the Requirements

for the Degree of Master of Science (Chemistry) at

Concordia University

Montreal, Quebec, Canada

September 2015

CONCORDIA UNIVERSITY
School of Graduate Studies

This is to certify that the thesis prepared

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Entitled: The Cycling of Organic Carbon in the St. Lawrence Estuary

and submitted in partial fulfillment of the requirements for the degree of

Master of Science (Chemistry)

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Abstract

The St. Lawrence River is one of the most important in the world in terms of water discharge to the global ocean. Several studies have been made to describe the environment, from its water dynamics to the activity of its phytoplankton communities. Despite this, a thorough characterization of the St. Lawrence Estuary (SLE) with respect to its organic carbon (OC) sources and sinks has not been done, and shortcomings pertaining to information needed for a comprehensive OC budget for the SLE have not been identified. Using samples collected over several sampling missions since 2003, quantitation and characterization of organic matter (OM) has been performed on dissolved, particulate and sedimentary samples. Measurements, using a DOC-analyzer coupled to an isotope mass spectrometer (IRMS), and elemental analyzer (EA) coupled to an IRMS, have shown that dissolved OC (DOC) and particulate OC (POC) concentrations decreased closer to the St. Lawrence Gulf. In addition, DOC, POC and sedimentary OC (SOC) samples closer to the gulf showed ^{13}C enrichment in, and a decrease in C/N atomic ratios in particulate samples. Parallel to these trends, an increase in Fe-OC association was observed. In this thesis, major sources and sinks have been identified and a gradual shift from terrestrial to marine OM characteristics have been observed in carbon stable isotope signatures, C/N atomic ratios and degree of Fe-OC association. Furthermore, a simple budget was constructed to help direct future research efforts towards a more complete understanding of the SLE.

Acknowledgements

To try to thank every person that has helped me in this achievement would be an exercise in futility, as there are just too many. Therefore I would like to start with a general “thank you” to everyone who has helped me, supported me and otherwise contributed to shaping me into the person I am today.

Having said that, there are some notable individuals whose presence and support have directly affected me since the beginning of my graduate studies and that I want to thank specifically. Yves, my supervisor, has had the most direct influence on me these last few years. Always ready to offer counsel, Yves has guided me through my master’s project by suggesting new avenues to explore and occasionally letting me stumble and learn from those mistakes. For that, Yves, I thank you. I would also like to thank my supervisory committee, Dr. John Capobianco and Dr. Cameron Skinner, for their support and guidance. I would like to thank my fellow lab members, past and present, for the type of support that can only be offered by others in the same position at the same time, so thank you Andrew Barber, Amanda Gabriel, Anja Moritz, Azadeh Joshani and Karine Lalonde for making LEGO lab completely unique.

A very big “thank you” to my friends and family for their unending support and patience during my stay at Concordia, you have helped keep things in perspective. Specifically, thank you mom and dad for watching me do my own thing during university without judgement and offering unconditional support through it all. Finally, thank you Caroline, my love. You have brightened every day and have always been supportive of me. It has been just over one year since we tied the knot, and here’s to countless more. I dedicate this thesis to you.

Contribution of authors

Sample collection was performed by numerous students working with Dr. Gélinas over 10 years. All DOC and $\delta^{13}C$ analyses of dissolved samples collected prior to 2007 were performed by Robert Panetta during his PhD at Concordia University, and all $\delta^{13}C$ analyses performed on dissolved samples collected thereafter were performed by Karine Lalonde during her PhD at Concordia University.

Table of Contents

List of Figures viii

List of Tables x

List of Acronyms xi

1 General introduction 1

1.1 Global Carbon Cycle 1

1.2 Estuaries 3

1.2.1 Carbon cycle in aquatic systems 3

1.2.2 Hypoxia in aquatic systems 4

1.2.3 St. Lawrence Estuary 6

1.3 Stable Isotopic Signatures of Organic Carbon 10

1.4 Historical Review 10

1.5 Scope of the Thesis 16

2 Materials and Methods 17

2.1 Sampling 17

2.2 Carbon Stable Isotopic Signature 18

2.3 EA-IRMS 18

2.4 DOC-IRMS 19

2.5 Iron Reduction Method 19

3 Results 20

3.1 Dissolved Organic Matter 20

3.2 Particulate Organic Matter 27

3.3 Sedimentary Organic Matter 35

4 Discussion 41

4.1 Dissolved Organic Matter 41

4.1.1 General trends and important processes 41
4.1.2 DOM in the USLE 42
4.1.3 DOM in the LSLE 43
4.2 Particulate Organic Matter 46
4.2.1 General trends 46
4.2.2 POM in the USLE 46
4.2.3 POM in the LSLE 48
4.2.4 The role of iron 49
4.3 Sedimentary Organic Matter 50
4.4 Preliminary Budget and Comparison to Similar Systems 53
5 General Conclusion 58
References 60
Appendix A: Raw Data 64

List of Figures

Figure 1.1: The St. Lawrence Estuary. Adapted from the Fisheries and Oceans Canada (2014) 6

Figure 1.2: Thermocline of the water column from Station 23 (300 km from Quebec City) showing the three strata based on the water temperature: surface layer (lightest shade); cold intermediate layer (CIL, intermediate shade), the part of the water column below 1°C; deep layer (darkest shade) 7

Figure 1.3: Estuarine water circulation in the St. Lawrence Estuary. Image from Merriam and Amos

(2006) 7

Figure 1.4: The St. Lawrence Gulf and source waters. The black arrow represents the warmer, saltier North Atlantic Central waters, and the gray arrow represents the cooler, fresher Labrador Current waters. Adapted from Fisheries and Oceans Canada (2014) 9

Figure 2.1: Map with the geographical location of all sampling stations of the Upper and Lower Estuary

..... P.17

Figure 3.1: DOC concentration in the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average DOC concentration over 7 sampling missions, starting at Quebec City (0 km) and moving away, seaward; (b) Average DOC concentration values for all Lower Estuary samples (6 sampling missions) (b) The shaded section in (a) is the same data series as plot (b)..... 21

Figure 3.2: The $\delta^{13}C$ stable isotope signatures measured on DOC samples from the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average $\delta^{13}C$ of DOC over 7 sampling missions, starting at Quebec City (0 km) and moving away, seaward; (b) Average $\delta^{13}C$ of DOC for all Lower Estuary samples (6 sampling missions). The shaded section in (a) is the same data series as plot (b) 23

Figure 3.3: Relationship between $\delta^{13}C$ DOC and DOC concentration: concentration and $\delta^{13}C$ for water samples from the surface (typically between 0 - 25 m) layer of each station of the Estuary and Gulf from all 7 sampling missions. 24

Figure 3.4: Depth profile of DOC concentrations. All Lower Estuary stations from (a) the 2013 sampling mission, and (b) from the 2011 sampling mission 25

Figure 3.5: Depth profiles of DOC concentrations at station 23 from sampling missions in 2010, 2011 and 2013 26

Figure 3.6: POC concentration in the surface (typically between 0 - 25m) layer along the entire St. Lawrence Estuary and Gulf. (a) Average POC concentration over 7 sampling missions, starting at Quebec City (0 km) and moving away, seaward; (b) Average DOC concentration values for all Lower Estuary samples (6 sampling missions). The shaded section in (a) is the same data series as plot (b) 28

Figure 3.7: The $\delta^{13}C$ stable isotope signatures measured on POC samples from the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average $\delta^{13}C$ of POC over 7 sampling missions, starting at Quebec City (0 km) and moving away, seaward; (b) Average $\delta^{13}C$ of POC for all Lower Estuary samples (6 sampling missions). The shaded section in (a) is the same data series as plot (b) 29

Figure 3.8: The carbon to nitrogen atomic ratios (C/N) measured on POM samples from the surface (typically between 0 - 25 m) layer along the entire St. Lawrence Estuary and Gulf. (a) Average C/N of POM over 7 sampling missions, starting at Quebec City (0 km) and moving away, seaward; (b) Average C/N of POM for all Lower Estuary samples (6 sampling missions). The shaded section in (a) is the same data series as plot (b) 31

Figure 3.9: Relationship between $\delta^{13}C$ POC and POM C/N atomic ratio: $\delta^{13}C$ and atomic ratios for particulate samples from the surface layer (typically between 0 - 25 m) of each station of the Estuary and Gulf from all 7 sampling missions 32

Figure 3.10: Depth profiles of POC concentration from the 2010 sampling mission at all Lower Estuary stations sampled 33

Figure 3.11: Depth profiles for (a) the isotopic signatures and (b) C/N atomic ratios of POC from all the Lower Estuary stations sampled in 2013 34

Figure 3.12: OC associated to iron in the POM of the LSLE (a) as a percentage of total OC and (b) as an atomic ratio 35

Figure 3.13: Average stable isotope signature of SOC moving seaward from surface sediments (top 4 cm with a resolution of 1 cm; n=4) collected during the 2006 and 2007 sampling missions 36

Figure 3.14: Average C/N atomic ratio of SOM moving seaward from surface sediments (top 4 cm with a resolution of 1 cm; n=4) collected during the 2006 and 2007 sampling missions 37

Figure 3.15: Sedimentary depth profiles of carbon content from the 2007 sampling mission at all Lower Estuary stations sampled 38

Figure 3.16: Depth profiles for (a) the isotopic signatures and (b) the C/N atomic ratios of sediments from the 2007 sampling mission at all Lower Estuary stations sampled 39

Figure 3.17: Relationship between $\delta^{13}C$ SOC and SOM C/N atomic ratio: average $\delta^{13}C$ and atomic ratios for the sediment cores of each station sampled during the 2007 sampling mission 40

List of Tables

Table 4.1: Water flows from sources to the St. Lawrence Estuary and Gulf with their respective DOC and POC concentrations. a) Data from Gingras, 1997; b) Data from Benke and Cushing, 2005; c) Data from Hélie and Hillaire-Marcel, 2006; d) Data from Thomas, 2013. *Calculated by subtracting Saguenay flow from combined flow of USLE and Saguenay (16 000 m^3/s). ** Calculated by multiplying the provided suspended matter concentration (67.54 mg/L) by average OC content observed in Saguenay (2.70 ± 1.16 %) 54

List of Abbreviations

DIC: Dissolved Inorganic Carbon

DOC: Dissolved Organic Carbon

DOM: Dissolved Organic Matter

EA: Elemental Analyzer

IC: Inorganic Carbon

IRMS: Isotope Ratio Mass Spectrometer

LSLE: Lower St. Lawrence Estuary

OC: Organic Carbon

OM: Organic Matter

PN: Particulate Nitrogen

POC: Particulate Organic Carbon

POM: Particulate Organic Matter

SLE: St. Lawrence Estuary

SPM: Suspended Particulate Matter

SOC: Sedimentary Organic Carbon

SOM: Sedimentary Organic Matter

TOC: Total Organic Carbon

USLE: Upper St. Lawrence Estuary

1 General Introduction

In biogeochemistry, cycles describe the circulation of molecules or elements across the biotic and abiotic "spheres" of the Earth (*e.g.* biosphere, atmosphere, and geosphere). These cycles allow us to understand how the molecules or elements move from one reservoir, or pool, to another (Schlesinger, 1991). Consider the water cycle: lakes and oceans form obvious reservoirs, keeping water sequestered from broader circulation for various amounts of time, but they are not the only ones. Water is also found in the atmosphere and in ice caps as well as in all living organisms. These reservoirs are interconnected through numerous processes such as evaporation, ingestion by living organisms and precipitation. With an understanding of the relative importance of individual processes in biogeochemical cycles, it becomes possible to model these cycles and predict the outcome of a number of hypothetical scenarios, and ultimately help in decision making regarding policies or large projects. Coming back to the example of the water cycle, a good understanding of the effect of precipitation on a river system could help the local communities strategically build dams and levees. These biogeochemical cycles are deeply intertwined and changes to one cycle often affect several other cycles. This leads to very complex and convoluted schemes that are exceedingly difficult to study. For this reason, biogeochemical cycles are often treated as separate and isolated cycles that are then to be integrated with other cycles by studying processes linking these elements or molecules.

1.1 Global Carbon Cycle

Some biogeochemical cycles seem particularly relevant considering the increased popular awareness concerning the environment, and few cycles seem more relevant than the carbon cycle. Today's society is one where individuals are becoming concerned with their "carbon footprint" and the effect of anthropic activity on the atmospheric pool of carbon. Since the industrial revolution, carbon dioxide

(CO_2) concentrations in the atmosphere have been on the rise. This increase in CO_2, a known greenhouse gas, has been associated to climate change (IPCC 2013).

This pool represents only a small portion of the global carbon cycle, which describes the numerous processes, sources and sinks that affect carbon, both organic and inorganic, on a planetary scale. The distinction between organic and inorganic carbon is one based on the redox state of the carbon in question: when discussing the fully oxidized forms of carbon (oxidation state +4), it is deemed to be inorganic carbon (IC), whereas any carbon that is reduced (oxidation state +3 or less) is referred to as organic carbon (OC). In the global biogeochemical cycle of carbon, inorganic carbon is fixed into organic matter (OM) by primary producers, organisms capable of photosynthesis such as plants and algae. This freshly produced OM is then consumed by heterotrophic organisms by the process of respiration, altering some of it and returning some inorganic carbon to the environment. As carbon moves through the biosphere, it gets altered and reworked by various organisms and is ultimately remineralized to IC or buried in soils or sediments. In soils, OC can be taken up by new primary producers, or transported to aquatic systems by water runoff. In sediments, OC undergoes diagenesis, alteration by local organisms following sediment deposition, and eventual burial on geological timescales by subduction. All the mentioned pools sequester carbon for various lengths of time. Of these, sediments offer the only link between the processes occurring outside the Earth's mantle and the Earth's mantle itself, and as such are the only sink acting on geological timescales. This long term sink, namely sedimentary rocks, marine and lacustrine sediments, has been estimated to hold over 22,000 times more carbon than the atmosphere (Hedges and Keil 1995). Recent estimates of marine sediments and OC sequestered therein suggest that this sink accounts for approximately 7.8×10^{22} g of carbon (Mackenzie *et al.*, 2004). The importance of this sink, and its ultimate link to atmospheric CO_2 and climate change, emphasizes the necessity of studying the way carbon behaves in aquatic systems in general.

1.2 Estuaries

The areas of the world where sediment sequestration and recycling and sequestration of OC are most important are continental shelves and margins (Macdonald *et al.*, 1998 and references therein). As such, these are areas of particular interest when deconvoluting the carbon cycle. Estuaries are the transition systems between inland freshwater systems and coastal saline systems, which are typically areas of strong sedimentation (where sedimentation rates are high). Coastal areas significantly impact long-term sequestration of carbon and estuarine systems leading to these costal environments can have a serious effect on the carbon transported to these coastal sediments, it is therefore essential to study and understand these estuaries (Hedges *et al*., 1997). In these systems, fresh waters from rivers mix with salt waters from the coast and gradually become more and more saline. Differences in temperature and salinity of the water with increasing depth typically leads to stratification of the water column, or vertical separation of water masses based on density, which in turn severely limits vertical mixing. There are a number of estuarine mixing models, each with its own physicochemical characteristics determining the stratification of the water column (Kennish, 1986). All these models feature a seaward current at the surface, bringing water from tributaries to the ocean, and a landward current at depth, bringing oceanic waters to mix with waters of this surface current. These estuarine systems lead to coastal environments and can have an effect on coastal sedimentation, but they can also be areas of important sedimentation and important players in the global carbon cycle.

1.2.1 Carbon cycle in aquatic systems

In aquatic systems, carbon is found in a few forms: dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC) and sediment organic carbon (SOC). DIC refers to dissolved carbon dioxide ($CO_{2(d)}$) as well as all species of the carbonate system, namely carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). POC is operationally defined as all organic carbon molecules that are retained on a filter of 0.45 µm pore size. In contrast, DOC is defined as the organic

carbon molecules of a continuum of molecular weights found in the filtrate. SOC is the organic carbon found associated with the sediment samples from these systems.

Several processes affect the various pools of carbon in estuaries and are therefore involved in estuarine carbon cycling. To start, the OC found in these estuaries is imported from various tributaries and the estuaries themselves export OC to coastal environments. During transit in the estuaries, OC is affected by production, respiration, sedimentation, UV-oxidation, DOC coagulation, POC degradation, and sediment resuspension (McCallister *et al.* 2006, Helms *et al.* 2013, Lalonde *et al.* 2014). The mechanism by which DOC and POC is imported to, and exported from, estuaries is advection, or transport due to bulk motion of the carrying waters. Production refers to the fixation of CO_2 by primary producers such as algae. This is the main process that consumes dissolved inorganic carbon (DIC) in marine systems, adding to the POC pool. Respiration processes are in competition with production, remineralizing DOC, POC and SOC to DIC via biotic and abiotic reactions. Another process that affects OC in estuaries is UV-oxidation, by which DOC exposed to UV radiation is decomposed and, to some extent, remineralized back to CO_2. The DOC and POC pools are interconnected, with DOC coagulation increasing the POC pool at the expense of the DOC pool, and the effects of POC degradation being opposed to coagulation, as well as contributing to the DIC pool. As particles sink in the water column and are deposited on the sediment bed, the process of sedimentation adds to the SOC pool at the expense of the POC pool. Under the effect of deep eddies, the counter-current swirling motion of sea water as it passes over sediments, SOC can return to the bottom of the water column as POC by resuspension.

Recently, the importance of iron has been demonstrated in preserving OC in sediments, with an average of approximately 20% of OC in sediments being associated to reactive iron species (Lalonde *et al.*, 2012). Iron and OC form associations in the sediments, but also in the water column (Helms *et al*., 2013), affecting the transport of OC to the sediments and long term preservation of OC in these sediments.

1.2.2 Hypoxia in aquatic systems

Because physical mixing is highly limited in strongly stratified estuaries, bottom waters are often isolated from shallower water masses and oxygen sources. Thus, these systems can be particularly susceptible to hypoxia. Hypoxia refers low concentrations of dissolved oxygen. In aquatic systems, it is deemed severe hypoxia when the oxygen concentration falls below 62.5 µmol/L (or 1 mg/L), a point at which most animal life cannot be sustained. If the concentration falls to 31.25 µmol/L (or 0.5 mg/L), the system is said to be anoxic according to the USGS definition of anoxic waters (USGS, 2006). Although there are a number of mechanisms by which hypoxia can develop in aquatic environments, one thing is necessary for hypoxia to occur: oxygen consumption must exceeds the oxygen supply. Hypoxia can occur via natural means or as a result of anthropic activity. In the case of naturally occurring hypoxic regions, these are systems with very limited vertical mixing and therefore very restricted oxygen supply (limited to diffusion) that, when coupled with typical oxygen consumption, can lead to low oxygen concentration and hypoxia. In environments where hypoxia is caused by anthropic activity, nutrients which would typically limit phytoplankton growth, such as nitrates and phosphates, are introduced to the surface of the system and cause eutrophication, an intense bloom of phytoplankton production. These blooms inevitably lead to an increased flux of biomass to the deep waters which can then be respired in this deep environment, consuming oxygen and leading to hypoxia.

1.2.3 St. Lawrence Estuary

The aquatic system of particular interest in this study is the St. Lawrence, more specifically its lower estuary. The St. Lawrence River (Figure 1.1), one of the world's top 15 largest rivers in terms of annual water flux, flows from the Great Lakes to Quebec City. At Quebec City, it starts mixing with salt water and is named the St. Lawrence Estuary (SLE), which is the section of the system between Quebec City and Pointe-des-Monts. This estuary is further subdivided into two sections, the upper estuary (USLE) between Quebec City and Tadoussac, where the salinity of the system increases from typically riverine

(around 0.1 on the practical salinity scale) to values that are closer to typically marine waters (around 30 on the same scale), and the lower estuary (LSLE) where salinity values are less variable and which features the Laurentian channel, a deep underwater trench that spans the entire lower estuary, well into the gulf. Finally, before exporting waters into the ocean, the St. Lawrence system flows into the Gulf of the St. Lawrence, a semi-enclosed sea bordered by Quebec and Labrador to the North, Newfoundland to the East, and Atlantic Canada to the South and West.

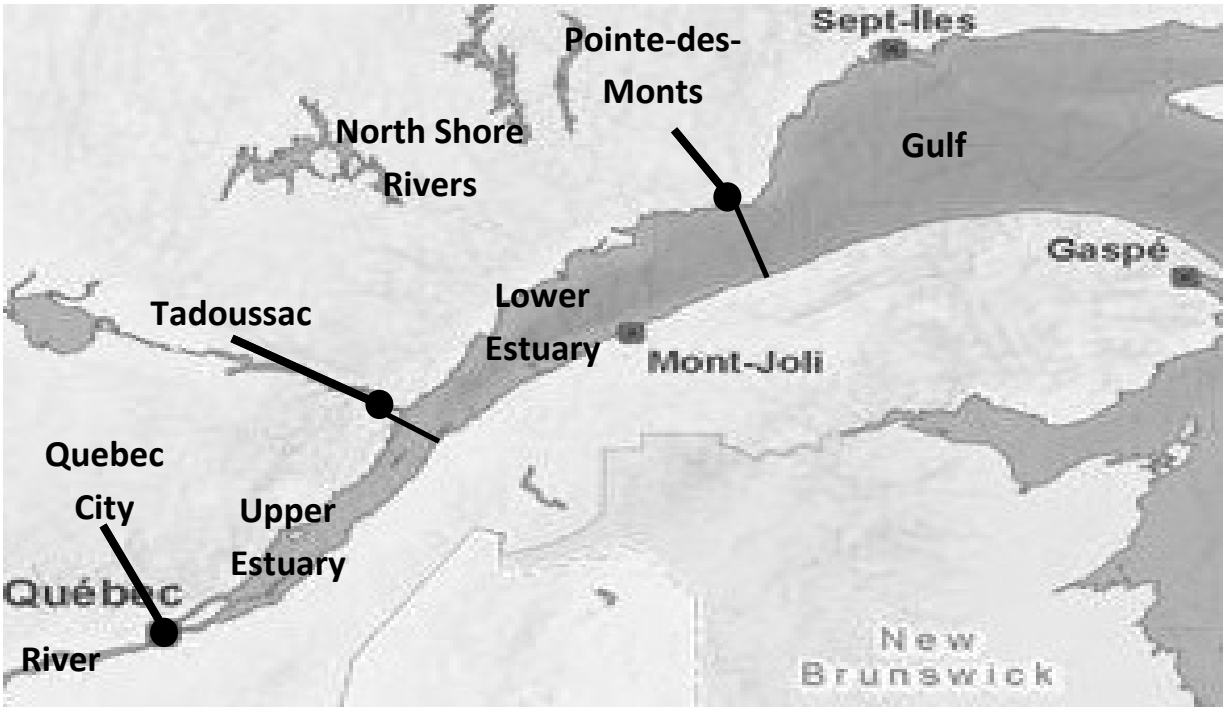

Figure 1.1. The St. Lawrence Estuary. Adapted from the Fisheries and Oceans Canada (2014).

In the St. Lawrence system, water flows along the river from the Great Lakes to Quebec City, where it begins to mix with salt water and gradually becomes more and more saline as the estuary flows between Quebec City and Tadoussac. At Tadoussac, the Saguenay River and the upper estuary meet, forming the surface current of the lower estuary. In the lower estuary, the water column features 3 distinct masses (Gilbert *et al*. 2005, Dufour and Ouellet 2007): the surface layer, water flowing seaward towards the

Gulf, the cold intermediate layer (CIL), a slow, landward moving mass of water that is defined as the portion of the water column at or below 1°C, and the deep layer, a landward moving water mass that is faster than the CIL (Figure 1.2). It is at Tadoussac that the head of the Laurentian Channel is found, where the deep landward current meets the strong slope of this channel head and upwells to mix with surface waters. As the surface current of the lower estuary travels seaward, rivers from the North Shore flow into the St. Lawrence system (Figure 1.3). At Pointe-des-Monts, the lower estuary flows into the Gulf of the St. Lawrence. In the Gulf, the parent waters of the deep layer of the lower St. Lawrence estuary mix in the Laurentian Channel and begin their landward transit.

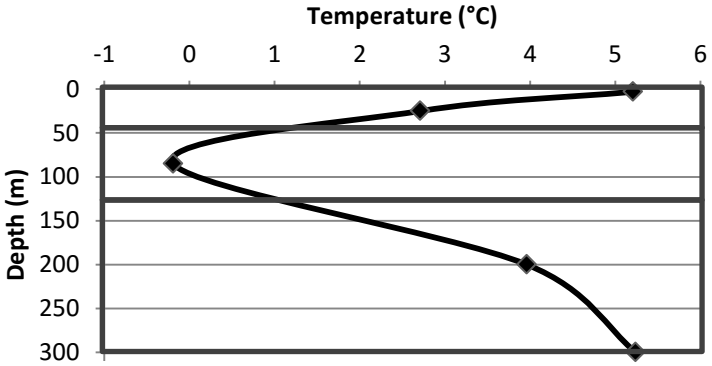

Figure 1.2. Thermocline of the water column from Station 23 (300 km from Quebec City) showing the three strata based on the water temperature: surface layer (0 - 50 m); cold intermediate layer (CIL, 50 - 125 m), the part of the water column below 1°C; deep layer (125 - 300 m).

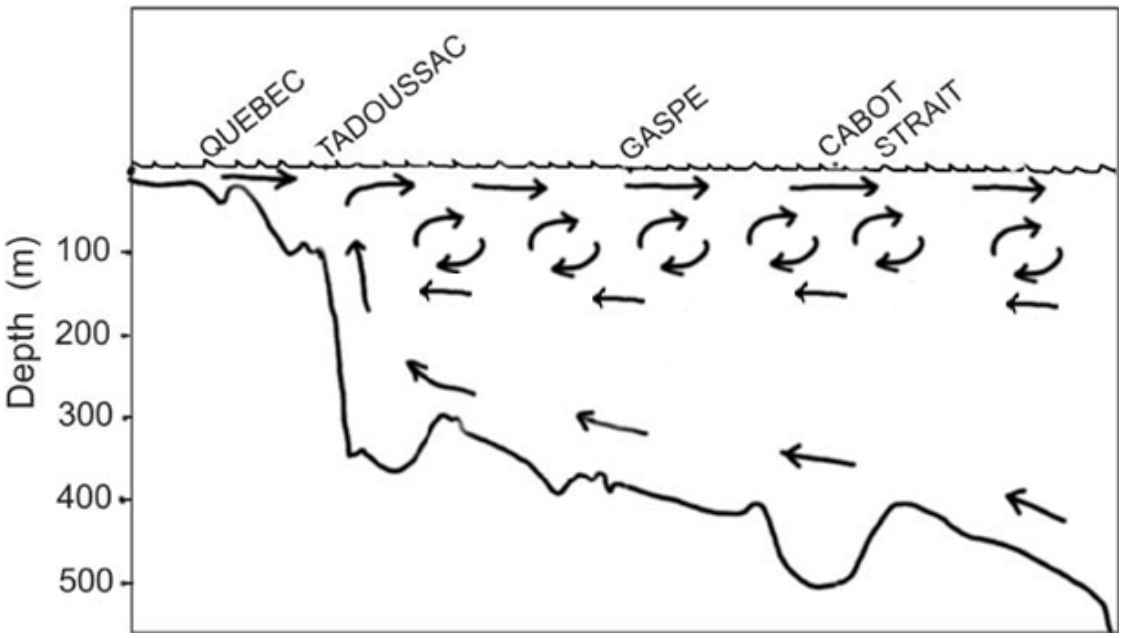

Figure 1.3. Estuarine water circulation in the St. Lawrence Estuary. Image adapted from Merriam and Amos (2006).

Being such a large system with an important water contribution to the global ocean, it stands to reason that its carbon cycle is also of global importance and should therefore be investigated. Systems of this size affect OC distribution to the coastal ocean and have a significant impact on the global biogeochemical cycle (Milliman and Farnsworth, 2011). Furthermore, the St. Lawrence system is of interest for phenomena that have been observed historically, namely eutrophication and a reduction in deep water oxygen concentration that has been observed since the 1930's (Gilbert *et al.*, 2005). Indeed, O_2 concentrations in the deep waters of the lower St. Lawrence Estuary have decreased from values of around 130 µmol/L in the 1930's to averages of less than the severe hypoxia threshold (62.5 µmol/L) in the 1980's and since then, oxygen concentrations have stabilized to this low level (Gilbert *et al.*, 2005). In 2005, Gilbert and collaborators determined that 50 - 66% of this observed decrease in oxygen concentration can be attributed to a change in proportion of source waters, with a gradually increasing contribution of North Atlantic Central waters, which are warmer, saltier and less oxygenated, at the expense of Labrador Current waters, which are colder, less salty and more oxygenated (Figure 1.4). This

leaves 33 - 50% of the oxygen depletion that could not be explained at the time. Since then, a number of studies have suggested that the remaining oxygen depletion could be attributed to eutrophication in the lower St. Lawrence Estuary (Thibodeau *et al*. 2006). However, since this historically observed oxygen depletion was accompanied by an increase in temperature, it has also been suggested the remaining 33 - 50% of the oxygen depletion might be at least in part due to increased oxygen demand due to increased bacterial activity in the water column and in the sediment (Gilbert 2005). A thorough understanding of carbon cycling in this system could be invaluable to understanding how anthropic activity affects the St. Lawrence system in general and specifically the hypoxic deep waters of its lower estuary.

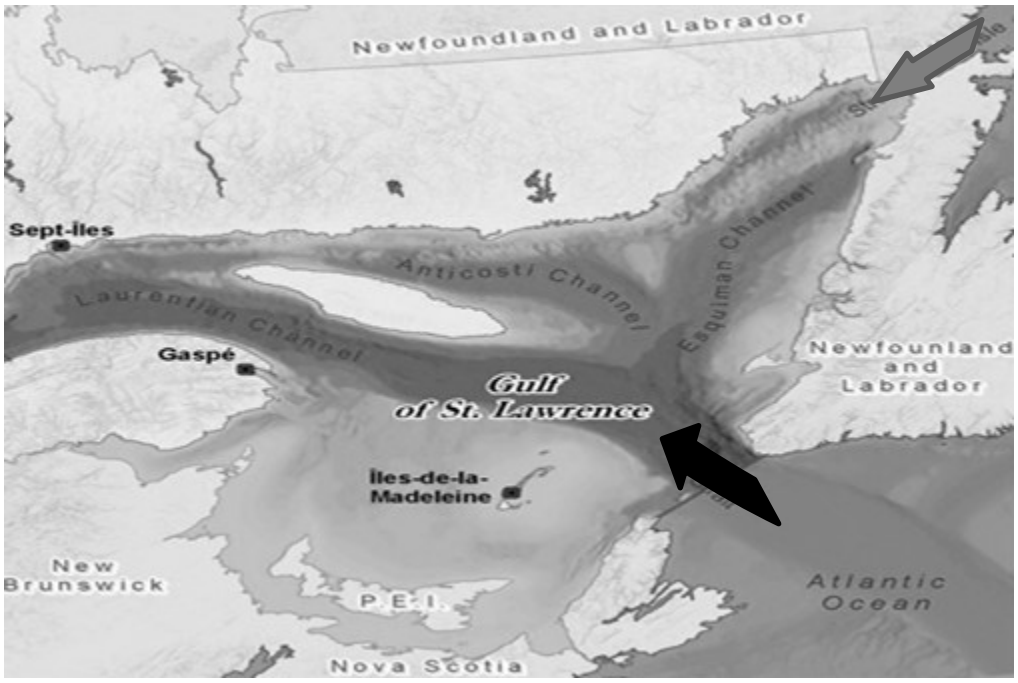

Figure 1.4. The St. Lawrence Gulf and source waters. The black arrow represents the warmer, saltier North Atlantic Central waters, and the gray arrow represents the cooler, fresher Labrador Current waters. Adapted from Fisheries and Oceans Canada (2014).

1.3 Stable Isotopic Signatures of Organic Carbon

Differences in OC source often leads to differences in C stable isotope composition. Because the source of inorganic carbon, and its isotopic content, is different between primary producers on land and at sea, differences arise in the isotopic signature of OC generated by these primary producers. Terrestrial primary producers fix their carbon from atmospheric CO_2, which has an average isotopic signature of -7‰ with respect to Vienna Pee Dee Belemnite (VPDB), the international reference standard. In contrast, oceanic primary producers, such as phytoplankton, fix their carbon from DIC, which has an average isotopic signature around 0‰. The difference in isotopic signatures between atmospheric CO_2 and DIC is due to the combustion of fossil fuels, which have been adding CO_2 that is depleted in ^{13}C to the atmospheric pool since the industrial revolution. Both terrestrial and marine primary producers fix CO_2using the enzyme Ribulose - 1,5-Bisphosphate Carboxylase/Oxygenase (RuBisCo), which leads to a ^{13}C fractionation, or preferential utilization of the ^{12}C isotope, of about -20‰ with respect to the starting CO_2. Because of the isotopic differences in the starting materials coupled with the fractionation due to RuBisCo, terrestrial OC has an isotopic signature between -27 to -30‰ whereas marine OC has an isotopic signature around -20‰ (Meyers 1994).

Carbon to nitrogen elemental ratios can be used in addition to the isotopic signature as a way to infer OM source. This is based on the fact that terrestrial plant matter is abundant in carbon-rich structural molecules, such cellulose and lignin, in addition to containing nitrogen-rich molecules, such as proteins. These latter proteins are the main component in the biomass of marine primary producers (Hedges *et al*., 2002). As such, OM from vascular land plants is considered to have a carbon to nitrogen elemental ratio greater than 20 whereas fresh marine OM from algae has a lower carbon to nitrogen ratio, typically between 4 and 10 (Meyers 1994).

1.4 Historical Review

In 1973, Pocklington described the composition of the particulate and sedimentary organic matter (POM and SOM) from the St. Lawrence Estuary and Gulf, as well as the Saguenay River. He reported that the percentage by mass of organic carbon (%OC) in sediments was highest in rivers and close to riverine sources, and lowest values found further away from important rivers. The C/N atomic ratios measured for these sediment samples were lowest for samples from the Gulf and highest for riverine samples, or samples with strong riverine input. In the analysis of POM, it was noticed that both POC and particulate nitrogen (PN) decreased in concentration with depth. Pocklington pointed out a direct correlation between concentration of POC and dissolved oxygen concentration throughout the sampling area. The C/N ratios measured in POM were typically higher at depth or in riverine systems. Pocklington thus produced the first set of quantitative data for organic carbon and nitrogen in the St. Lawrence Estuary and Gulf.

A 1989 study by Lucotte investigated the isotopic composition of OC in the maximum turbidity zone in the Upper St. Lawrence Estuary (Lucotte, 1989). From the isotopic data of particles collected in the area, the year-round average $\delta^{13}C$ value for the downstream samples represented an average long-term mixture of organic matter derived from terrestrial sources and planktonic cells. Further upstream, the seasonal variations of the isotopic signature were linked to changes in factors controlling the POC composition, (*e.g.* spring freshet carrying terrigenous particles in May and sedimentary exchanges between tidal platforms and estuarine platforms leading to a blurring of isotope characteristics between June and October). It was suggested that particles in this zone have a relatively long residence time (between 6 and 12 months) in the maximum turbidity zone, possibly by sediment exchange with adjacent tidal marshes.

Using free-drifting sediment traps, Colombo *et al.* collected sinking particles at two different sites and two different depths at each site in the Laurentian Trough and characterized the total organic carbon composition of these particles (Colombo *et al.*, 1996a). They reported 2.6 - 6.7% OC content by mass in the sinking particles, consisting of 17 - 37% lipids, 7.9 - 16% carbohydrates, 8.4 - 16% hydrolysable amino acids, 0.3 - 2.6% labile proteins, and 40 - 64% uncharacterized compounds. Based on C/N and C/pigment ratios, they estimated that approximately half of the carbon flux was of terrigenous origin.

In addition to the sediment traps, Colombo *et al.* used a box corer to collected bottom sediment samples from the same sites as the sediment traps in order to characterize the OC content of these sediments (Colombo *et al.*, 1996b). They reported 1.3 - 2.4% OC content by mass in the dried sediments, consisting of 1 - 5% lipids, 15 - 22% carbohydrates, 7 - 13% hydrolysable amino acids, 0.3 - 1% labile proteins, and 62 - 74% uncharacterized compounds. Based on the differences in concentration between the sinking particles and the deposited sediments, a reactivity trend was deduced (lipids > proteins > amino acids > carbohydrates). Lipids were identified as a dominant substrate near the sediment-water interface, with carbohydrates and amino acids providing most of the energy deeper in the sediments. A comparison between sampling sites showed that OC content and C/N were higher at the landward site due to higher rates of sedimentation, bioturbation and terrestrial input. In contrast, sedimentation and bioturbation were lower at the marine site, and marine production having a stronger influence on composition, leading to a lower C/N ratio and more complete decay of OM within the top 35 cm of the sediment.

In 1998, Louchouarn and Lucotte studied the flux of inorganic contaminants and terrestrial organic molecules (lignin) to the Saguenay and St. Lawrence systems since preindustrial times (Louchouarn and Lucotte, 1998). Sediment profiles representing 100 - 200 years of chronology were analyzed and from these analyses, a strong input of lignin was observed in samples representing the years 1940 - 1975. It

was determined that this input of terrestrial OM was likely due to the growth of chlor-alkali industry and the pulp and paper industry during this timeframe.

In 1999, Louchouarn *et al.* described the geographical variations in terrestrial organic matter as well as their sources and transport in the St. Lawrence system (Louchouarn *et al.*, 1999). They determined that an increase in discharge of organic wastes to the Upper St. Lawrence Estuary as a result of the expansion of the pulp and paper industry has affected the sources of terrestrial organic matter. The anthropogenic fraction of lignin in the sediments from the Lower St. Lawrence Estuary ranged from 2 - 30%. In this environment, 60 - 80% of the sedimentary OM was of allochtonous origin, a proportion that dropped to 15 - 30% in the Gulf and continental shelf sediments. On a global scale, it was estimated that half of the OM carried from riverine sources was degraded and that the remaining half accumulated primarily in the continental shelf and slope sediments.

In 2002, Hélie *et al*. observed sources and fluxes of DIC in the St. Lawrence River, tracking seasonal changes in $\delta^{13}C$ (Hélie *et al,*. 2002). The flux of inorganic carbon from the River to the Estuary (at the Quebec City outlet) represented approximately 1.5% of the world river contribution to the oceans. Important seasonal variability was reported, ranging from an 80% of the St. Lawrence outflow supplied by the Great Lakes (summer low) to 80% of the St. Lawrence outflow supplied by tributaries (spring snowmelt). Alongside these seasonal source differences, important differences were observed in the DIC $\delta^{13}C$ signatures, with values close to isotopic equilibrium with atmospheric CO_2 during the summer and values showing strong ^{13}C depletion in the spring. Hélie *et al.* suggest this variability may be due to a combination of several factors, namely the increased input of ^{13}C depleted inorganic carbon from soils and ground waters, increased oxidation of ^{13}C depleted organics, and a decrease in photosynthesis.

In 2006, Hélie and Hillaire-Marcel studied POC and DOC in the St. Lawrence River between the Great Lakes and Quebec City (from its origin to the estuary) and two of its tributaries (Hélie and Hillaire-Marcel,

2006). They paid special attention to the isotopic composition of both POC and DOC, C/N ratios of POM and ^{14}C activities of DOC in an attempt to determine their dominant sources. They found that in the St. Lawrence River, a relatively small difference in $\delta^{13}C$ between the POC and DIC pools (POC being 12‰ depleted in ^{13}C compared to DIC) was indicative of local production dominating POC from terrestrial sources. In contrast, DOC in the River appears to be mostly derived from terrestrial OM, with a young ^{14}C age, possibly suggesting recent matter from topsoils as the source material.

In 2006, Thibodeau *et al.* investigated the link between eutrophication and hypoxia in the Lower St. Lawrence Estuary (Thibodeau *et al.*, 2006). Two sediment cores from the Lower St. Lawrence Estuary were recovered and analyzed to document recent primary productivity and carbon transfer to the bottom waters. An important increase in dinoflagellate cysts was interpreted as increase in pelagic and benthic production. Furthermore, the presence of benthic foraminiferal species were assumed to reflect significant changes in physicochemical conditions of bottom waters over the last 40 years. These changes in benthic biota were correlated with an increase in OC content and a shift in isotopic signature to less depleted values, along with a decrease in C/N atomic ratio. This suggests an increase in burial of marine OM over terrestrial OM, which in turn implies an increase in Lower St. Lawrence Estuary primary productivity since the 1960's. This was deemed to be consistent with the hypothesis that the recent eutrophication of the LSLE may be, in part, responsible for the depletion of dissolved oxygen in the Estuary.

In 2009, Tremblay and Gagné investigated the reactivity of estuarine DOM and POM and found that DOM appeared less reactive and more altered than POM and that most of its humic substances were of terrestrial origins, even in marine locations (Tremblay and Gagné, 2009). Conversely, POM appeared to be highly labile, with terrigenous POM being remineralized or retained within the upstream portion of the estuary and POM from the downstream portion exhibiting a significant marine signature. The rapid

remineralization of labile POM in the water column represented a large O_2 demand, suggesting that water column respiration is not negligible as it was previously thought to be.

In 2010, Bourgoin and Tremblay studied the reworking of OM from terrigenous and marine sources in the water column and sediments of the LSLE (Bourgouin and Tremblay, 2010). By quantifying bacterial biomarkers in ultrafiltered DOM (UDOM), POM and SOM, they attempted to describe the fate of terrigenous and marine OM and quantify the bacterial contribution to OM composition and diagenesis. They found a decrease in amino acid yields in POM as samples were collected deeper in the water column, followed by an up to 3-fold increase in amino acid yields in newly deposited sediments. Along with bacterial biomarker measurements, this indicated *in situ* synthesis of amino acids by benthic bacteria. They also found a N dependent degradation or enrichment of N and amino acids, with terrigenous POM (N-poor) showing incorporation of N and an increase in amino acids whereas marine POM (N-rich) showed preferential degradation or use of organic N. Based on their measured yields, they estimated bacterial OM to represent an average of 20% of bulk C and approximately 40 - 70% of bulk N in POM and SOM, except in deep marine POM, where bacterial contribution was approximately two times lower.

In 2010, Thibodeau *et al.* measured fluxes of oxygen and inorganic nitrogen dissolved in the water column and in the sediments throughout the St. Lawrence Estuary (Thibodeau *et al.*, 2010). The goal was to assess the nitrogen budget and determine the impact of the hypoxic bottom waters of the LSLE on removal of fixed nitrogen. They found that the nitrogen budget appears almost balanced over the entire St. Lawrence system, indicating that nitrogen rich fertilizers that get introduced to the St. Lawrence River and Estuary do not lead to an imbalance in the overall budget, despite causing eutrophication in both the river and estuary.

In 2011, using solid-state NMR, Mao *et al.* reported structural changes between POM and surface SOM in order to better understand sources and preservation of OM in the SLE (Mao *et al.*, 2011). Based on the relative composition of either pools, they found that lipids and proteins or peptides (which are more abundant in POM than SOM) are more reactive than carbohydrate-like structures, supporting the selective degradation theory of the more reactive components in a pool of complex OM.

In 2012, Lalonde *et al.* demonstrated that an average of approximately 20% of OC in sediments is associated to reactive iron species (Lalonde *et al*., 2012). It was suggested that OC and iron form these associations primarily through co-precipitation or chelation, which could help preservation of OM over geological timescales. As such, iron, and its interactions with OC, was described as being important in the global cycles of carbon, oxygen and sulphur.

1.5 Scope of the Thesis

These studies all highlight the importance of the St. Lawrence Estuary in the global carbon cycle and provide insight on important processes and measurable phenomena related to the carbon cycle. Despite the efforts to study the SLE and its contribution to the global carbon cycle, no comprehensive organic carbon budget exists for this system. Several factors have contributed to making the SLE a difficult system to describe in terms of year-round OC dynamics, such as the extreme difficulty of sampling the water column during the autumn and winter, as well as a lack of reliable data on annual water flows from the Estuary to the Gulf (and values for the deep current flowing into the Estuary from the Gulf) to name a few examples. This work cannot address these issues, but rather is meant as a description of the concentration and composition (isotopic composition and C/N atomic ratio composition) of the OC cycling in the SLE based on 10 years of sampling missions during the summer season. It is also a collection of currently available data useful in the eventual construction of a carbon budget. Thus, this

work will help identify areas where more knowledge is needed to fully understand the contribution of the SLE to the global carbon cycle.

2 Methods

2.1 Sampling

The samples were collected aboard the research vessel *Coriolis II*. These missions occurred in the spring or summer of 2003, 2006 (twice), 2007, 2009, 2010, 2011, and 2013. During these missions, water and sediments were sampled in the St. Lawrence upper Estuary and lower Estuary, St. Lawrence Gulf and Saguenay River. Water was collected using a rosette with a CTD probe holding 12-L Niskin bottles. The CTD probe measured physicochemical properties of the water as the rosette moved through the water column. These properties, namely oxygen concentration (mg/L), salinity (psu), density (σ), temperature (°C), fluorescence, and transmittance, were collected to describe the environment from which the samples were collected. Sediments were obtained using a box-core, and the first 30 - 40 cm were sliced and kept at -80°C until they could be lyophilised.

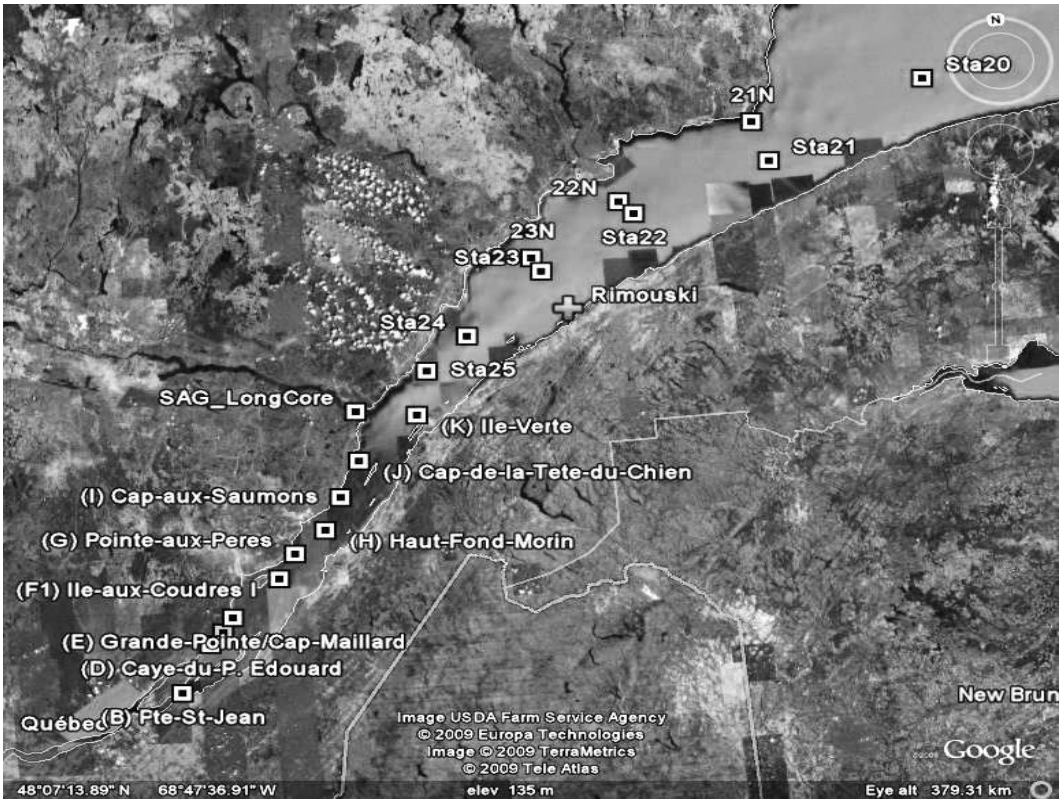

Figure 2.1. Map with the geographical location of all sampling stations of the Upper and Lower Estuary.

As soon as the water was collected, it was vacuum filtered using pre-weighed and pre-combusted (450°C for 6 hours) GF/F filters (pore size 0.7 µm). Filters used in this way captured particulate matter from the water column and were used for POC analyses. These filters were stored at -80°C until they could be lyophilised and weighed. Once filtered, part of the water was transferred to pre-combusted 30-mL glass vials with PTFE-lined screw caps, acidified to pH 2 to stop all biological activity and stored at 4°C for later analysis.

2.2 Carbon Stable Isotope Signature

Stable isotope ratios for organic carbon samples were reported as isotopic signature with respect to the international standard VPDB using Equation 1.

$$\delta^{13}C_{Sample} = \left(\left(\left(\frac{^{13}C}{^{12}C} \right)_{Sample} \Big/ \left(\frac{^{13}C}{^{12}C} \right)_{Standard} \right) - 1 \right) \times 1000 \qquad \text{Equation 1.}$$

The isotopic signature, expressed in per mil (‰), is the relative deviation in the isotope ratios of the sample and the standard. The isotope ratio carbon of the calcite found in the fossils of Vienna Pee Dee Belemnite (VPDB) has been set as the international standard for this equation (0 ‰) with a $^{13}C/^{12}C$ ratio of 0.0112372.

2.3 EA-IRMS

All solid phase samples (filters with particulate matter and sediment samples), were analysed for carbon content, nitrogen content, as well as $\delta^{13}C$ signature using an Eurovector elemental analyzer coupled to an Isoprime isotope ratio mass spectrometer (EA-IRMS). Prior to analyses, all particulate and sediment

samples were decarbonated by exposing them to HCl fumes for 10 hours in order to measure only OC content and isotope signatures. Isotope calibration was done using a certified sucrose standard ($\delta^{13}C$ -10.45 ± 0.03‰, IAEA-CH-6) and an in-house β-alanine standard ($\delta^{13}C$ -26.18 ± 0.33‰, SigmaAldrich).

2.4 DOC-IRMS

Samples in the dissolved phase were analysed for carbon content using a Shimadzu high temperature catalytic (HTC) TOC-Analyzer. Isotopic analyses were done on more recent (3 years or less) samples on an OI Analytical HTC TOC-Analyzer coupled to a Graden-100 CO_2 chemical trap and the Isoprime IRMS. The acidification step of the sample collection allows for quick removal of inorganic carbon species by purging with the carrier gas immediately before analysis. Isotope calibration was done using the same sucrose and β-alanine standards as for the EA-IRMS.

2.5 Iron Reduction Method

Reactive iron oxides in particulate samples were reduced using a procedure first described by Mehra and Jackson (1960) and adapted by Lalonde *et al.* (2012). Particulate matter on filters was ground to homogeneity and was transferred to PTFE tubes for reduction. One aliquot of the homogenized particulate matter was rinsed with a salt solution of the same ionic strength as the reducing solution (1.6 M), heated at 80°C, subjected to an increase in ionic strength (0.25 M) and kept at 80°C for 15 minutes (control). The slurry was centrifuged (at 3000 g for 10 minutes). This was done to determine the amount of OC released by the reaction conditions as opposed to the reduction itself. On a second aliquot, the reduction was performed in the same ionic strength and temperature conditions as the control using a mixture of trisodium citrate (0.27M) as a complexing agent, sodium bicarbonate (0.11M) as the buffer, and sodium dithionite (0.1M) as the reducing agent to be added once the solution was at 80°C. The sodium dithionite was added as a solid directly to the buffered solution containing the particles and the

citrate only after its temperature reached 80°C. The samples were then rinsed, lyophilized and analyzed using the EA-IRMS.

3 Results

3.1 Dissolved Organic Matter

The DOC concentration in surface waters for the entire St. Lawrence Estuary (Upper and Lower) and Gulf showed a decreasing trend (Figure 3.1), starting at a concentration of 4.57 ± 0.31 mg C/L at Station A (0 km, Quebec City) and levelling off at an average concentration of 1.18 ± 0.19 mg C/L in the Gulf (Stations 19, 18, 17, and 16). These values agreed to the 95% confidence interval with previous studies for the St. Lawrence River (Hélie *et al*., 2002; Hélie and Hilaire-Marcel, 2006) and Gulf (Packard, 2000, Panetta, 2008). When narrowing the focus on the Lower Estuary, increased DOC concentration was observed at the boundary between the USLE and LSLE (200 km), followed by a decreasing trend (Pearson coefficient -0.57) as samples were from more seaward stations (*i.e.* further away from Quebec City). The increase in concentration was due to the upwelling of landward flowing water from the deep LSLE, which brought more nutrients to the surface and stimulates primary production, and the input from the Saguenay River, which had waters rich in DOC and nutrients to stimulated primary production. The decrease in concentration as DOC sources became more marine was a result of the gradual mixing of riverine water with high DOC concentration (4.57 ± 0.31 mg C/L from the St. Lawrence River) with water from oceanic sources, which were much less concentrated in DOC (0.82 ± 0.22 mg C/L in the deep LSLE). An increase in DOC concentration was also generally observed at 400 km from Quebec City (Station 21), a region just downstream from where large rivers from the North Shore (Betsiamites River: 323 m^3/s, Aux-Outardes River: 391 m^3/s, and Manicouagan River: 877 m^3/s) discharged in the Estuary.

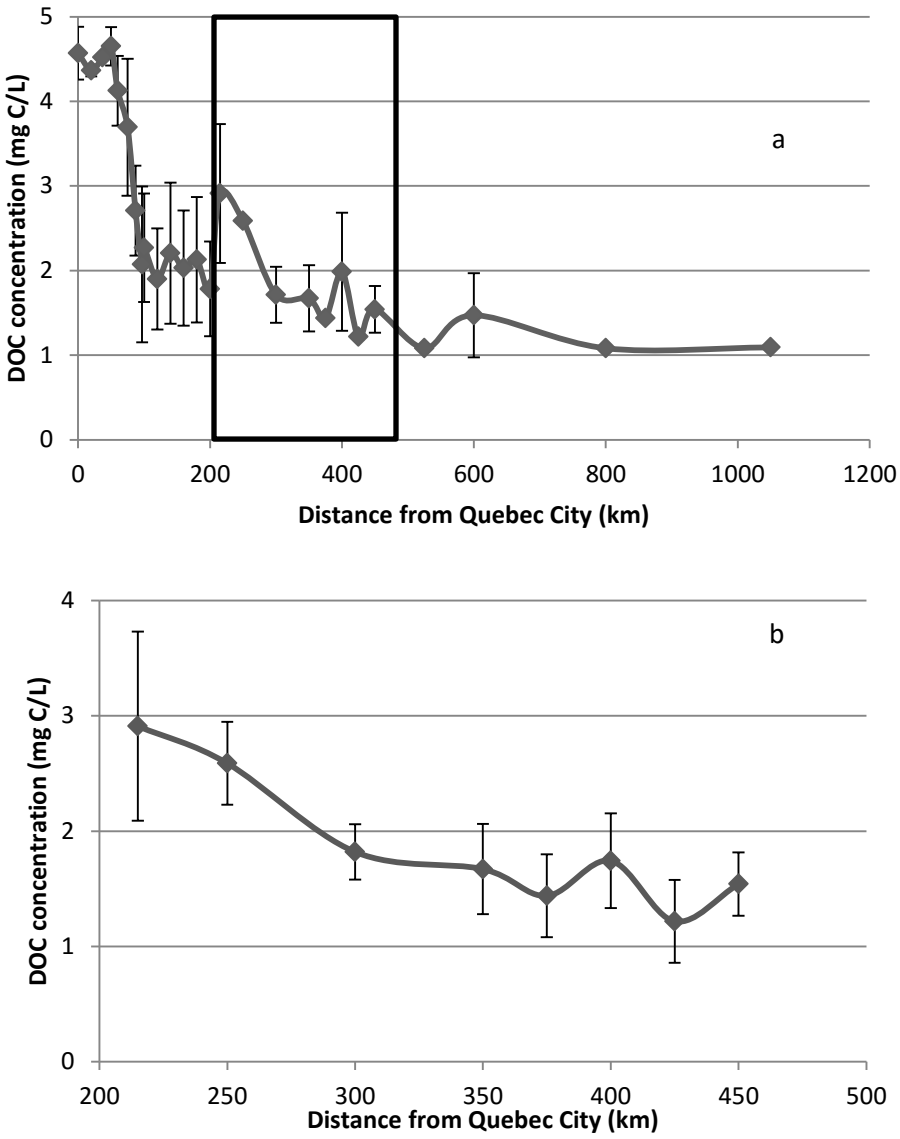

Figure 3.1. DOC concentration in the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average DOC concentration over 10 years (8 sampling missions), starting at Quebec City (0 km) and moving away, seaward; (b) Average DOC concentration values for all Lower Estuary samples over 7 years (6 sampling missions) (b) The boxed section in (a) was the same data series as plot (b).

The $\delta^{13}C$ stable carbon isotope signatures (Figure 3.2) were also in good agreement with previous studies (Hélie *et al.*, 2002; Hélie *and* Hilaire-Marcel., 2006; Panetta, 2008). Stable isotope signatures for DOC from the Upper Estuary showed more depletion in ^{13}C than samples from the Lower Estuary and the

Gulf, starting at -26.75 ± 0.35 ‰ near Quebec City (Figure 3.2a). This ^{13}C depletion relative to the rest of the Estuary was due to a more important contribution of riverine organic matter from the St. Lawrence River ($\delta^{13}C$ signatures typically between -27 ‰ to -30‰, in contrast to marine $\delta^{13}C$ signatures which were typically between closer to -20‰). The $\delta^{13}C$ of DOC increased in the Upper Estuary, indicating a relative enrichment in ^{13}C as samples were from more seaward stations to a maximum of -22.25 ± 1.06 ‰, before decreasing again to 24.57 ± 1.16 ‰ at the head of the Lower Estuary (Station 25, 215 km from Quebec City), and increasing again to less depleted values averaging -21.01 ± 2.11 ‰ in the Gulf (Stations 18 and 19). Focusing on the Lower Estuary (Figure 3.2b), an enrichment trend (Pearson coefficient: 0.66, considered to be high in geochemistry due to variability of natural samples) was observed as samples were from stations further away from Quebec City, which has been reported in previous studies with isotopic analyses performed on DOC in this region (Panetta, 2008). The data point at Station 21 (400 km) stood apart from the trend, with an isotopic signature that was more depleted than would be expected (-24.15 ± 1.00‰, rather than approximately -21.3 ‰, if this station followed the trend). This was the same station that also shows differences in the DOC concentration plots, suggesting the influx of riverine water had an important impact on DOC, a station that has been consistently different in all sampling missions.

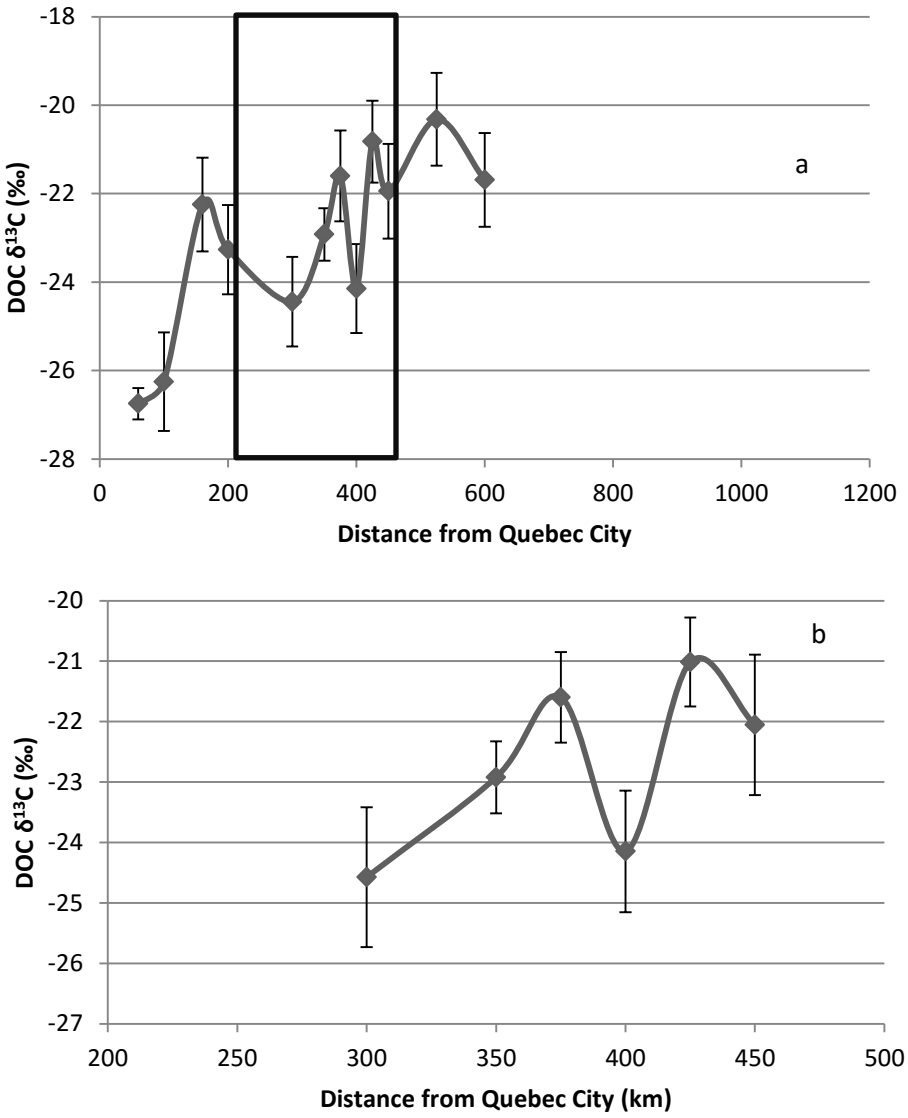

Figure 3.2. The $\delta^{13}C$ stable isotope signatures measured on DOC samples from the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average $\delta^{13}C$ of DOC over 7 years (7 sampling missions), starting at Quebec City (0 km) and moving away, seaward; (b) Average $\delta^{13}C$ of DOC for all Lower Estuary samples over 7 years (6 sampling missions). The boxed section in (a) was the same data series as plot (b).

Isotopic mass balance calculations were made to estimate the contribution from terrestrial DOC exported to the LSLE by the rivers of the North Shore using the a 2-end-member mixing analysis. End-member mixing analyses use the distinctive features of different sources (in this case, two sources with

different concentrations and $\delta^{13}C$ signatures) to estimate the contribution of each source to the sample of interest. A mixing is defined by such an analysis and if all sources have been accounted for, it is possible to describe the sample of interest in terms of relative contributions from either source. For this analysis, the difference between the expected isotopic signature at station 21 (-21.3 ‰) was compared to the average isotopic signature at station 21 (-24.15 ‰) and the typical range of terrestrial OC (-30 to 27 ‰) for DOC from the rivers of the North Shore. The mass balance calculations predicted a riverine contribution between 33 % and 50 %, with -30 ‰ and -27 ‰ signatures respectively, which was not in agreement with the observed increase in DOC, of which only 24 % was above what would have been expected if the station followed the observed trend for the LSLE. Other processes, such as biological processes (affecting concentrations) or photochemical processes (affecting concentrations and signatures, Lalonde *et al.*, 2014), that influenced DOC concentrations and/or signatures were probably not captured using this simple 2-end-members mass balance model, leading to the disagreement between observations and the end-member analysis .

DOC concentrations decreased as $\delta^{13}C$ signatures increased (Pearson coefficient: -0.68) (Figure 3.3). This trend was in agreement with typical observations of riverine sources, which have higher DOC concentrations than estuarine and marine sources coupled with lower $\delta^{13}C$ signatures, mixing with marine waters in the estuarine transition systems. This also confirmed that the data that seem to fall away from the trend were not merely outliers, but representative of riverine DOC and thus, his trend, while clearly decreasing, was not linear. DOC concentration decreased rapidly as the carbon stable isotope signature slightly increased, followed by a much slower decrease of DOC concentration over a much larger span of stable isotope signatures. This underlined the removal of terrestrial DOC, likely via

coagulation and sorption to mineral particles in the high turbidity zone, as well as bio- and photo-oxidation, as this DOC mixed with marine DOC.

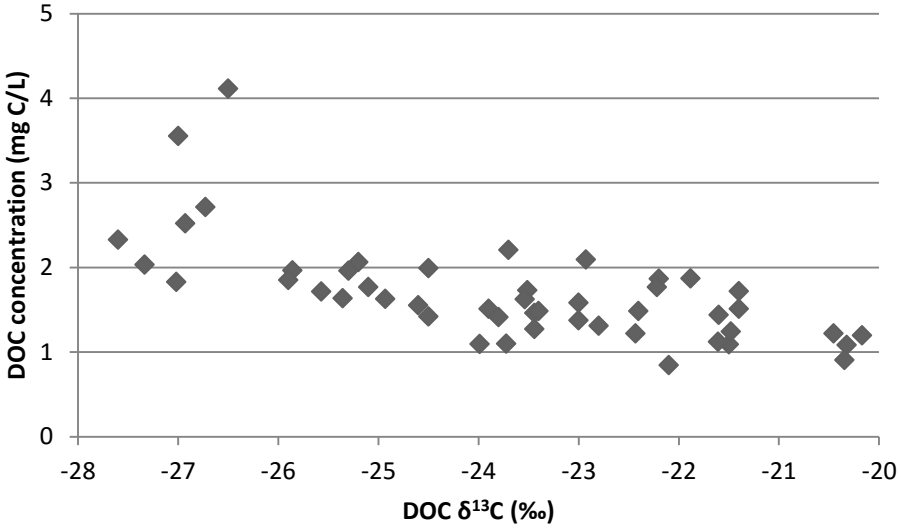

Figure 3.3. Relationship between $\delta^{13}C$ DOC and DOC concentration: concentration and $\delta^{13}C$ for water samples from the surface (typically between 0 - 25 m) layer of each station of the Estuary and Gulf over 7 years (6 sampling missions).

The DOC concentration depth profiles for the 2013 sampling mission showed great similarity throughout the water column (Figure 3.4), with the exception of station 20.5, which was different from the other stations in the surface layer (1.25 mg C/L compared to an average of 1.73 ± 0.08 mg C/L for the rest of the Lower Estuary stations). Despite this observed difference, all depth profiles had similar features, with higher concentrations observed in the surface mixed layer and a decrease in concentration in the top 50 - 100 m to reach a more uniform profile down the water column of around 0.75 to 1 mg C/L (Figure 3.4). These profiles were in good agreement (95% confidence interval) with what has been observed in other studies (Panetta, 2008). Furthermore, values from samples taken at greater depth (0.85 ± 0.15 mg C/L for 2013 and 1.09 ± 0.25 mg C/L for 2011) were in good agreement with measurements made on deep samples from the St. Lawrence Gulf (Packard *et al.,* 2000; Alkhatib *et al.,* 2012). Like the 2013 depth

profiles, the 2011 depth profiles were mostly similar, albeit generally more concentrated in DOC (Figure 3.4b). The most important differences observed at the same station for different years were in surface waters. At depth, DOC concentrations were more similar from year to year.

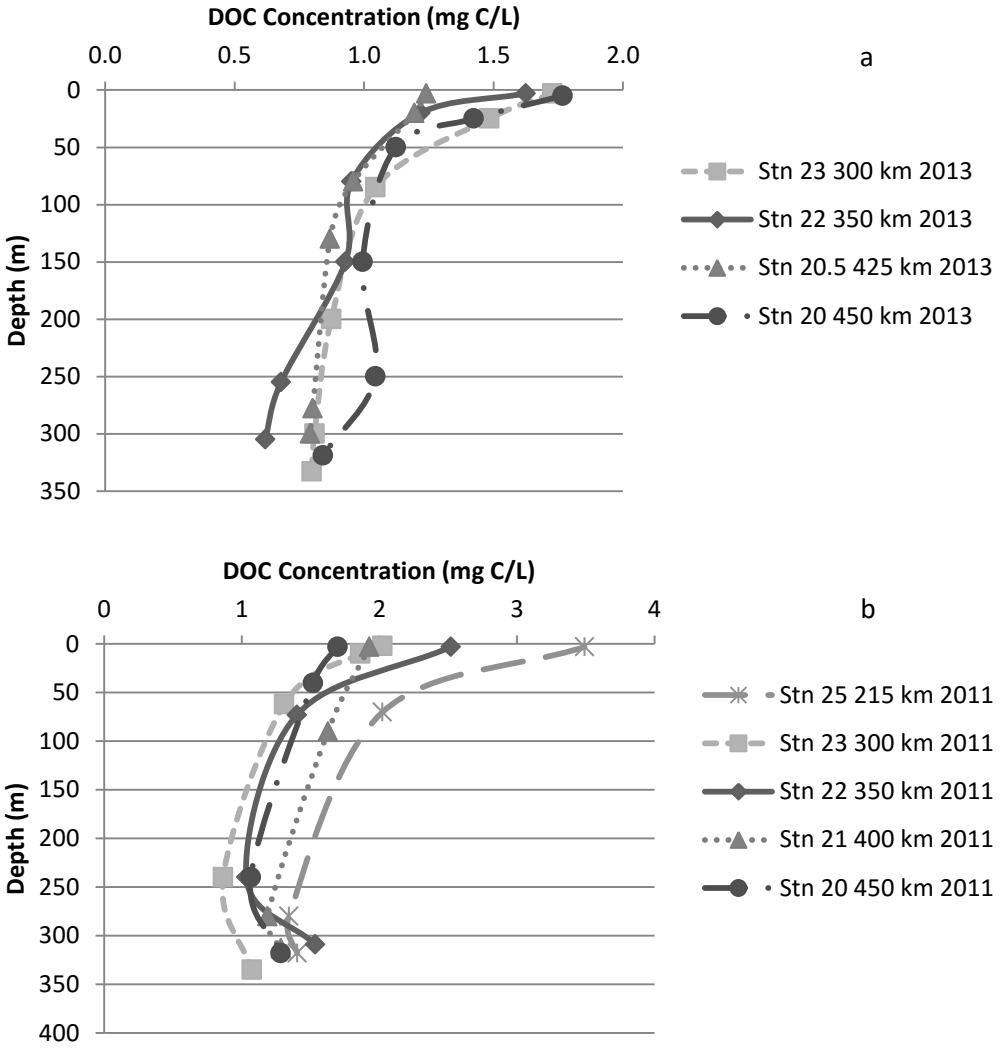

Figure 3.4. Depth profile of DOC concentrations. All Lower Estuary stations from (a) the 2013 sampling mission, and (b) from the 2011 sampling mission.

The comparison between the DOC depth profiles for Station 23 from samples collected in 2010, 2011 and 2013 gave a sense of the annual variability observed in the Lower St. Lawrence Estuary. Figure 3.5

showed very good agreement between the depth profiles from 2013 and 2010. Both 2010 and 2013 depth profiles began with surface concentrations around 1.75 mg C/L (1.72 mg C/L for 2010 and 1.73 mg C/L for 2013). This value dropped rapidly in the top 50 - 100m to stabilize around 1 mg C/L. The 2011 DOC depth profile showed a higher concentration at the surface (around 2 mg C/L) and more variable concentration at certain points down in the water column. The most notable of these deviations appeared to be at the deepest point (335m), where the concentration was 0.2 mg C/L higher than the previous point (330m) and higher than the deep DOC concentration from both 2010 and 2013. This depth corresponded to the deep nepheloid layer, a water layer with a high load of resuspended sediments and higher DOC concentration owing to the dispersion of high-DOC pore water upon resuspension of the surface sediment. These depth profiles of OC are typical of those found in most water columns.

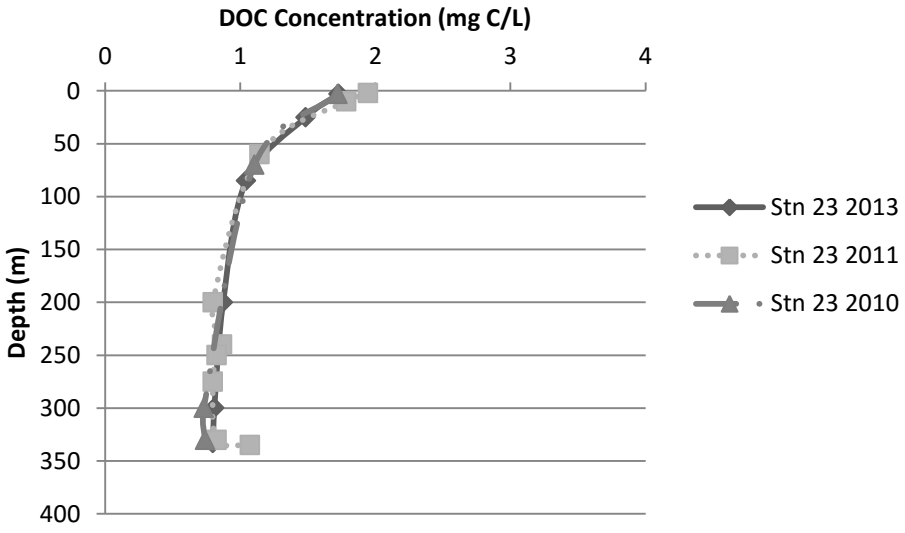

Figure 3.5. Depth profiles of DOC concentrations at station 23 (300 km) from sampling missions in 2010, 2011 and 2013.

3.2 Particulate Organic Matter

The POC concentrations in surface waters of the Estuary were variable, with the Upper Estuary showing most variability (Figure 3.6a), tapering off in the Lower Estuary and stabilizing in the Gulf at around 98 ± 17 µg C/L. The upper Estuary showed extreme variability in the first 75 km after Quebec City (Stations A to E inclusively) with Station D having the highest average POC concentration and a relative standard deviation of more than 100% (4410 ± 5025 µg C/L). There were several major causes of variability of POC concentration in this area: increased particle import from rivers during freshet events, which often coincided with sampling missions, coagulation of riverine DOC due to increasing salinity, algal blooms and dilution with upwelling marine water from the deep LSLE, which had low POC concentrations.

When only considering the Lower Estuary, POC concentrations in surface waters appeared variable (Figure 3.6b), as shown by very large error bars, which suggested a minimum POC concentration throughout the system around 100 µg C/L, but to which much POC could be added, mainly by primary production due to the import of nutrient. As temperatures rose during the spring, snow packs melted and the runoff carried with it soil detritus and nutrients that were typically limited in these water systems. This injection of nutrients boosted primary production, leading to an algal bloom. It was interesting to note that the areas of highest variability for the Lower Estuary coincided with Station 21, previously identified as a station of interest based on the DOC results, both in terms of isotope signature and DOC concentration. The increased POC concentration observed there was due to the export of riverine POC from rivers of the North Shore to the LSLE and the increased primary production caused by the influx of nutrients from these same rivers.

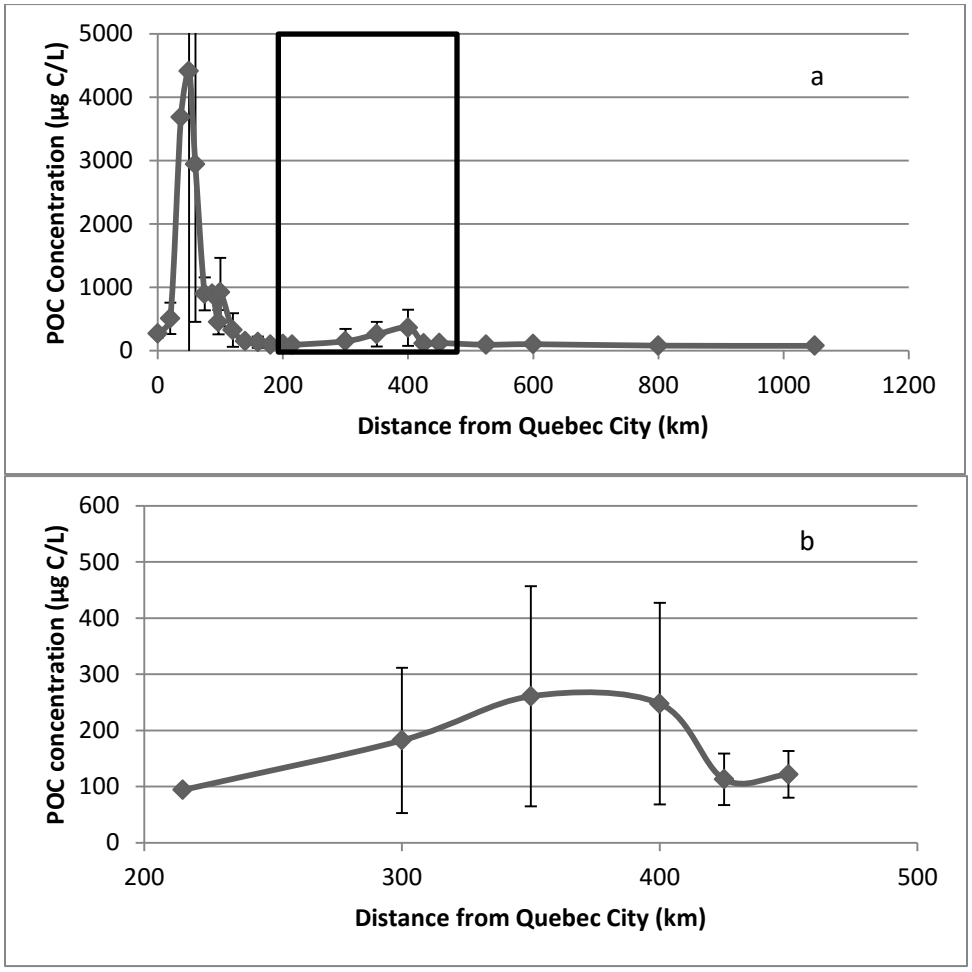

Figure 3.6. POC concentration in the surface (typically between 0 - 25m) layer along the entire St. Lawrence Estuary and Gulf. (a) Average POC concentration over 10 years (8 sampling missions), starting at Quebec City (0 km) and moving away, seaward; (b) Average DOC concentration values for all Lower Estuary samples over 7 years (7 sampling missions). The boxed section in (a) was the same data series as plot (b).

Similarly to the average POC concentration, the carbon stable isotope signature of POC also showed high variability, but in this case, the Lower Estuary showed the highest variability (Figure 3.7a). POC from the Upper Estuary were more depleted in ^{13}C and showed a small enrichment (Pearson coefficient: 0.65) in stations that were further from Quebec City. This was because particles in the Upper Estuary were mostly terrestrial debris carried to the estuary by rivers, with increasing contribution of marine primary productivity as the samples were from stations closer to the Lower Estuary. The high variability observed

in LSLE POC (Figure 3.7b) lead to difficulty describing this system in terms of trends. Once more, Station 21 (400 km) stood out from the other LSLE stations, although significantly less so than when looking at DOC and POC concentrations or DOC isotopic signatures. Here, the $\delta^{13}C$ values for surface POC at Station 21 (average of -22.66 ± 2.41 ‰) was, on average, less depleted than the stations upstream (-23.88 ± 0.25 ‰, -24.00 ± 1.35 ‰, and -23.67 ± 2.08 ‰), and the downstream stations of the Lower Estuary (-24.63 ± 0.11 ‰ and -22.92 ± 2.06 ‰). This suggested that primary production was the major contributor to the increase in POC concentrations observed at Station 21.

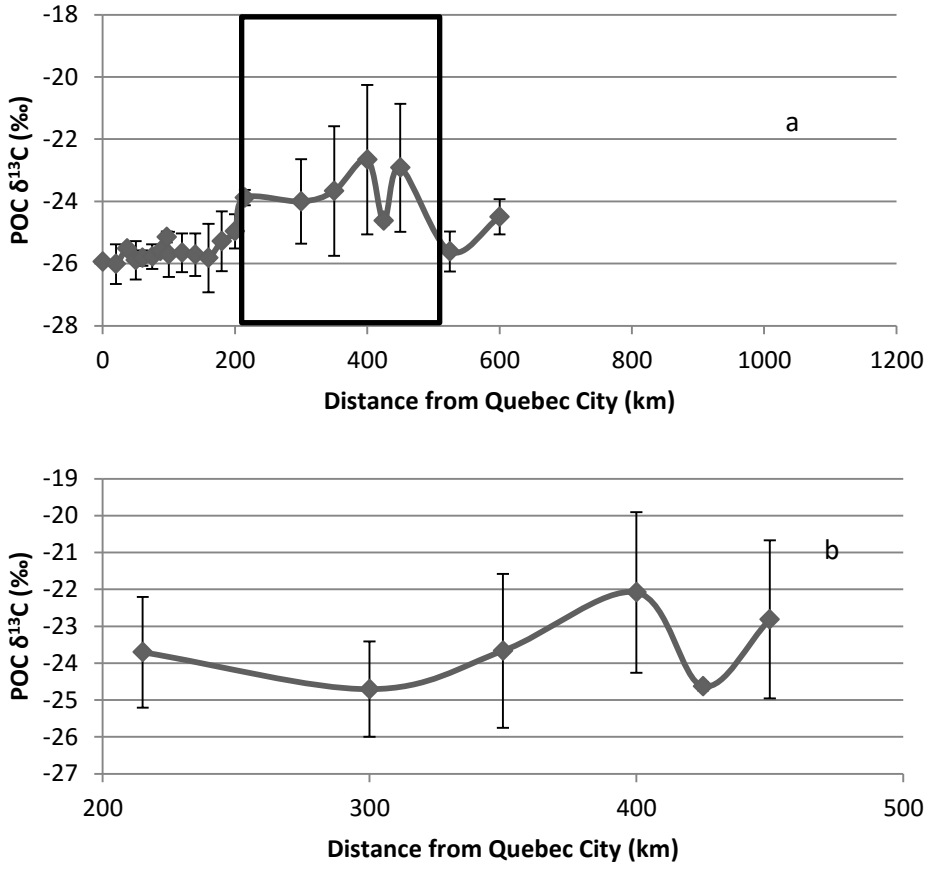

Figure 3.7. The $\delta^{13}C$ stable isotope signatures measured on POC samples from the surface layer (typically between 0 - 25 m) along the entire St. Lawrence Estuary and Gulf. (a) Average $\delta^{13}C$ of POC over 10 years (8 sampling missions), starting at Quebec City (0 km) and moving away, seaward; (b) Average $\delta^{13}C$ of POC for all Lower Estuary samples over 7 years (7 sampling missions). The boxed section in (a) is the same data series as plot (b)

The general observations made for $\delta^{13}C$ of POC as samples increasingly further from Quebec City were mirrored in the C/N of POM (Figure 3.8a). The atomic C/N ratios of POM samples from the Upper Estuary were more depleted in nitrogen, leading to a higher C/N ratio, as was typically observed in terrestrial OM. As with the isotopic signatures of POC, a decreasing trend was observed in the Upper Estuary for POM C/N (Pearson coefficient: -0.66), which was in agreement with the increasing importance of nitrogen-rich marine primary production. The change of C/N atomic ratio of POM in the LSLE as sampling stations were further away from Quebec City mirrored the fluctuations observed in the carbon stable isotope signature of POC (Figure 3.8): as $\delta^{13}C$ signatures became less depleted, C/N ratios became smaller, with Station 21 showing the lowest C/N ratio (average of 7.04). This decreasing trend of C/N ratio as POC isotopic signatures became less depleted could be seen throughout the Estuary and Gulf (Pearson coefficient: -0.64; Figure 3.9) and were a good indication of the change in provenance of the POM, going from a terrestrial source in the Upper Estuary to a marine source in the Lower Estuary.

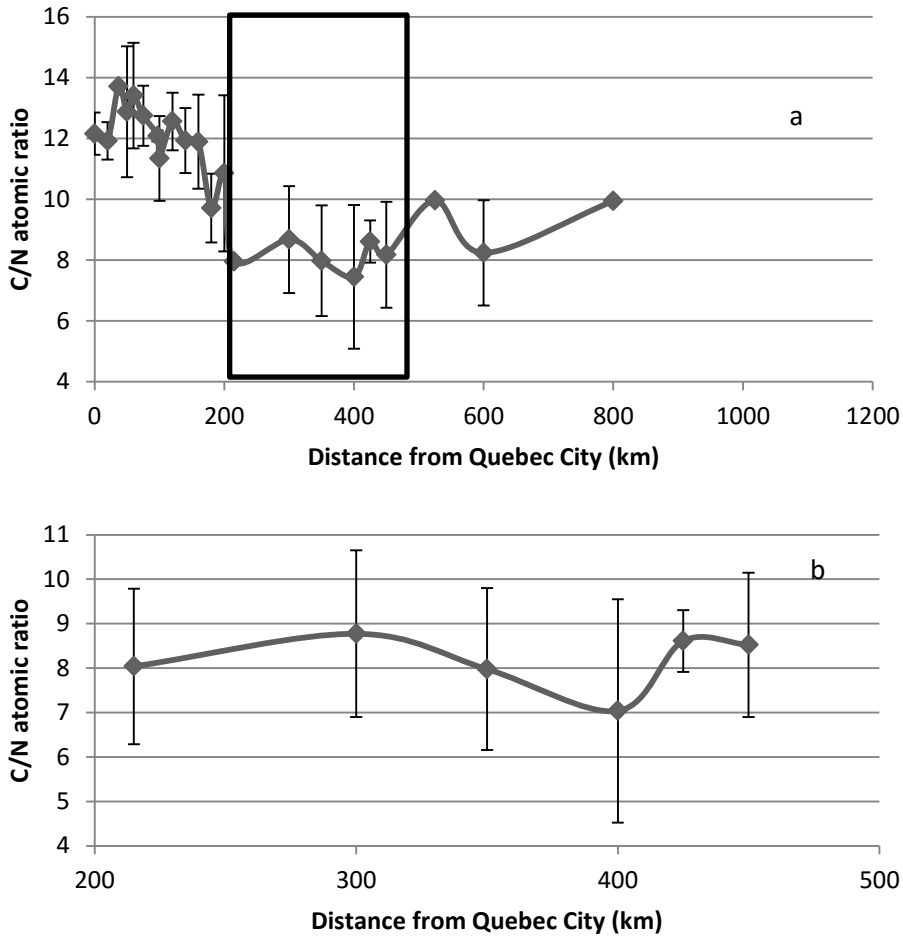

Figure 3.8. The carbon to nitrogen atomic ratios (C/N) measured on POM samples from the surface (typically between 0 - 25 m) layer along the entire St. Lawrence Estuary and Gulf. (a) Average C/N of POM over 10 years (8 sampling missions), starting at Quebec City (0 km) and moving away, seaward; (b) Average C/N of POM for all Lower Estuary samples over 7 years (7 sampling missions). The boxed section in (a) is the same data series as plot (b).

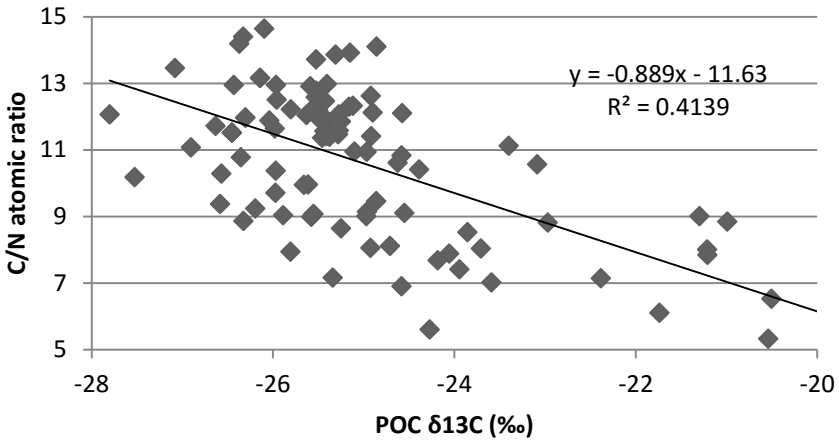

Figure 3.9. Relationship between $\delta^{13}C$ POC and POM C/N atomic ratio: $\delta^{13}C$ and atomic ratios for particulate samples from the surface layer (typically between 0 - 25 m) of each station of the Estuary and Gulf over 10 years (8 sampling missions).

Depth profiles from the LSLE showed a decrease in the surface concentration of POC as samples were collected more seaward, tapering off before going into the Gulf (Figure 3.10), from 385.8 µg C/L at Station 23 to 135.2 µg C/L at Station 21 and 164.2 µg C/L at Station 20. It appeared that values for samples collected deeper than 100 m were more uniform in the LSLE, averaging 60.3 ± 16.9 µg C/L, a result that had also been observed in previous studies (Pocklington 1973; Panetta 2008). This decreasing trend seaward was a result of riverine POC sedimenting in the LSLE and primary producers becoming less productive as limiting nutrients became more dilute seaward: less concentrated limiting nutrients lead to lower production which lead to lower POM concentrations.

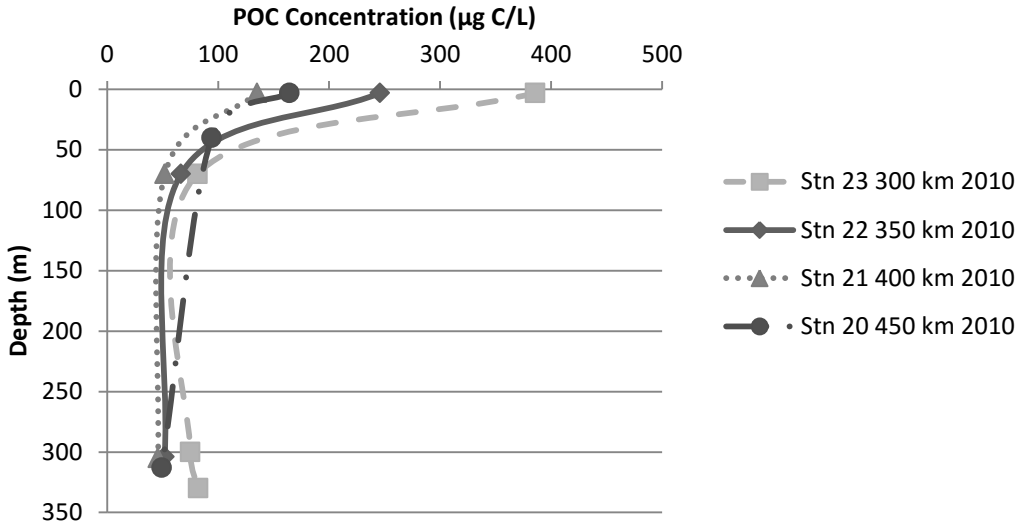

Figure 3.10. Depth profiles of POC concentration from the 2010 sampling mission at all Lower Estuary stations sampled.

Depth profiles of POC isotopic signature showed that $\delta^{13}C$ of POC was more variable in surface waters than at depth (Figure 3.11b). Surface POC from Station 23 was the sample most depleted in ^{13}C (-25.81 ‰) from the 2013 mission and surface POC from Station 20 the least depleted (-23.94 ‰), underlining a transition in source of POC in the LSLE from mostly terrestrial with some marine primary production at the mouth of the LSLE, to a more even mix of terrestrial and marine POC. Further down the water column, POC isotopic signatures became much closer to one another. This was due to the degradation of POC in the surface layer by marine life, leaving more recalcitrant molecules as the main component of deeper POC, which resulted in a depletion of the $\delta^{13}C$ for POC.

Unlike the relationship between surface POM C/N atomic ratio and isotope signature, the depth profiles of POM C/N atomic ratios did not mirror the depth profiles of the isotopic signatures of POC (Figure 3.11b). Nonetheless, all depth profiles had similar C/N atomic ratio in surface POM (7.60 ± 0.55), all of which were typical of important marine primary production. The depth profiles also showed an increase in C/N ratio going from the surface layer to the CIL, indicative of OM degradation, before stabilizing to

intermediate values at depth throughout the LSLE. This again pointed to reactive POM being degraded in the surface portion of the water column and more recalcitrant molecules as the main component of deeper POM.

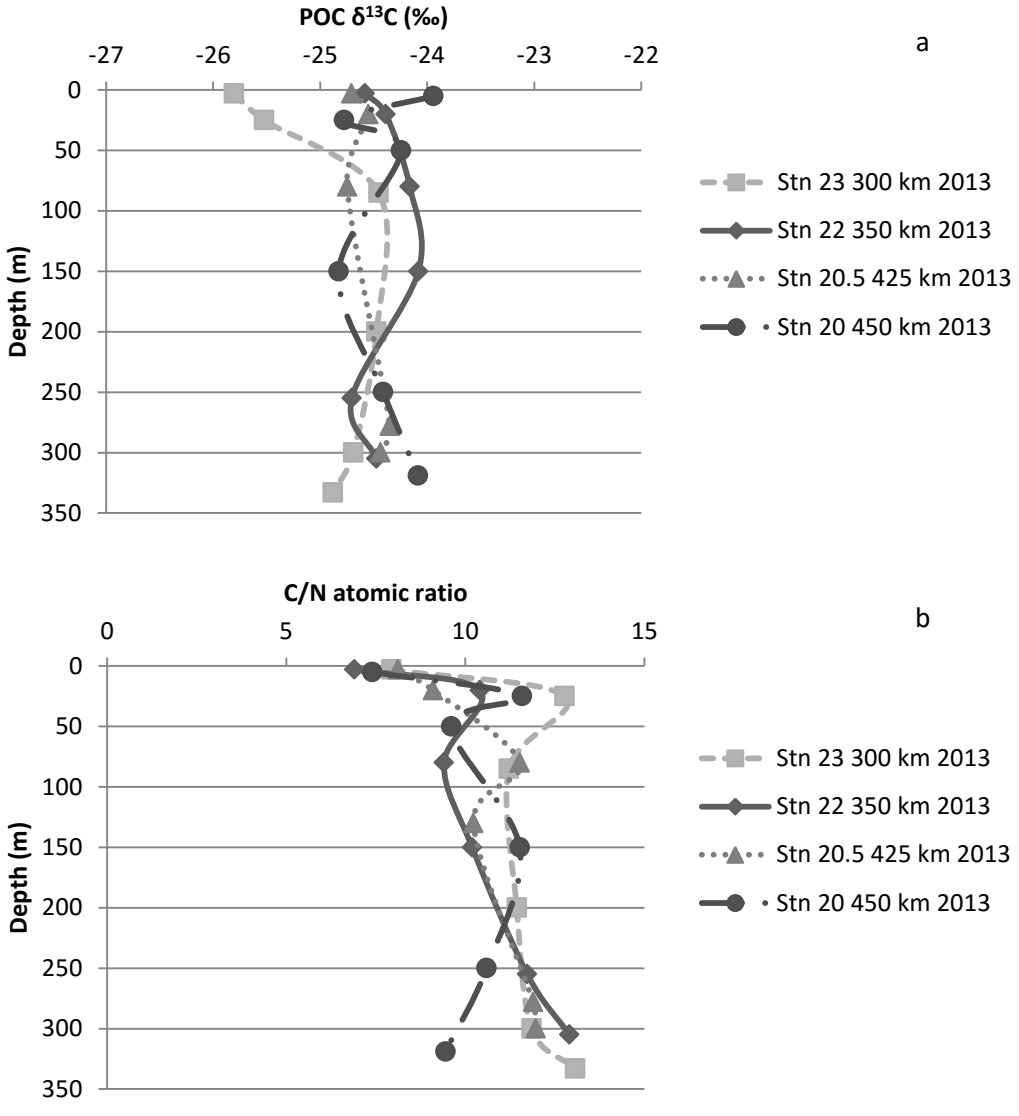

Figure 3.11. Depth profiles for (a) the isotopic signatures and (b) C/N atomic ratios of POC from all the Lower Estuary stations sampled in 2013.

The relationship between iron and POC in the SLE showed interesting trends (Figure 3.12). As sample origin became more marine (moving away from Quebec City), a higher percentage of the total POC was associated to reactive iron oxides (Figure 3.12a). By looking at the OC:Fe atomic ratios (Figure 3.12b), it was clear that this increase in percentage of POC associated to iron was accompanied by an increase in the atomic ratio of OC to iron upon reduction of these iron oxides. This increasing seaward trend observed in both %OC associated to iron and OC:Fe atomic ratios suggested that iron played a role in the cycling of POM.

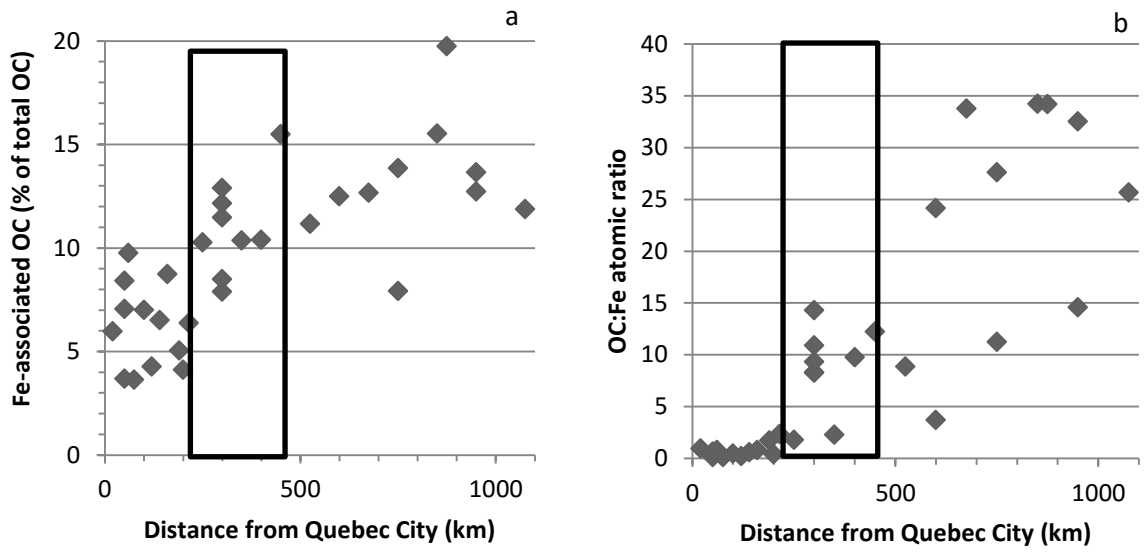

Figure 3.12. OC associated to iron in the POM of the LSLE (a) as a percentage of total OC and (b) as an atomic ratio. The boxed sections corresponds to samples from the LSLE.

3.3 Sedimentary Organic Matter

The OC content in the top 4 cm of the LSLE sediments was fairly constant throughout at 1.82 ± 0.18% OC by dry weight. The percentage of OC varied by less than 10% from station to station, which suggested that the processes controlling the preservation of OC were not governed by the magnitude of the flux of OM to the sediments.

The isotopic signatures of SOC in the LSLE showed a distinct ^{13}C enrichment trend (Pearson coefficient of 0.92) moving seaward (Figure 3.13), going from an average of -24.56 ± 0.17 ‰ at station 25 for the top 4 cm (at a 1 cm resolution) to -22.64 ± 0.07 ‰ at station 20. The small standard deviations between 0 and 4 cm suggested that the isotopic composition of the top 4 cm of the sediment was uniform at each station, which is consistent with observations of bioturbation mixing sediments over several centimeters. The observed enrichment trend was independent of OC content, suggesting that while sources of OC to the sediments might have been different (*i.e.* relative input from primary production increased and relative input from terrestrial sources decreased as samples were from more seaward stations) and gross flux of particles to the sediment bed decreased as the transition was made from a riverine to a coastal marine system, the product of degradation processes occurring during early sedimentation was a uniform OC content in this system.

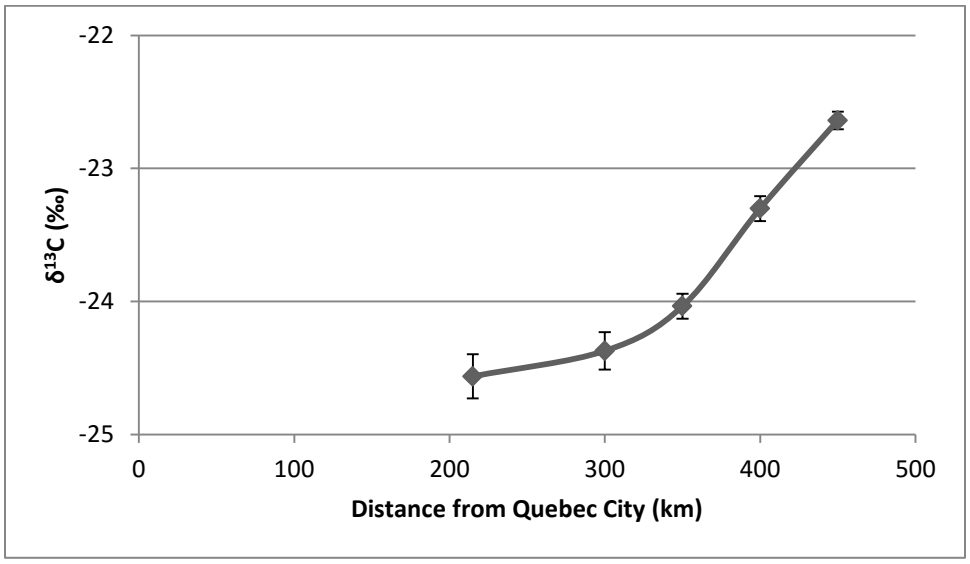

Figure 3.13. Average stable isotope signature of SOC moving seaward from surface sediments (top 4 cm with a resolution of 1 cm; n=4) collected during the 2006 and 2007 sampling missions.

The C/N atomic ratio of SOM in the LSLE followed a general decreasing trend (Pearson coefficient of -0.72) (Figure 3.14). This trend, although not as strong as the increasing trend for the isotopic signature, was correlated (Pearson coefficient of -0.88) with ^{13}C enrichment observed in SOC from the same station. Together, these trends suggested a change in the source of SOM accumulating in the sediments throughout the LSLE, despite the percentage of carbon not changing significantly.

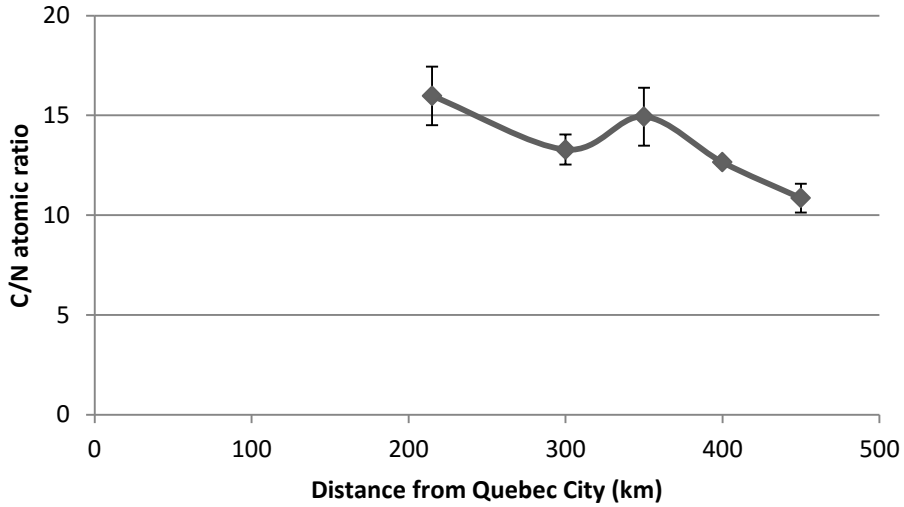

Figure 3.14. Average C/N atomic ratio of SOM moving seaward from surface sediments (top 4 cm with a resolution of 1 cm; n=4) collected during the 2006 and 2007 sampling missions.

The OC depth profiles of the sediments from the LSLE showed great similarities, both in values for %OC and in trends (Figure 3.15). At the surface of the sediment (0 - 1 cm), values were close to the OC average for the top 4 cm of LSLE sediments (1.82 ± 0.18%). Thereafter, the depth profiles showed a decreasing trend with depth of very similar magnitude, reaching 1.35 ± 0.02 % at a depth range of 26 - 31 cm, with the exception of station 25, which had an OC content of 0.96% at the same depth. This decrease in %OC was the result of OC degradation processes following deposition on the sea floor.

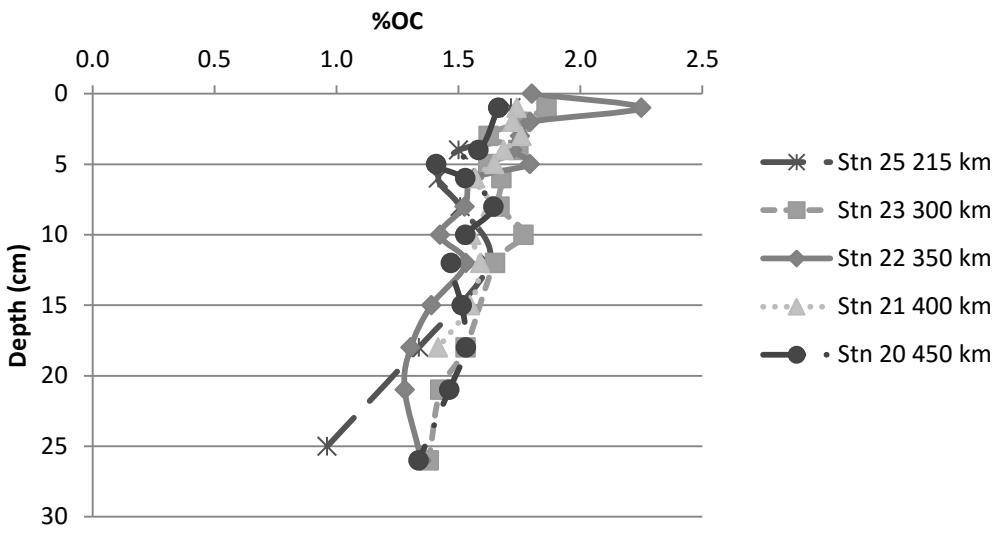

Figure 3.15. Sedimentary depth profiles of carbon content from the 2007 sampling mission at all Lower Estuary stations sampled.

The sediment depth profiles for the isotopic signatures and C/N atomic ratios agreed with the trend observed in surface sediments along the LSLE for the isotopic signature and C/N atomic ratio, namely that sedimentary organic matter (SOM) became less depleted in ^{13}C and had lower C/N values as samples were from more seaward stations. This was observed at all depths of the collected samples, with $\delta^{13}C$ values becoming increasingly enriched (Figure 3.16a) and C/N values decreasing (Figure 3.16b) as sampling station was further seaward. In addition, all depth profiles showed a depletion trend in $\delta^{13}C$ and an increase in C/N atomic ratio. A negative correlation between the $\delta^{13}C$ and C/N atomic ratio of sedimentary organic matter was observed (Figure 3.17; Pearson Coefficient: -0.74), which would indicate that despite the gradual change from a terrestrial to a marine source, SOM bacterial degradation had the same effect throughout the Lower Estuary and Gulf.

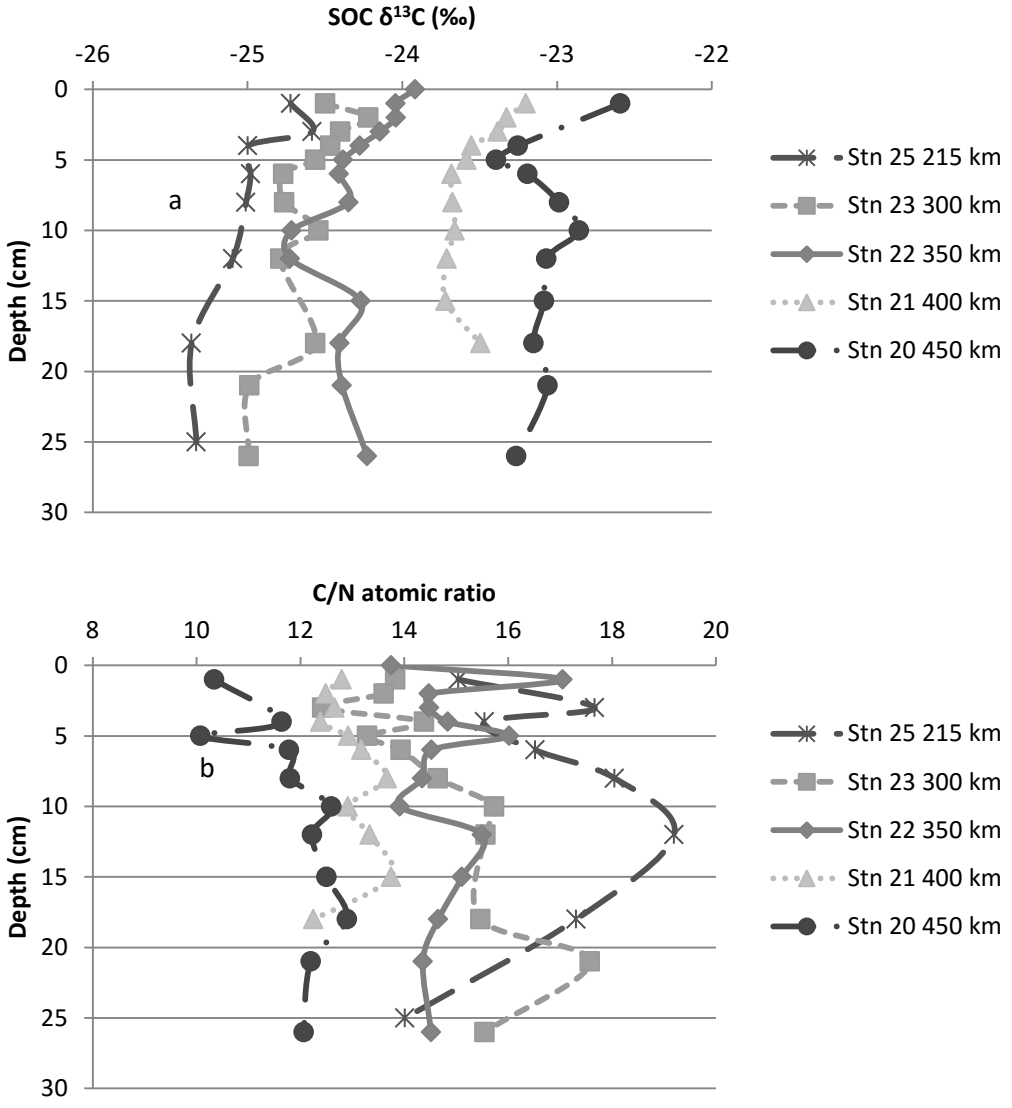

Figure 3.16. Depth profiles for (a) the isotopic signatures and (b) the C/N atomic ratios of sediments from the 2007 sampling mission at all Lower Estuary stations sampled.

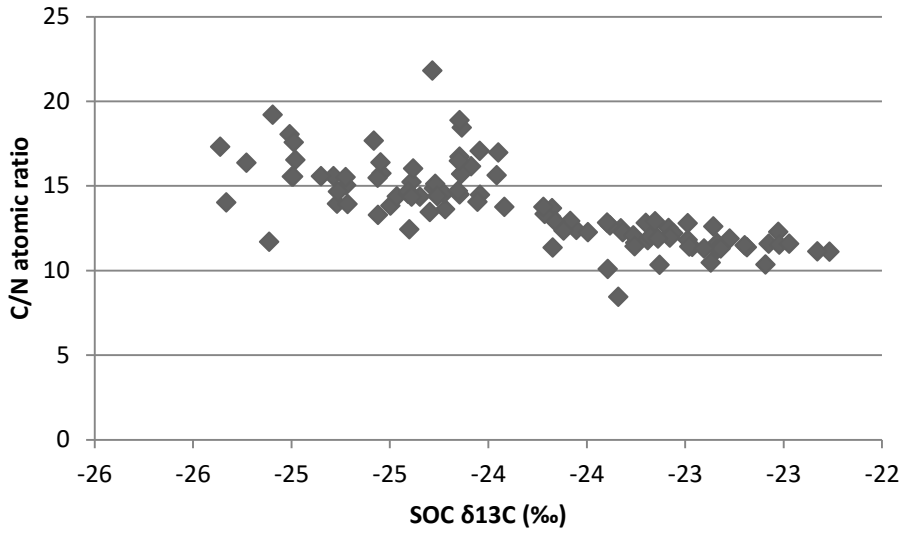

Figure 3.17. Relationship between $\delta^{13}C$ SOC and SOM C/N atomic ratio: average $\delta^{13}C$ and atomic ratios for the sediment cores of each station sampled during the 2007 stations mission.

4 Discussion

4.1 Dissolved Organic Matter

4.1.1 General trends and important processes

In the SLE, a decreasing trend in surface DOC concentration (Figure 3.1a) was reported at more seaward stations. This had been observed before (Panetta, 2008), and could be explained by the mixing of seawater with fresh riverine water. Because rivers drain carbon-rich terrestrial ecosystems, their water is more concentrated in DOC than marine water (Hynes, 1963), and the water flowing into the SLE from various sources could attest to that: the average concentration of DOC from the St. Lawrence River was more concentrated (4.41 ± 0.10 mg C/L), as was that from the Saguenay (4.27 ± 1.37 mg C/L), and from the rivers of the North Shore (6.49 mg C/L; Thomas 2013). Meanwhile, water in the Gulf was less concentrated in DOC, as is typical for marine environments, with surface concentrations of DOC averaging 1.18 ± 0.19 mg C/L. As water from these sources mixed, DOC concentration decreased and ultimately reached concentrations typical of marine systems. This transition, however, was not as gradual as one would have expected if this were strictly dilution, especially when looking at the sharp decline in DOC concentration in the Upper Estuary (Figure 3.1a). This sudden decline therefore was a result of one or more processes acting parallel to dilution, resulting in a removal of DOC, namely bacterial respiration of DOC, UV photo-oxidation of DOC or DOC coagulation as salinity increased and dissolved cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and other metals neutralized the negative charges of dissolved organic compounds (Buffle *et al*. 1998). Each of these processes could have affected the pool of DOC in a different way: bacterial respiration is the removal of DOC, the result of which is a net flux to DIC by consuming labile molecules, which are enriched in ^{13}C relative to the more refractory components (Hwang and Druffel, 2003), resulting in a depletion of $\delta^{13}C$ in the remaining DOC pool; UV photo-oxidation is the removal of DOC, the result of which is a net flux to DIC via the UV catalyzed oxidation of

chromophores, resulting in an enrichment of $\delta^{13}C$ in the remaining DOC pool (Lalonde *et al.* 2014); DOC coagulation is the removal of DOC, the result of which is a net flux to POC, resulting in an increase in POC concentration to accompany the decrease in DOC concentration. To our knowledge, the effect of coagulation on the $\delta^{13}C$ signature of the residual riverine DOC has never been assessed but likely is small.

The general trend of ^{13}C enrichment of DOC in the Estuary and Gulf was correlated to a decrease in concentration (Figure 3.3). This correlation was due to DOC of riverine water being more concentrated and more depleted in ^{13}C than DOC of marine waters. However, if this correlation were strictly the result of mixing between marine and riverine sources, a linear relationship, called conservative mixing (Mantoura and Woodward 1983), would have been expected when plotting concentration and isotopic signature. Instead, the plot showed deviation from linearity in the range of isotopic signatures associated with terrestrial OM, indicating removal of terrestrial DOC as riverine and marine waters mixed. The processes that could be involved in the removal of DOC are coagulation and sorption to mineral particles, both of which lead to an increase in POC, and photo-oxidation, which leads to an increase in DIC. Since an increase in POC concentration was observed at station D (Figure 3.6a.) without any significant difference in Fe:OC and %OC associated to iron (Figure 3.12), it is very likely that the main mechanism of removal of terrestrial DOC was DOC coagulation. To confirm this, DIC measurements and CO_2 degassing estimates for this station should be performed to constrain the extent of photo-oxidation, even though it is likely negligible given the very shallow light penetration depth in these highly turbid waters.

4.1.2 DOM in the USLE

Additional information can be added to the observed decrease in DOC concentration, namely the isotopic signature of these DOC samples and the POC concentration at these stations. This information pointed to DOC coagulation as being a major process, perhaps even the main process behind the loss of DOC observed in the Upper Estuary. The very high POC concentrations observed at station D (50 km from

Quebec City) coincided with the onset of the decrease in DOC concentrations, and difference in POC concentration between station D and stations closer to Quebec City was of the same order of magnitude as the decrease in DOC concentration (Figure 3.6a). It is important to note that DOC coagulation was not the only process occurring in the Upper Estuary, UV photo-oxidation and bacterial respiration were both occurring throughout the St. Lawrence Estuary and Gulf (Lalonde *et al.,* 2014). However, the water in this transition zone was very turbid and UV rays did not penetrate below the air-water interface thus UV photo-oxidation rates were low, and the importance of this mechanism was minor compared to the other removal processes. In contrast, bacterial respiration of DOC would be difficult to detect from the isotopic signatures alone since the labile molecules that would have been respired in the Upper Estuary were of the same isotopic signature as the recalcitrant molecules, resulting in little to no change in the isotopic signature of the resulting DOC.

Following the drop in DOC concentration starting at station D, there was no significant difference in DOC concentration in the Estuary until it reached station 25, or the beginning of the Lower Estuary (Figure 3.1a). At this station, the DOC concentration was higher than it was in nearby stations from the Upper Estuary. The reason for this was fresh input from the Saguenay River and Fjord, which had higher DOC concentrations than the USLE. This was consistent with the observed depletion in ^{13}C of DOC at this station (Figure 3.2): DOC from the Saguenay River was not only more concentrated (average DOC: 4.59 ± 0.99 mgC/L), but more depleted in ^{13}C (average $\delta^{13}C$: -26.08 ± 1.12), as is typical for terrestrial sources.

4.1.3 DOM in the LSLE

Throughout the LSLE, surface DOC decreased as samples were from stations further from Quebec City (more seaward), with the exception of station 21 (Figure 3.1b). The increase in DOC concentration observed at 400 km (station 21) could be explained by two DOC inputs: firstly, the direct input of riverine DOC from the North Shore Rivers would have led to an increase in DOC concentration around this location, and secondly, the heightened primary production observed in this region would have increased

the DOC concentration following the death of phytoplankton and the release of fresh organic matter to the surface waters. Furthermore, there was a ^{13}C enrichment trend in the isotopic signature of surface DOC moving seaward (Figure 3.2) and a break from that trend at station 21 in the form of a depletion in ^{13}C. This supports a strong riverine contribution at this station. This region also had an increase in POM production (Figures 3.6b, 3.7b and 3.8b), which would have been expected to lead to an increase in DOC concentration following degradation of this freshly produced marine OM. If such a process were the major source of DOC at station 21, there would also have been an increase in the $\delta^{13}C$ as opposed to the observed decrease. Thus, the higher DOC concentration observed at station 21 was likely due in greater part to the influx of riverine DOC. However, the simple addition of ^{13}C depleted riverine DOC to the estuarine DOC pool might not be in agreement with mass balance calculations based on isotopic signatures described earlier in this document (section 3.1). Based on the isotopic signature and on the DOC increase with respect to the rest of the Lower Estuary, the riverine DOC exported to the LSLE would have had to have been very depleted ($\delta^{13}C$ = -32.5 to -33‰) for it to have been the sole cause of depleted DOC at station 21. Since no isotopic values were found for DOC of the North Shore Rivers, that possibility was not dismissed, but these values would have been highly depleted for a sample of purely terrestrial OM and it therefore seems likely that another process is involved, leading to a depletion in ^{13}C.

DOC depth profiles from LSLE (Figure 3.4) stations were consistent with depth profiles previously measured in these locations (Panetta, 2008) and were typical of a strongly stratified estuary. In these systems, DOC at the surface was isolated from that in the CIL and Deep layers. The higher DOC concentration in the surface layer could be explained by two sources: riverine DOC imports and degradation of freshly produced POC. For these sources, riverine DOC was imported directly to the surface of the SLE, where it was mixed with upwelling water from the deep SLE. As for the second source, the surface layer, or euphotic zone, was the site of primary production in the water column and

was therefore a zone with readily available, fresh POC. Coupled with the higher water temperature, which increased biodegradation rates (Thamdrup *et al.,* 1998), that made the euphotic zone a region of consumption of freshly synthesized POC, which was partially degraded to DOC. The cold intermediate layer (CIL) was the coldest part of the water column, a water mass at a temperature below 1°C, and featured a sharp decline in DOC concentration in all LSLE depth profiles. This layer was formed during the winter when frigid temperatures cool the surface waters. Upon the melting of snow packs, and the influx of warmer waters, the water mass that had cooled during the winter sank and partially mixed with the deep layer, which carried the CIL landward (Gilbert *et al.,* 2005). The observed decline in DOC concentration in the depth profiles was due to degradation processes occurring in the summer, as well as when the surface water cools during autumn and winter, namely photo-oxidation and bacterial respiration, albeit at a slower rate in the fall and winter than during warmer months, with little input from rivers (much lower discharge rate at the end of the summer and in the fall compared to the spring and early summer; Hélie *et al.*, 2002) and virtually no input from primary production and degradation of POC, since photosynthesis is undetectable during winter months (Roy *et al.*, 1996). In the depth profiles of DOC samples collected in 2011 and 2013, some differences were observed between stations at depth, likely due to differences in surface primary productivity at the surface, leading to differences in POC sinking rates and degradation through the water column, and thus small differences in the production of POC-derived DOC at depth. Despite this, concentrations were much more variable in the surface layer than at depth and that was due to the uniform nature of the oceanic DOC source and the extent of degradation of DOC in the water column. Water from the deep layer of the LSLE travelled up the Laurentian Channel from the deep Gulf and that water was a mixture of North Atlantic Central Waters (NACW) and Labrador Current Waters (LCW). Since NACW originates from the deep Atlantic, the organic carbon dissolved in these waters is old and therefore recalcitrant. Thus, the DOC found in the deep LSLE should be low in concentration and highly reworked, resulting mostly in a quasi-uniform pool of DOC.

The year-to-year comparisons of DOC concentrations at a single station, station 23, showed that despite some annual differences at the surface, the DOC concentrations in the rest of the water column remained very constant (Figure 3.1). Surface DOC concentration depended on DOC influx from the rivers and degradation of POC, and therefore could greatly vary from season-to-season and year-to-year, as was seen in the 2011 depth profile of station 23. Below the surface layer, the processes affecting DOC (respiration) and the sources of DOC (cooling and sinking of the surface waters and influx of deep Atlantic water) were similar from year to year and did not lead to significant differences in DOC concentration. Thus, while surface DOC concentration was dependent on sampling time (*e.g.* shortly after the freshet or at the height of summer), DOC in the CIL and deep layer was relatively unaffected by these conditions. Therefore samples from these depths are relevant for the entire spring and summer season, if not the entire year.

4.2 Particulate Organic Matter

4.2.1 General Trends

Another interesting observation of the Upper Estuary was the variability of POC concentration, both in spatial and temporal terms (Figure 3.6a). Spatially, POC concentration dramatically rose within the first 50 km after Quebec City and, over the next 50 km, returned to a concentration similar to that observed at the head of the Upper Estuary. From that point onward, the POC concentration showed a decreasing trend until the Lower Estuary, where average POC concentrations were not significantly different from station to station.

4.2.2 POC in the USLE

The most striking feature when looking at the spatial distribution of POC concentration in the Upper Estuary was its extreme increase within the first 50 km and the very high variability associated with it. Since the area over which POC concentration increased coincided with a transition from fresh water to

brackish water (St. Lawrence River to Upper St. Lawrence Estuary), DOC was expected to coagulate in a "salting out" type of phenomenon, by which the increase in ionic strength of the solution causes hydrophobic moieties to aggregate. Thus, this sharp increase in POC concentration was likely due in part to the *in situ* formation of POC from coagulating DOC from terrestrial sources. However, despite being of the same order of magnitude as the POC increase, the change in the DOC pool was not sufficiently large to account entirely for the increase in POC concentration (DOC concentration prior to decrease: 4.52 ± 0.24 mg/L; DOC concentration after decrease: 2.06 ± 0.66 mg/L; POC maximum concentration: 4.41 ± 5.03 mg/L). Thus, other possible sources to the POC pool had to be investigated, such as influx from tributaries and particle resuspension as strong currents met a shallow sediment bed (Lucotte, 1989). Along the bottom of the USLE, there are areas that favour the resuspension of sediment particles, such as the waters becoming shallower between l'Ile d'Orleans and l'Ile aux Coudres (from depths of 40 + m to depths between 20 - 30 m) and strong currents passing over shallow flats (1 - 2 m) on the southern banks near stations DE and E. Sediment resuspension was further supported by the fact that little variation was observed in either the isotopic signatures of POC or the POM C/N atomic ratios along with the increase in POC concentration (Figure 3.7 and 3.8). Since USLE sediments are flushed annually during spring and ice melt events (Drapeau, 1990), they do not accumulate or undergo extensive diagenesis and thus should have very similar characteristics to POM of the USLE. As a whole, the data for the USLE point to a transition system from a riverine environment to a marine environment in which several processes occur, as can be seen by changes in POC concentration, but these have no net effect on POC $\delta^{13}C$ and POM C/N atomic ratio. It is likely that the spring freshet and the influx of riverine water were causes for all the variation in POC in the USLE, importing a large quantity of DOC and particulate matter, stimulating coagulation, resuspending particles from the sediment bed and directly adding to the POC pool.

4.2.3 POM in the LSLE

This effect of the spring freshet was observed throughout the SLE, explaining the large year-to-year variations observed in POC. In the LSLE, POC concentrations showed large variations (Figure 3.6b), albeit not to the extent observed in the USLE. These variations were largest at station 21 (400 km from Quebec City), where an increase in the average $\delta^{13}C$ and a decrease in the C/N atomic ratio were observed alongside the increase in average concentration and variability (Figure 3.7b and 3.8b respectively), but these variations were not only localized to that part of the Lower Estuary. In fact, based on standard deviations of POC concentrations in the LSLE, there was a minimum concentration of approximately 100 µg C/L for the system to which processes such as primary production and influx of riverine POC could add to varying degrees. The main source of added POC at station 21 was primary production, since marine photosynthesis lead to the enrichment in ^{13}C of POC and a decrease in C/N atomic ratio of POM. Upstream from station 21 are three large rivers, the Betsiamites river, the Rivière aux Outardes and the Manicouagan River, from which a combined annual average of approximately 1590 m^3/s flows into the LSLE (1591 m^3/s according to Gingras 1997, 1593.61 according to Thomas 2013, no uncertainty provided in either source) compared to the St. Lawrence River, whose average flow is 12 086 m^3/s (12 309 m^3/s according to Gingras 1997, 12 101 according to Benke and Cushing 2005, 11 335 ± 2663 according to Hélie and Hillaire Marcel 2006, and 12 600 according to Thomas 2013, only Hélie and Hillaire-Marcel provided uncertainty). As snow packs melt in the late spring, this flow is much higher, carrying with it a large amount of limiting nutrients (nitrogen, phosphorus and sulfur containing nutrients). This annual phenomenon, the freshet, initiates a short burst of intense primary production in the LSLE in the form of algal blooms. Because of this, and because sampling missions were often close in to POC concentrations at station 21 were more variable and showed isotopic signatures and C/N atomic ratios associated with increased primary production.

The POC in the SLE was more enriched in ^{13}C and had lower C/N atomic ratios in the LSLE than in the USLE (Figure 3.7b and 3.8b), indicating a shift from terrestrial to marine sources as the main contributing OM to the POM pool. This shift was due to the sinking of the terrestrial fraction of POM and its degradation the further downstream it traveled, thus unmasking POM derived from local primary production. For the most part, C/N atomic ratios and isotopic signatures were a good indicator of OM source, but they do not always show the same picture (Figure 3.9), as degradation processes can affect one measurement or the other to different extents and, in particular, lead to the decoupling of particulate carbon and nitrogen. A good example of this is the preferential degradation that was observed in the depth profiles (Figures 3.10 and 3.11). POC depth profiles of the LSLE, like DOC depth profiles, showed a sharp decrease in concentration in the top 50 m of the water column (Figure 3.10). In this top portion of the water column, a large portion of the POC pool was removed through degradation. Based on the depth profiles of the C/N atomic ratio of POM (Figure 3.11b), the observed decrease in concentration was accompanied by an increase in C/N atomic ratio, indicating a preferential removal of nitrogen containing compounds from the surface particles as they sank. However, no clear trend could be observed in the isotopic signature depth profiles (Figure 3.11a), which means that the recalcitrant POC observed at greater depths in the LSLE were from similar sources as the surface material (*i.e.* predominantly from primary production with decreasing contributions from terrestrial POM as samples were from more seaward stations), but with much less proteinaceous material, as it these were rapidly consumed in the water column (Colombo *et al.* 1996a, Colombo *et al.* 1996b, Bourgoin and Tremblay 2010).

4.2.4 The role of iron

In addition to the processes described above, the cycling of POM appears to have been affected by iron. In fact, the percentage of OC associated to iron as well as the OC:Fe atomic ratio increased as POM samples were from more seaward stations (Figure 3.12). This could point to an important role of iron in

the formation of POM in areas with higher DOC concentrations, such as the USLE, something that was observed by Helms *et al.* (2013). Furthermore, the LSLE, in which POC isotopic signatures transitioned from predominantly terrestrial to more marine, was the region of the St. Lawrence where important increases in OC:Fe atomic ratios were observed, confirming that POM shifted not only in source (terrestrial or marine source) but also in mechanism of formation, from one in which iron played an important role to one in which iron was much less present. The first mechanism could have been a form of iron mediated coagulation of DOM, analogous to the onion model of Mackey and Zirino (1994) and found in systems with high DOC concentrations such as the USLE, where terrestrial organic matter is the main source to the DOC pool. The second mechanism would have been one where the role of iron was less generalized, or its presence was incidental, such as during primary production, where iron is not the direct cause for the formation of particles, but rather is essential to the algal organisms that constitute the major source of particles. As the more labile components of POM were degraded under oxic conditions in the water column, Fe-associated OM would have been preferentially preserved, either because of their intrinsic or acquired (through Fe complexation) refractoriness (Lalonde *et al.*, 2012), thus leading to an increase in the percentage of POM associated with Fe going seaward and down the water column (Figure 3.12).

4.3 Sedimentary Organic Matter

The final pool of OC in the SLE before long-term burial is SOC. In the LSLE, the percentage of OC in surface (top 4 cm) SOC samples was 1.82 ± 0.18%, varying by less than 10% across the LSLE. This percentage was observed for both 2006 and 2007 sampling missions, suggesting that SOC was not very susceptible to annual variations. This was not surprising when considering the sedimentation rate in the LSLE: from 0.70 cm/year at the head of the Laurentian Channel (station 25) to 0.04 cm/year in the Gulf

(station 19 and lower) (Smith and Schafer, 1999). From these sedimentation rates, it appears that it would take decades of sample collection before observing changes in SOC content and composition of SOM at a single station. Bioturbation, the reworking of sediments by local lifeforms which leads to homogenization of the top few centimeters of sediment, further muddled any annual differences that could have been observed, supporting the suggestion that decades of sample collection would be needed to observe changes in SOC content and SOM composition. A comparison (t-test, C.L. 95%) between this data and the data measured by Pocklington *et al.* in 1973 revealed an increase in percentage of OC in sediments at station 23 (1.72 ± 0.12 % compared to 1.07 % at station 51 in Pocklington *et al.,* 1973) and station 21 (1.74 ± 0.02 % compared to 1.39 % at station 82 in Pocklington *et al.,* 1973). This higher percentage could have been the result of an increase of the amount of OC that was deposited in LSLE sediments, but it could also have been the result of the harsher method designed to eliminate carbonates in the sediment: Pocklington *et al.* used direct addition of an acid, which would lead to losses of OM that is soluble in water or acid, whereas this method used acid in the vapor phase. The lack of observable difference in percentage of OC in sediments, despite a distinct shift in the composition of the OM, as attested by the important increase in $\delta^{13}C$ (Figure 3.13) and decrease in C/N atomic ratio (Figure 3.14), pointed to processes other than the sedimentation of freshly produced OM as the main controlling factors behind the preservation of SOM in the sediments of the LSLE.

Some potential factors controlling the preservation of OC in sediments have been suggested such as O_2 concentration (Gilbert *et al.*, 2005, Katsev *et al.*, 2007, Alkhatib *et al*., 2012) and temperature (Thamdrup *et al.,* 1997, Gilbert *et al.*, 2005). Furthermore, iron oxides have also been linked to OC preservation in sediments (Lalonde *et al.,* 2012). Both oxygen concentration and water temperature are certainly factors in the degradation and bacterial reworking of SOM, but they cannot explain the uniformity of the OC content in sediments. Oxygen concentration in bottom waters of the SLE decreases as bottom waters travel from the Gulf to the head of the Laurentian Channel (Gilbert *et al.*, 2005), reaching a minimum at

station 23, where the concentration is at the threshold for hypoxia (62.5 µmol/L). The concentration gradient observed along the Laurentian Channel is attributed to the consumption of oxygen with the deep landward current as the only source of replenishment (Gilbert, 2005). Oxygen is consumed in this system by bacterial respiration of OM in sinking particles and surface sediments (Gilbert *et al.*, 2005, Katsev *et al.,* 2007, Alkhatib *et al.,* 2014), and thus its concentration may be controlled to some extent by the local sedimentation rate (higher rate, more oxygen consumption). If oxygen concentration controlled respiration of sinking particles and freshly deposited SOC, higher respiration rates would have been expected where oxygen was most readily available (*i.e.* the more marine locations). This is not the case: marine locations, which have a lower sedimentation rate, had the same OC content in sediments, suggesting lower respiration rates despite the higher oxygen availability. As for temperature, it is controlled by the relative proportions of source waters (NACW and LCW) and therefore, at any one time, it does not significantly vary in bottom waters along the Laurentian Channel (Gilbert *et al.*, 2005) and therefore cannot account for the inferred differences in respiration rates that would lead to a uniform OC contents in sediments of the LSLE. In contrast, the iron content of sinking particles could explain, at least in part, the differences in respiration rates. Interactions between iron oxides and OC have been linked to OC preservation in sediments (Lalonde *et al.,* 2012), and as shown in Figure 3.12a, a greater percentage of OC in sinking particles was associated to iron as samples were from more seaward stations. It is conceivable that the OC interactions with iron in particles serve to protect it from respiration during sedimentation and early diagenesis and thus go some way towards explaining the inferred differences in respiration rates in the deep LSLE.

In contrast to POM where C/N atomic ratio and isotopic signatures were generally correlated with frequent deviations from the trend, C/N atomic ratio and isotopic signatures of SOM showed stronger correlation (Pearson coefficient -0.74) (Figure 3.17). This suggests that the cumulative effect of the extensive degradation and reworking of OM prior to burial affected C/N atomic ratios and isotopic

signatures proportionally and leaved the recalcitrant OM with characteristics that are shifted from those of the source OM, rather than unrecognizable.

As with the percentage of OC at the surface of sediments, depth profiles of SOC in the LSLE were very similar to one another (Figure 3.17), starting at OC contents that were not statistically different from one another and exhibiting strong to very strong negative correlations with sediment depth (coefficients of -0.86 for station 25, -0.87 for station 23, -0.83 for station 22, -0.95 for station 21, and -0.70 for station 20). All stations, with the exception of station 25, showed a decrease of the same magnitude in the top 30 cm, a result of bacterial degradation after the deposition of OM on the LSLE floor. The decrease in OC content in depth profiles was accompanied by a depletion in ^{13}C and an increase in C/N atomic ratio, both of which are characteristic of biochemical fractionation due to bacterial respiration (Figure 3.16). During respiration, bacteria consume labile compounds such as proteins (less depleted in ^{13}C than the bulk OC, and lower C/N atomic ratio than the bulk OM) and sugars (less depleted in ^{13}C than the bulk OC), leaving behind more refractory compounds (lipids and lignin that are more depleted in ^{13}C and have higher C/N atomic ratios) and thus changing both of these characteristics in the remaining OM by biochemical fractionation rather than isotopic fractionation. Depth profiles of C/N atomic ratio of SOM and isotopic signatures showed a continuation of the trend observed in surface sediments, namely an enrichment of ^{13}C and a reduction of C/N atomic ratio as samples were from more seaward stations. This suggested that despite the extensive degradation and reworking of the OM in sediments, some identifying characteristics of the original source of this OM remained. Based on sediment extractions and isotopic measurements performed by our lab in recent years, these identifying characteristics may be measurable in the refractory components composing the bulk of OM in sediments: they are less depleted in ^{13}C at marine stations than they are in stations with a stronger terrestrial influence. For example, lipids and fatty acids in sediments at station 25 might have a more depleted signature than lipids in sediments of station 20.

4.4 Preliminary Budget and Comparison to Similar Systems

When information about OC pool sizes and fluxes from other studies of the SLE and its tributaries, briefly described in the introduction, is added to the information collected in this project (summarized in Table 1), a preliminary OC budget could be calculated. This type of calculation is useful to evaluate how a system is behaving at a large scale, and whether current models can accurately describe or predict the general flux of OC in the system. Systems like the SLE are typically described as transition areas between rivers, which are usually net sources of carbon to the atmosphere, and marine systems, which are net sinks of carbon for the atmosphere. In other words, rivers annually export and sequester less OC than they import, leading to a positive flux of OC to the atmosphere, and marine systems annually export and sequester more OC than they import, leading to a net uptake of atmospheric CO_2. Furthermore, continental shelves around the world have been speculated to function as "carbon pumps", acting as net sinks for atmospheric CO_2 and being a source of carbon for the open ocean (Tsunogai *et al.,* 1999). Some areas, such as the East China Sea (Tsunogai *et al.,* 1999) and the North Sea (Thomas *et al.,* 2005, Bozec *et al.,* 2005) have been confirmed as acting this way. Thus, the SLE is expected to have characteristics from both riverine and marine systems, of being a system that transitions from the net source that is the St. Lawrence River to what could be a "carbon pump" in the St. Lawrence Gulf.

Source	Water Flow (m^3/s)	DOC Concentration (mg C/L)	POC Concentration (µg C/L)
St. Lawrence River	12 086 ± 514[a,b,c,d]	3.85 ± 0.81[c]	287 ± 53
USLE	15 185 ± 191*[b]	1.78 ± 0.56	107 ± 50
Saguenay	1615 ± 191[a,d]	4.27 ± 1.37	1975 ± 769
North Shore Rivers	1592[d]	6.49[d]	1824 ± 783**[d]
LSLE	21 000[a]	1.54 ± 0.28	122 ± 42

Table 4.1. Water flows from sources to the St. Lawrence Estuary and Gulf with their respective DOC and POC concentrations. a) Data from Gingras, 1997; b) Data from Benke and Cushing, 2005; c) Data from Hélie and Hillaire-Marcel, 2006; d) Data from Thomas, 2013. *Calculated by subtracting Saguenay flow from combined flow of USLE and Saguenay (16 000 m^3/s). ** Calculated by multiplying the provided suspended matter concentration (67.54 mg/L) by average OC content observed in Saguenay (2.70 ± 1.16 % OC)

Flowing into this system at Quebec City are $1.20 \pm 0.05 \times 10^4$ m^3/s of freshwater (average of 4 yearly fluxes taken from Gingras (1997), Benke and Cushing (2005), Hélie and Hillaire-Marcel (2006), and Thomas (2013)), and the average DOC concentration at the head of the USLE is 3.85 ± 0.81 mg C/L (annual average based on samples collected every two weeks between June 1997 and June 2003, Hélie and Hillaire-Marcel, 2006), resulting in $1.47 \pm 0.32 \times 10^{12}$ g of DOC flowing each year into the USLE. To that is added POC (287 ± 53 µg C/L, results from this study), resulting in $0.110 \pm 0.021 \times 10^{12}$ g of POC each year, for a total of $1.58 \pm 0.32 \times 10^{12}$ g of OC entering the USLE at Quebec City. No flows specific to the USLE were found for the region prior to reaching the Saguenay River, but the combined flows of the USLE and the Saguenay River are 16 800 m^3/s (Benke and Cushing, 2005; no uncertainty provided), and flow from the Saguenay has been documented at 1615 ± 191 m^3/s (Gingras, 1997, Thomas, 2013), leaving 15 185 ± 190 m^3/s for the USLE. Based on the average DOC and POC concentration for the USLE at station K (1.78 ± 0.56 mg C/L and 107 ± 50 µg C/L respectively), the USLE exports $0.853 \pm 0.269 \times 10^{12}$ g of DOC and $0.051 \pm 0.024 \times 10^{12}$ g of POC to the LSLE each year, to which is added $0.148 \pm 0.072 \times 10^{12}$ g of DOC and $0.101 \pm 0.041 \times 10^{12}$ g of POC from the Saguenay. The total OC contribution to the LSLE from the USLE amounts to $0.904 \pm 0.273 \times 10^{12}$ g of OC per year, whereas the Saguenay contributes $0.248 \pm 0.083 \times 10^{12}$ g per year, resulting in $1.153 \pm 0.282 \times 10^{12}$ g of OC flowing into the LSLE. It is interesting to note here that there is a significant difference between the OC flowing into and out of the USLE ($0.674 \pm 0.416 \times 10^{12}$ g of OC per year), with more flowing in than there is flowing out. Since sediments are annually flushed from the USLE during spring and ice melt events (Drapeau, 1990), it is difficult to truly account for this temporary removal of OC from this system. However, considering the sedimentation for the entire LSLE accounts for less than the difference calculated above, it is safe to assume that the USLE is a net sink for OC. Furthermore, this OC must be removed from the system, in this case by degradation processes resulting in a positive net flux of inorganic carbon (carbonates and CO_2). To this flux of inorganic carbon from degradation processes is added the degassing of CO_2 from

freshwater discharged by rivers, which are supersaturated in CO_2 due to the high activity of respiration processes in these systems, which exceed photosynthetic uptake (Kling *et al.,* 1991). This is in agreement with the expectation that, as the terrestrial section of a transition system, the USLE is a net source of carbon to the atmosphere.

In addition to water from the USLE and Saguenay, several major rivers on the North Shore contribute to the LSLE, with two sources stating their combined flow as being 1592 m^3/s (1 591 m^3/s as per Gingras, 1997, 1 593.61 m^3/s as per Thomas, 2013; no uncertainty provided in either case). Thomas' 2013 study (based on sampling missions in May, August, and November of 2010, as well as March and May of 2011) also reports average DOC concentrations for these rivers (6.49 mg C/L, no uncertainty provided) and average suspended particle matter concentration (67.54 mg/L, no uncertainty provided), without providing information on the OC content of these particles. For the purposes of this estimated budget, particles were assumed to have the same OC content as Saguenay particle, namely 2.70 ± 1.16 %. With these data and approximations, the North Shore Rivers are estimated to contribute 0.326×10^{12} g of DOC and $0.092 \pm 0.039 \times 10^{12}$ g of POC each year for a total of $0.418 \pm 0.039 \times 10^{12}$ g of OC per year. The combined effect of these sources amounts to $1.340 \pm 0.426 \times 10^{12}$ g of OC per year. Unlike the USLE, sediments deposited in the LSLE accumulate for long-term burial at a rate of 8.8×10^{12} g of raw sediment per year (estimated average for the entire LSLE, integrated from variable sedimentation rates along the Laurentian Channel by Smith and Schafer, 1999). Considering the percentage of OC in the LSLE (1.82 ± 0.18 %), sedimentation accounts for the removal of $0.160 \pm 0.016 \times 10^{12}$ g of OC per year, to which is added the LSLE exports to the Gulf, 21 000 m^3/s flow into the Gulf (Environment Canada, 1997, no uncertainty provided), accounting for $1.02 \pm 0.19 \times 10^{12}$ g of DOC and $0.081 \pm 0.028 \times 10^{12}$ g of POC each year, for a total of $1.10 \pm 0.19 \times 10^{12}$ g of OC exported to the Gulf each year. These flux values do not allow for a clear picture in the LSLE: when accounting for all the OC fluxes calculated here, the LSLE appears to import more OC than it exports ($0.078 \pm 0.465 \times 10^{12}$g of OC per year), but the uncertainty on

this value is such that it cannot be said for certain whether or not the LSLE is a net source or sink of carbon.

The magnitude of OC fluxes calculated here are similar to those observed in the Baltic Sea. The sum of OC imported annually from riverine sources (St. Lawrence River, Saguenay River and North Shore Rivers) amounts to $2.24 \pm 0.33 \times 10^{12}$ g of OC per year, from a combined water flow of 15 293 m^3/s. This value is significantly less, but comparable to that from the riverine sources to the Baltic Sea: $4.09 \pm 0.77 \times 10^{12}$ g of OC per year, from a combined flow of 10 429 m^3/s (Kuliński and Pempkowiak, 2011). The Baltic Sea also has a higher sedimentation rate, accounting for a net $3.87 \pm 1.12 \times 10^{12}$ g of OC per year (Kuliński and Pempkowiak, 2011), compared to the removal of $0.160 \pm 0.016 \times 10^{12}$ g of OC per year in the SLE. Considering the differences in OC delivered to the Baltic Sea (between 1.3 and 2.5 more OC imported from tributaries each year) with a fraction of the annual water flow (approximately 0.70 times the amount flowing into the SLE), the main tributaries to the Baltic Sea are much more concentrated in OC than those of the SLE. This greater OC flux coupled to the much higher sedimentation rate of OC in the Baltic Sea (17 times more OC sequestered through sedimentation), points to a system that is much more dynamic in terms of OC turnover.

The description of the carbon cycle in the Baltic Sea is much more complete than the current description of the carbon cycle in the SLE. The former includes reliable water fluxes accounting for 80% of the total river runoff, well documented water exchanges between the Baltic Sea and North Sea (flow is restricted between these bodies and exchanges occur in episodes of large volume transfers), and fluxes of inorganic carbon, allowing for reliable identification of OC and IC sources and sinks. For this to be possible in the SLE, several key pieces of information are needed: accurate and up to date flows from the SLE's tributaries, including deep water flowing into the LSLE from the Gulf (most of the information available is almost 20 years old, and none of it includes confidence intervals); reliable DOC and POC

concentrations for the North Shore Rivers (only averages without standard deviations were available, despite riverine POC concentrations varying by 1 to 2 orders of magnitude in a typical year); IC information for the entire system (fluxes from tributaries, flux to the Gulf and uptake from the atmosphere); and, in the interest of making a budget that reflects the cycling of carbon for the entire year, samples that have been collected throughout the year.

5 General Conclusion

To our knowledge, this work is the most complete description of the cycling of OC in the SLE. With the information at our disposal, we can say with some confidence that the USLE is a net sink for OC, despite not have a quantitative value for the annual flushing of USLE sediments, as there is much more OC flowing into this portion of the SLE than out of it. Based on the fact that the USLE has no means of long term storage for OC and that the riverine water flowing in is supersaturated with CO_2, it can be inferred that the USLE is also a net source of carbon to the atmosphere.

The LSLE is more difficult to label since the calculations done with the information available do not conclusively point to it being a net source or sink of OC, much like the Baltic Sea, which has uncertainties greater than its net fluxes for OC and IC. What can be said about it is that the LSLE acts as a sink for 0.160 $\pm$ 0.016 $\times 10^{12}$ g of OC per year through sedimentation, of which a portion escapes degradation and is sequestered on geological timescales. It is important to note that the samples on which these calculations were made were collected during periods of high primary production in the LSLE, periods during which the potential as a net sink for atmospheric carbon would be greatest. It is therefore very likely that on an annual basis, the LSLE would act as a net sink for OC and a net source of carbon to the atmosphere.

However, this speculation points to an unfortunate truth: we are still far from a comprehensive carbon budget for this system. The most important limitation to the relevance of the data presented here is that it is only representative of the SLE during the summer months, since all sampling occurred during May, June and July. In order to create a budget representative of the seasonal changes in the SLE, samples would have to be collected throughout the year. Furthermore, there is a need for up-to-date information on annual water fluxes and accurate concentrations of DOC, POC and DIC associated with these fluxes in order to constrain the carbon exchanges that occur at the set boundaries. Finally, to truly identify the

importance of the USLE and LSLE as carbon sources to the atmosphere, more information is needed on CO_2 exchanges between the atmosphere and the SLE.

In comparison to the Baltic Sea, the SLE is a system that involves much less OC. The annual water flow to the Baltic Sea is lower, but carries much more OC (between 1.3 and 2.5 times more OC) and the sedimentation rate of OC in the Baltic Sea is an order of magnitude greater than sedimentation in the SLE. Although the SLE's role in the global carbon cycle might be muted when compared to its annual water flux, it is still a significant system, especially in the light of climate change. Current global warming trends may very well indicate wetter climate for the St. Lawrence and its tributaries, which could mean an increase in runoffs from agricultural lands to the SLE which, coupled with higher temperatures, would lead to an increase in primary production, which in turn would lead to an increased flux of fresh OM to the deep waters of the LSLE and exacerbate the hypoxia observed there, potentially expanding the hypoxic zone or further depleting the oxygen concentration in waters that are currently hypoxic.

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Appendix A: Raw Data

In the following tables, several abbreviations and symbols were used to reduce the size of the column headers: [DOC] and [POC] for the DOC and POC concentrations, $\delta^{13}C$ for the isotopic signatures of DOC and POC, [SPM] for the concentration of suspended particulate matter, [PN] for the concentration of particulate nitrogen, and C/N for the atomic ratio in the particulate phase. A cell with "n.a." indicates a sample for which the dimension in question was not measure because the sample was lost or was not collected, ran out, or was too old to reliably measure.

Table A.1: Raw data for the samples collected in 2003.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
A	3	0	4.38	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	8.79	0.11
A	5	0	4.59	n.a.	8.33	0.24	-25.98	23.64	11.63	8.78	0.11
A	10	0	4.38	n.a.	10.07	0.36	-25.97	32.48	12.94	8.79	0.46
A	25	0	4.39	n.a.	8.01	0.28	-26.04	27.71	11.88	8.77	0.12
B	5	20	4.30	n.a.	9.86	0.27	-25.96	25.25	12.50	8.68	0.11
B	20	20	4.44	n.a.	13.40	0.40	-25.80	38.57	12.21	8.63	0.11
C	10	37	4.52	n.a.	147.73	3.68	-25.52	313.26	13.71	8.01	0.10
D	10	50	4.49	n.a.	361.33	7.96	-25.46	818.14	11.36	7.43	1.30
E	5	75	4.30	n.a.	50.00	0.98	-25.63	94.65	12.04	6.52	5.54
E	15	75	3.45	n.a.	50.20	0.63	-25.58	60.10	12.17	4.36	11.10
E	20	75	3.07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.06	13.25
E	27	75	2.89	n.a.	62.44	0.76	-25.53	70.32	12.58	3.33	17.00
F1	4	100	2.87	n.a.	51.23	0.63	-25.42	58.66	12.46	4.35	14.44
F1	10	100	1.98	n.a.	56.83	0.38	-25.37	38.50	11.39	3.40	13.38
F1	20	100	1.61	n.a.	131.79	0.99	-25.33	98.85	11.67	1.64	25.49

F1	40	100	1.53	n.a.	158.80	1.72	-25.51	167.29	11.98	1.42	26.41
F1	60	100	2.37	n.a.	180.00	1.95	-25.59	176.52	12.91	1.37	26.63
F2	4	97	3.28	n.a.	58.03	0.37	-24.90	36.08	12.12	3.74	16.33
F2	10	97	2.30	n.a.	32.50	0.22	-25.16	20.91	12.29	3.05	19.99
F2	30	97	1.38	n.a.	82.00	0.56	-25.27	54.04	12.06	1.07	27.90
F2	45	97	1.33	n.a.	86.00	0.65	-25.25	63.93	11.85	1.04	28.05
G	5	120	2.80	n.a.	24.20	0.22	-25.27	21.72	11.58	4.49	14.03
G	20	120	1.85	n.a.	31.83	0.21	-24.92	19.45	12.62	2.06	23.89
G	40	120	1.43	n.a.	64.00	0.82	-24.86	67.70	14.10	1.18	27.44
G	87	120	1.16	n.a.	100.00	0.64	-25.40	57.76	12.97	0.55	30.06
G	5	120	2.36	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.79	17.08
G	20	120	1.66	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.49	26.27
G	40	120	1.41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.13	27.67
G	87	120	1.41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.73	29.39
G	5	120	2.66	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.15	16.02
G	20	120	2.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.75	21.46
G	40	120	1.54	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.36	26.91
G	87	120	1.25	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.88	28.79
G	20	120	1.65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.73	25.34
G	40	120	1.52	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.43	26.46
G	87	120	1.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.68	29.60
G	5	120	2.64	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.15	16.48
G	20	120	1.57	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.46	26.41
G	40	120	1.41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.01	28.20
G	87	120	1.17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.68	29.61
G	5	120	2.82	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.52	15.26
G	20	120	1.99	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.60	22.38
G	40	120	1.47	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.48	26.53
G	87	120	1.63	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.77	29.27
H	5	140	3.20	n.a.	20.90	0.20	-25.43	20.51	11.56	4.92	13.77
H	20	140	1.62	n.a.	33.40	0.18	-24.97	19.47	10.94	0.99	28.52

H	50	140	1.23	n.a.	21.65	0.14	-25.30	13.50	11.78	0.41	30.73
I	5	160	2.75	n.a.	18.53	0.16	-25.15	13.54	13.92	4.46	16.83
I	20	160	1.99	n.a.	28.70	0.13	-25.12	12.77	12.32	1.77	25.64
I	100	160	1.33	n.a.	10.45	0.06	-25.31	5.37	13.86	0.47	30.92
J	5	180	2.46	n.a.	28.25	0.17	-25.41	17.31	11.41	3.27	20.65
J	20	180	1.39	n.a.	27.34	0.10	-25.25	13.83	8.64	1.13	29.11
J	100	180	1.32	n.a.	21.25	0.09	-24.62	9.42	10.61	0.33	31.48
K	10	200	1.97	n.a.	33.20	0.17	-24.53	19.64	10.24	2.84	24.95
K	46	200	1.35	n.a.	36.89	0.11	-24.92	12.67	9.86	0.58	31.26
K	90	200	1.13	n.a.	35.40	0.13	-24.52	11.69	12.90	0.33	32.37

Table A.2: Raw data for the 2006 mission in the USLE and Station 23.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	δ^{13}C DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	δ^{13}C POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
A	40	0	5.10	-26.80	6.26	0.22	-25.80	n.a.	n.a.	17.17	0.11
EF	3	87	2.33	-26.45	60.25	0.90	-25.60	n.a.	n.a.	12.04	9.66
EF	10	87	3.08	-27.46	n.a.	n.a.	n.a.	n.a.	n.a.	11.42	10.89
F1	3	100	1.76	-25.10	91.67	1.29	-25.60	n.a.	n.a.	10.61	13.41
F1	11	100	1.96	-25.86	n.a.	n.a.	n.a.	n.a.	n.a.	7.50	19.99
F1	45	100	2.52	-26.93	n.a.	n.a.	n.a.	n.a.	n.a.	6.21	22.70
F1	3	100	2.71	-26.73	n.a.	n.a.	n.a.	n.a.	n.a.	9.63	15.30
F1	11	100	2.03	-27.34	n.a.	n.a.	n.a.	n.a.	n.a.	8.10	18.62
F1	43	100	1.83	-27.02	n.a.	n.a.	n.a.	n.a.	n.a.	5.88	23.44
G	20	120	2.18	n.a.	29.29	0.06	-25.86	n.a.	n.a.	7.33	20.55
23	70	300	0.95	-22.71	n.a.	n.a.	n.a.	n.a.	n.a.	1.05	31.94
23	100	300	0.79	n.a.	4.41	0.00	-25.02	n.a.	n.a.	1.04	32.47
23	150	300	0.82	-22.00	5.49	0.01	-24.06	n.a.	n.a.	3.33	33.72

23	200	300	0.74	-21.68	4.26	0.00	-24.71	n.a.	n.a.	4.37	34.18
23	250	300	0.68	-21.49	6.12	0.01	-26.15	n.a.	n.a.	4.77	34.35
23	300	300	0.72	-21.67	9.58	0.01	-25.36	n.a.	n.a.	5.10	34.50
23	330	300	0.73	-21.63	9.52	0.01	-26.55	n.a.	n.a.	5.20	34.55

Table A.3: Raw data for the 2006 mission in the LSLE and Gulf.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	δ^{13}C DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	δ^{13}C POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
23	0.5	300	1.71	-25.57	7.83	0.03	-23.34	n.a.	n.a.	8.80	25.68
23	10	300	1.63	-25.36	5.28	0.02	-23.42	n.a.	n.a.	8.83	26.80
23	20	300	1.63	-24.93	9.28	0.03	-22.99	n.a.	n.a.	8.47	27.06
23	30	300	1.55	-24.60	3.45	0.01	-23.38	n.a.	n.a.	5.64	28.01
23	40	300	1.09	-23.99	3.98	0.01	-24.10	n.a.	n.a.	4.59	29.65
23	50	300	1.10	-23.72	4.56	0.01	-23.95	n.a.	n.a.	2.69	30.41
22	5	350	1.46	-23.44	7.20	0.08	-25.40	n.a.	n.a.	10.90	25.80
22	60	350	0.79	-22.47	8.20	0.03	-24.50	n.a.	n.a.	0.72	32.19
22	300	350	0.76	-20.12	7.60	0.04	-23.30	n.a.	n.a.	5.35	34.65
21	5	400	1.27	-23.44	12.70	0.30	-24.98	n.a.	n.a.	12.57	26.87
20	10	450	1.22	-20.45	7.00	0.09	-25.10	n.a.	n.a.	13.91	29.32
20	40	450	0.78	-21.01	n.a.	n.a.	n.a.	n.a.	n.a.	0.60	32.06
20	210	450	0.58	-19.72	8.10	0.03	-24.76	n.a.	n.a.	4.95	34.43
20	320	450	n.a.	n.a.	8.40	0.02	-25.20	n.a.	n.a.	5.44	34.75
19	10	525	1.08	-20.32	8.40	0.08	-24.70	n.a.	n.a.	13.00	29.08
18	1	600	1.12	-21.61	7.60	0.15	-24.33	n.a.	n.a.	15.07	28.91
18	15	600	0.91	-20.34	7.90	0.14	-24.69	n.a.	n.a.	12.60	28.95
18	60	600	0.64	-20.54	n.a.	n.a.	n.a.	n.a.	n.a.	0.51	31.94
18	100	600	0.66	-20.82	n.a.	n.a.	n.a.	n.a.	n.a.	1.00	32.72
18	370	600	0.69	-20.79	10.20	0.02	-24.23	n.a.	n.a.	5.37	34.80
23	0.5	300	1.71	-25.57	7.83	0.03	-23.34	n.a.	n.a.	8.80	25.68

Table A.4: Raw data for the samples collected in 2007.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
DE	2	60	4.11	-26.50	252.39	5.70	-25.79	n.a.	n.a.	9.45	4.89
DE	15	60	3.55	-27.00	n.a.	n.a.	-25.90	n.a.	n.a.	9.38	5.07
F1	2	100	2.06	-25.20	77.00	0.86	-25.10	91.63	10.95	7.02	12.32
F1	15	100	2.33	-27.60	44.20	0.62	-27.52	71.16	10.18	4.46	20.03
F1	40	100	1.42	-24.50	94.00	1.27	-24.92	184.24	8.05	2.17	26.64
I	2	160	2.14	-27.70	n.a.	n.a.	-27.08	n.a.	13.45	4.42	21.02
I	25	160	1.37	-23.00	9.41	0.06	-26.57	7.25	10.28	1.76	27.79
I	140	160	1.09	-21.50	22.55	0.10	-27.80	9.47	12.06	0.58	30.92
K	2	200	1.51	-23.90	12.24	0.10	-25.38	6.85	17.31	2.68	26.99
K	25	200	1.41	-23.80	8.61	0.05	-25.35	7.23	8.66	1.27	29.82
K	90	200	0.84	-22.10	9.09	0.05	-25.26	7.64	7.86	1.31	32.72
23	5	300	n.a.	-24.42	6.99	0.12	-25.33	n.a.	n.a.	5.07	23.94
23	25	300	0.93	-22.29	n.a.	n.a.	n.a.	n.a.	n.a.	0.40	30.78
23	50	300	n.a.	n.a.	28.11	0.58	-23.90	n.a.	n.a.	-0.62	32.21
23	75	300	0.83	-22.43	n.a.	n.a.	n.a.	n.a.	n.a.	-0.38	32.49
23	150	300	0.70	-22.00	n.a.	n.a.	n.a.	n.a.	n.a.	2.83	33.54
23	200	300	n.a.	-28.07	29.89	0.03	-28.07	4.19	7.86	4.28	34.14
23	250	300	0.66	-21.59	35.03	0.25	-24.27	n.a.	n.a.	5.13	34.52
23	300	300	0.69	-21.80	27.30	0.03	-28.89	3.82	9.89	5.23	34.58
23	330	300	0.78	-21.64	24.30	n.a.	n.a.	n.a.	n.a.	5.23	34.58
22	2	350	1.87	-22.20	10.08	0.55	-19.78	107.23	5.95	6.41	22.66

22	50	350	n.a.	n.a.	30.60	0.44	-21.38	77.11	6.73	-0.58	32.17
22	240	350	n.a.	-22.61	3.32	0.02	-22.61	2.79	7.81	4.68	34.30
22	305	350	n.a.	-22.81	4.00	0.02	-22.81	3.92	7.06	5.14	34.53
21	2	400	1.96	-25.30	8.61	0.42	-19.43	95.17	5.13	5.48	25.34
21	19	400	n.a.	n.a.	3.38	0.05	-22.52	8.98	6.91	-0.68	32.20
21	60	400	n.a.	n.a.	3.74	0.02	-24.14	3.66	6.60	0.27	32.70
21	150	400	n.a.	n.a.	4.69	0.02	-25.11	3.28	7.81	0.27	32.70
21	250	400	n.a.	-23.74	3.41	0.02	-23.74	2.39	7.49	5.06	34.40
21	300	400	n.a.	-24.32	3.90	0.02	-24.32	3.27	7.18	5.43	34.70
20	2	450	1.31	-22.80	7.26	0.17	-21.21	25.41	7.84	3.65	31.80
20	25	450	1.48	-23.40	31.88	0.71	-20.90	n.a.	n.a.	1.43	32.08
20	75	450	n.a.	n.a.	24.10	0.04	-22.19	6.75	7.19	2.57	33.43
20	224	450	n.a.	-23.02	2.42	0.02	-23.02	2.71	8.02	5.36	34.62
20	250	450	n.a.	-25.98	54.40	0.43	-25.98	7.62	n.a.	5.47	34.69

Table A.5: Raw data for the samples collected in 2009.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
B	3	20	n.a.	n.a.	10.30	0.52	-26.90	54.28	11.07	15.34	0.11
D	3	50	4.81	n.a.	51.89	0.86	-26.33	69.36	14.39	12.71	5.55
DE	3	60	4.48	n.a.	142.40	2.27	-26.09	180.85	14.63	12.80	5.33
E	3	75	4.77	n.a.	65.00	1.22	-26.37	100.43	14.18	13.63	3.94
F1	3	100	2.44	n.a.	115.60	0.76	-26.43	68.78	12.94	8.63	15.75
F1	40	100	3.42	n.a.	24.00	0.23	-26.35	25.32	10.77	3.17	27.09
G	3	120	3.24	n.a.	14.60	0.15	-26.30	14.53	11.96	6.86	19.96
G	50	120	2.55	n.a.	26.40	0.18	-26.45	18.48	11.51	4.03	25.55
G	85	120	2.54	n.a.	55.17	0.35	-26.14	30.90	13.16	2.23	28.91
H	3	140	2.90	n.a.	16.87	0.13	-26.51	13.41	11.59	6.52	21.02
H	50	140	2.07	n.a.	15.85	0.11	-26.37	8.96	13.75	1.50	30.29

I	3	160	3.04	n.a.	n.a.	n.a.	-26.63	n.a.	11.71	6.75	20.97
I	30	160	2.38	n.a.	10.40	0.05	-26.32	6.29	8.86	2.50	28.99
I	144	160		n.a.	11.80	0.08	-25.67	7.08	13.10	1.78	30.59
J	3	180	3.02	n.a.	14.40	0.04	-26.58	5.11	9.37	6.45	22.00
J	20	180	2.45	n.a.	9.00	0.09	-23.85	11.97	8.53	3.32	28.77
J	114	180		n.a.	12.97	0.09	-25.97	10.89	9.70	1.89	30.56
K	3	200	2.47	n.a.	8.87	0.06	-25.85	6.48	10.44	3.64	27.14
K	10	200	2.32	n.a.	8.33	0.07	-26.03	8.83	9.64	3.22	27.78
K	50	200	2.32	n.a.	7.63	0.06	-24.59	7.94	9.02	2.32	29.77
K	90	200	2.37	n.a.	5.36	0.05	-24.65	6.81	9.39	1.43	30.95
25	3	215	2.33	n.a.	n.a.	n.a.	-24.05	n.a.	7.88	4.65	28.72
25	50	215	2.31	n.a.	n.a.	n.a.	n.a.	n.a.	12.08	-0.74	32.28
25	300	215	1.90	n.a.	13.03	0.06	-25.67	5.47	12.06	4.87	34.42
25	317	215	1.79	n.a.	12.73	0.06	-25.66	5.66	12.32	4.90	34.43
24	3	250	2.59	n.a.	n.a.	n.a.	-25.97	n.a.	10.37	4.01	28.09
24	50	250	1.92	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-0.48	32.44
24	300	250	1.90	n.a.	6.22	0.04	-25.86	3.83	11.50	5.01	34.47
24	310	250	1.78	n.a.	6.28	0.03	-26.05	3.05	11.8	5.01	34.47
23	2	300	2.45	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.41	27.84
23	3	300	n.a.	n.a.	11.72	0.39	-22.62	56.85	8.01	6.35	27.91
23	50	300	1.80	n.a.	8.90	0.09	-23.45	11.44	9.16	-0.36	32.31
23	300	300	1.83	n.a.						5.14	34.53
23	333	300	n.a.	n.a.	21.80	0.08	-25.67	7.96	12.10	5.17	34.55
23	338	300	1.66	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.17	34.55
22	3	350	1.66	n.a.	5.75	0.09	-24.96	11.33	9.13	6.23	27.16
22	50	350	2.04	n.a.	2.99	0.03	-25.63	2.74	10.95	-0.79	31.88
22	110	350		n.a.	2.97	0.02	-24.41	2.64	9.20	-0.16	32.56
22	300	350	0.70	n.a.	5.42	0.02	-25.81	3.06	9.31	5.09	34.51
21	300	400	1.74	n.a.	4.08	0.02	-25.91	2.59	10.19	5.22	34.57
21	3	400	3.19	n.a.	n.a.	n.a.	-25.55	n.a.	9.07	9.35	25.70
20	3	450	1.99	n.a.	4.92	0.05	-26.19	6.59	9.23	6.79	30.71

20	50	450	1.98	n.a.	3.88	0.04	-26.39	3.49	14.25	-0.77	32.31
20	300	450	n.a.	n.a.	3.93	0.02	-25.43	2.87	9.14	5.30	34.63
20	320	450	2.02	n.a.	7.73	0.03	-25.95	3.48	9.93	5.32	34.64

Table A.6: Raw data for the samples collected in 2010.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
23	3	300	1.72	n.a.	11.07	0.39	-22.97	51.48	8.82	6.13	28.69
23	70	300	1.11	n.a.	5.59	0.08	-22.73	10.44	9.10	0.59	32.08
23	300	300	0.73	n.a.	9.10	0.07	-24.88	6.40	13.65	4.71	34.35
23	330	300	0.74	n.a.	9.10	0.08	-25.02	7.03	13.61	4.72	34.36
22	3	350	1.44	n.a.	5.96	0.25	-24.97	31.86	9.00	9.56	27.25
22	70	350	1.74	n.a.	3.53	0.07	-23.18	6.95	11.17	0.17	32.01
22	304	350	0.78	n.a.	3.55	0.05	-24.13	4.84	12.47	4.78	34.38
21	3	400	1.35	n.a.	5.56	0.14	-23.08	14.93	10.56	11.27	29.22
21	70	400	0.90	n.a.	3.33	0.05	-22.41	5.87	10.32	0.10	32.09
21	305	400	0.71	n.a.	3.63	0.05	-24.42	4.27	12.50	4.74	34.37
20	3	450	1.18	n.a.	7.10	0.16	-23.40	17.23	11.12	12.07	29.69
20	40	450	1.00	n.a.	2.41	0.09	-22.15	7.51	14.63	0.09	31.93
20	313	450	1.09	n.a.	5.13	0.05	-24.20	4.22	13.65	5.17	34.55
19	3	525	n.a.	n.a.	7.50	0.11	-25.61	12.75	9.96	11.37	29.11
19	60	525	0.93	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-0.01	32.03
19	353	525	0.64	n.a.	5.53	0.05	-26.20	4.06	13.11	5.23	34.63
18	3	600	1.37	n.a.	5.75	0.10	-24.86	11.79	9.46	11.87	28.16
18	80	600	0.92	n.a.	3.26	0.04	-24.66	3.60	13.97	0.00	32.01
18	370	600	0.72	n.a.	5.10	0.03	-24.96	2.86	12.00	5.23	34.72
17	3	800	1.08	n.a.	4.28	0.08	-25.66	9.48	9.94	11.75	30.85
17	80	800	0.90	n.a.	3.12	0.02	-26.51	1.76	11.62	-0.03	32.38
17	388	800	1.46	n.a.	5.27	0.10	-25.66	11.67	9.94	5.23	34.75

16	3	1050	1.09	n.a.	4.94	0.08	-25.58	10.09	8.98	10.03	31.27
16	81	1050	0.89	n.a.	2.49	0.03	-25.93	2.64	11.45	-0.04	32.33
16	260	750	1.09	n.a.	3.41	0.03	-26.62	2.22	14.22	5.62	34.57
16	416	750	1.24	n.a.	3.15	0.02	-25.68	2.71	10.68	5.19	34.83
14	3	1155	1.87	n.a.	5.55	0.08	-24.87	10.41	8.94	12.75	30.29
14	85	1155	n.a.	n.a.	3.13	0.04	-25.26	3.90	12.44	1.05	32.67
14	420	1155	1.26	n.a.	3.57	0.05	-24.68	4.52	11.88	5.30	34.89

Table A.7: Raw data for the samples collected in 2011.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
B	5	20	4.35	n.a.	21.70	0.85	-25.40	83.34	11.88	10.63	0.08
DE	5	60	4.35	n.a.	23.36	0.87	-25.50	82.35	12.18	9.72	0.09
F1	3	100	2.52	n.a.	166.00	7.11	-25.97	450.71	18.41	5.87	12.68
F1	45	100	3.73	n.a.	21.05	0.39	-25.28	39.62	11.46	3.47	20.90
I	3	160	2.94	n.a.	7.90	0.16	-24.58	17.35	10.83	4.63	17.00
I	40	160	1.71	n.a.	15.40	0.15	-24.92	15.14	11.41	1.70	27.48
I	145	160	1.57	n.a.	25.53	0.34	-24.57	32.67	12.10	1.27	28.99
K	3	200	2.39	n.a.	11.48	0.19	-25.51	17.01	12.84	3.02	23.56
K	30	200	2.33	n.a.	13.80	0.18	-24.77	17.99	11.49	2.55	25.15
K	90	200	1.45	n.a.	8.43	0.11	-24.08	11.79	11.02	1.13	31.21
25	3	215	3.49	n.a.	3.45	0.09	-23.70	13.65	8.04	4.94	21.19
25	70	215	2.02	n.a.	3.79	0.06	-23.35	6.83	9.40	-0.03	31.70
25	280	215	1.34	n.a.	9.33	0.10	-24.49	9.84	12.38	4.64	34.33
25	318	215	1.40	n.a.	20.35	0.20	-23.84	19.11	12.17	4.71	34.36
23	2	300	2.02	n.a.	6.38	0.69	-21.21	100.34	8.00	4.76	24.04
23	3	300	1.87	n.a.						4.76	24.04
23	10	300	1.86	n.a.	4.42	0.10	-24.18	14.55	7.68	4.57	24.20
23	20	300	1.71	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.34	29.16

23	60	300	0.98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-0.19	31.69
23	62	300	1.31	n.a.	6.00	0.05	-23.24	7.05	7.85	-0.06	31.71
23	200	300	0.80	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.66	33.86
23	240	300	0.87	n.a.	3.46	0.06	-23.95	7.09	9.74	4.15	34.09
23	250	300	0.83	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.25	34.14
23	275	300	0.80	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.52	34.26
23	330	300	0.82	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.72	34.36
23	335	300	1.07	n.a.	6.52	0.15	-25.16	18.70	9.21	4.75	34.38
22	3	350	2.52	n.a.	9.00	0.53	-20.99	69.98	8.84	5.57	21.76
22	73	350	1.40	n.a.	2.87	0.09	-23.47	12.28	8.94	0.20	31.74
22	240	350	1.03	n.a.	3.15	0.10	-23.61	11.22	10.22	4.34	34.18
22	309	350	1.53	n.a.	6.28	0.06	-23.33	8.74	8.53	4.80	34.41
21	3	400	1.93	n.a.	2.86	0.14	-22.38	22.13	7.14	4.83	27.78
21	90	400	1.63	n.a.	2.98	0.12	-23.20	12.52	11.33	0.30	31.98
21	280	400	1.19	n.a.	3.15	0.08	-23.92	11.65	7.87	4.79	34.40
21	313	400	1.29	n.a.	5.70	0.09	-23.49	9.91	10.19	4.97	34.49
20	3	450	1.70	n.a.	2.76	0.12	-21.30	15.21	9.00	6.50	31.28
20	40	450	1.52	n.a.	1.91	0.09	-22.13	7.32	14.53	0.07	31.85
20	240	450	1.07	n.a.	1.60	0.04	-23.15	4.92	9.41	4.58	34.27
20	318	450	1.28	n.a.	3.59	0.06	-22.74	7.62	8.63	5.10	34.56

Table A.8: Raw data for the samples collected in 2013.

Station	Depth (m)	Distance from Quebec (km)	[DOC] (mg C/L)	$\delta^{13}C$ DOC (‰)	[SPM] (mg/L)	[POC] (mg C/L)	$\delta^{13}C$ POC (‰)	[PN] (µg N/L)	C/N	Temperature (°C)	Salinity
23	3	300	1.73	-23.51	8.05	0.17	-25.81	25.01	7.94	5.21	24.80
23	25	300	1.48	-22.40	4.67	0.10	-25.52	8.91	12.77	2.71	27.93
23	85	300	1.04	-19.38	3.08	0.05	-24.45	5.63	11.22	-0.19	32.14
23	200	300	0.87	-20.11	4.16	0.10	-24.47	10.07	11.44	3.96	33.93
23	300	300	0.81	-21.54	4.33	0.11	-24.69	11.02	11.85	5.24	34.51

23	333	300	0.80	-20.18	4.24	0.07	-24.88	5.84	13.06	5.24	34.51
23	330 (Nephloid Layer)	300	1.01	-19.72	45.01	0.59	-24.56	61.02	11.30	5.24	34.51
22	3	350	1.62	-23.54	4.81	0.18	-24.58	29.67	6.90	8.10	25.81
22	20	350	1.22	-22.43	2.68	0.08	-24.39	8.43	10.40	3.40	29.52
22	80	350	0.95	-21.69	3.26	0.07	-24.16	8.87	9.41	-0.22	32.01
22	150	350	0.93	-21.69	3.40	0.05	-24.08	5.69	10.19	2.35	33.26
22	255	350	0.68	-21.62	3.73	0.07	-24.70	6.48	11.73	4.94	34.36
22	305	350	0.62	-23.42	5.89	0.09	-24.47	8.37	12.91	5.22	34.49
20.5	3	425	1.24	-21.48	2.21	0.08	-24.71	11.59	8.12	6.49	29.17
20.5	20	425	1.19	-20.17	2.06	0.15	-24.55	18.67	9.10	5.84	29.59
20.5	80	425	0.96	-18.42	2.45	0.08	-24.75	7.88	11.52	-0.12	32.26
20.5	130	425	0.87	-19.17	2.23	0.05	-23.69	6.08	10.23	1.61	32.95
20.5	278	425	0.80	-18.95	3.45	0.08	-24.35	8.29	11.89	5.39	34.55
20.5	300	425	0.79	-19.77	5.09	0.10	-24.44	9.37	11.97	5.39	34.55
20	5	450	1.77	-22.22	4.52	0.12	-23.94	18.90	7.41	6.84	29.29
20	25	450	1.42	-22.19	3.50	0.07	-24.78	6.73	11.58	0.36	31.69
20	50	450	1.12	-22.73	2.55	0.05	-24.25	6.56	9.61	-0.37	32.11
20	150	450	0.99	-21.51	3.04	0.04	-24.83	4.39	11.52	3.63	33.69
20	250	450	1.04	-22.44	2.94	0.05	-24.41	5.09	10.59	5.34	34.51
20	319	450	0.84	-22.94	4.56	0.06	-24.09	7.38	9.44	5.50	34.64
18	3	600	2.09	-22.93	2.05	0.07	-23.59	11.14	7.02	6.75	27.43
18	25	600	1.87	-21.88	3.04	0.07	-25.02	4.92	16.49	1.85	30.60
18	85	600	1.44	-21.43	1.40	0.06	-24.49	5.83	11.17	-0.23	31.95
18	150	600	1.16	-20.34	2.31	0.05	-24.22	5.51	10.58	1.81	33.03
18	280	600	0.94	-20.71	2.61	0.04	-23.61	5.02	10.22	5.40	34.52
18	373	600	1.13	-20.78	2.27	0.05	-23.99	5.52	11.59	5.60	34.72