A multidisciplinary study of hypoxia in the deep water of the Estuary and Gulf of St. Lawrence: Is this ecosystem on borrowed time?

by

Stelly Lefort

Department of Earth and Planetary Sciences

McGill University, Montreal

December 2011

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Doctor of Philosophy

© Stelly Lefort 2011

"If we knew what it was we were doing, it would not be called research, would it?"

Albert Einstein

Acknowledgements

Although full of obstacles and challenges, this Ph.D. was a most positive and exciting experience. Nevertheless, the last years would have seemed much more difficult if the wonderful people who accompanied me throughout this journey would not have been there. I use these few lines to emphasize the impact they had on me and my research thesis.

First, I would like to thank my thesis supervisors, Alfonso Mucci, Bjørn Sundby, Yves Gratton and Denis Gilbert for their mentorship, their support, their patience and their encouragements during the past 5 years. I am grateful to Al for his critical eye, his enthusiasm, his scientific guidance and his relevant and wise advice. Al taught me the highest level of scientific rigor. I also want to express my gratitude for the many opportunities he gave me to travel around the world in the name of science. These experiences enriched my professional and personal life. I acknowledge Bjørn for his wise advice and his help on writing style, his kindness and his availability. I thank Yves for his contribution to this thesis as well as for making time to meet me on short notice despite his busy schedule. Without his strong knowledge of mathematics, the thesis could not have been completed. I am grateful to Denis for his enthusiasm and sharing his passion of science with me.

Although not an official member of my advisory committee, I want to thank Isabelle Dadou who played a crucial role in my stay at McGill. I also am grateful for her invitation and hospitality during my visit at the LEGOS. The time we spent together in Toulouse during the summer 2010 strongly advanced progress of my work.

I also want to give special thanks to Gwenaëlle Chaillou, Philippe Archambault and Sergei Katsev: Gwen for the good times we spend together in and out of the lab at ISMER in Rimouski during the summer 2007, as well as for her support and the many passionate discussions we had about the St. Lawrence ecosystem over the past 5 years; Philippe for welcoming and accommodating me in his lab at ISMER in Rimouski during the summer 2007, and for always taking the time to promptly reply my questions; Sergei for sharing his knowledge about the St. Lawrence and for the enjoyable time we spend together at several conferences.

I also express my gratitude to the thesis evaluators, Jack Middelburg and Eric Galbraith, for their critical and insightfull review. Thanks to the thesis jury committee for their enthousiam during the oral defense and their fruitfull comments.

I am grateful for the financial support that I received from various sources (GEOTOP; CMOS-CGU; IAGS; McGill University; Department of Earth and Planetary Sciences) as well as funding from NSERC-CRSNG for the research conducted during the hypoxia cruises.

I acknowledge Hervé Guyard for his support and his love through good and bad times. He never let me down; he comforted me and brought out the best in me. I would certainly not have gone this far without him by my side.

I will be forever grateful for the support of my family and my friends who I consider to be my family, Nathalie Epervrier and Manon Méheust-Roux who always believed in me and supported my decisions, even when it took me far away from them. I could not have written this thesis without their unconditional love and support.

Thanks also go to my friends Mlle Patate, Noémie Caron and Julien Lesnay for their encouragement, their patience and the support they gave me, especially over the last year. I am glad I made their acquaintance here in Montreal and will keep them in my heart wherever I go. I am grateful for the camaraderie of my colleagues and fellow students in the EPS Department, Cédric Magen, Dirk Shumann, Aleksandra Mloszewska, Bruno Lansard, Sean Crowe, Thais Lamana, Qiang Chen, Dominique Richard, Ting-ting Wang, Steve Pratt, Fatimah Sulu-Gambari, Maryon Strugstad, and many others. I also wish to acknowledge the GEOTOP students from UQAM and UQAR, with whom I shared unforgettable laughs and enjoyable times at each annual GEOTOP student symposium.

I also wish to give thanks to Anne Kosowski, Kristy Thornton, Angela Di Ninno and Brigitte Dionne for making life at McGill better in more ways than I can list.

I probably have forgotten people (I think it is the one rule of acknowledgments) so I will summarize this acknowledgment section by thanking all the persons who helped me to understand the science or myself... I still have a way to go, but now - thanks to them - I am on the right trail.

Contents

Acknowledgements	iii
Contributions of Authors	X
Statement of Originality	xii
Abstract	XV
Résumé	xvii
List of Tables	xix
List of Figures	xxi
1 Introduction	1
1.1 Hypoxia in the marine environment	1
1.1.1 Distribution and causes	1
1.1.2 Reported impacts	2
1.2 The St. Lawrence System: a persistent hypoxic system	5
1.3 Objectives: A multidisciplinary study	6
1.4 Thesis Outline	7
1.5 References	7
2 Sediment response to 25 years of persistent hypoxia	14
2.1 Abstract	
2.2 Introduction	
2.3 Geological setting	
2.4 Methods	19
2.4.1 Sampling	19
2.4.2 Analytical procedures	20
2.5 Results	22

2.5.1 Iron	22
2.5.2 Arsenic	23
2.5.3 Manganese	23
2.6 Discussion	24
2.7 Conclusions	28
2.8 Acknowledgements	29
2.9 References	30
2.10 Appendix: Supplementary data	42
2.10.1 Methods description of complementary analyses	42
2.10.2 Results	44
2.10.3 Short discussion	56
2.10.4 References	56
3 Fluxes and distribution of dissolved oxygen, nitrate, phosphate, iron and	
manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations	58
manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations	58 61
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 61
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 61
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 61 63 65
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 61 63 65 65
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 63 65 65 65
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 63 65 65 65
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 63 65 65 65 67 68
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract 3.2 Introduction 3.3 Site Description 3.4 Materials and Methods 3.4.1 Core collection. 3.4.2 Flux measurements 3.4.3 Pore-water profiling. 3.4.4 Chemical analysis 3.4.5 Statistical analysis. 	58 61 63 65 65 65 67 68
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract	58 61 63 65 65 65 67 68 68 70
 manganese in Laurentian Trough sediments exposed to different bottom- water oxygen concentrations. 3.1 Abstract 3.2 Introduction 3.3 Site Description 3.4 Materials and Methods 3.4.1 Core collection. 3.4.2 Flux measurements 3.4.3 Pore-water profiling. 3.4.4 Chemical analysis 3.4.5 Statistical analysis 3.5 Results 3.5.1 Fluxes across the sediment-water interface 	58 61 63 65 65 65 67 68 68 70 70

3.5.3 Experimental variations of bottom water O ₂ concentrations72
3.6 Discussion
3.6.1 Bottom water oxygenation and elemental fluxes across the sediment-water interface
3.6.2 Effects of chemistry and transport mechanisms on fluxes
3.7 Acknowledgments
3.8 References
3.9 Appendix: Supplementary information on manganese, arsenic and selenium fluxes
3.9.1 Methods
3.9.2 Results
4 Hypoxia in the Lower St. Lawrence Estuary: How physics controls spatial patterns
4.1 Abstract
4.2 Introduction
4.3 Model description
4.3.1 Oxygen transport
4.3.2 Oxygen sinks
4.3.3 Initial and boundary conditions
4.3.4 Tuning of physical parameters110
4.3.5 Model implementation
4.4 Model-data comparison
4.5 Sensitivity analysis
4.5.1 Physical parameters
4.5.2 Biogeochemical parameters
4.6 Interpretation and implication of the oxygen minimum
4.7 Conclusions
4.8 Acknowledgments

4.9 References	120
4.10 Appendix	143
4.10.1 Verification of boundary conditions for advective velocities in the case of a variable bathymetry	e 143
4.10.2 Recommendations for future work	147
5 Conclusions	148
5.1 Summary and suggestions for future work	148
5.2 References	153

Contributions of Authors

This thesis presents the result of the author's Ph.D. research project conducted in the Department of Earth and Planetary Sciences at McGill University, under the supervision of Alfonso Mucci and the co-supervision of Bjørn Sundby, Yves Gratton and Denis Gilbert. The thesis is a manuscript-based thesis composed of three scientific manuscripts, each one being a chapter of the thesis.

The first manuscript (Chapter 2) was written by the author and submitted to the journal Aquatic Geochemistry. Alfonso Mucci and Bjørn Sundby critically reviewed the scientific content and style of the manuscript. Field work and sample analyses were performed by the author with help from a technician (C. Guignard) and summer students (C. Gilbert and N. Molnar) to whom the author is grateful. The latter are acknowledged in the manuscript. The author conceived and carried out the experimental procedures as well as selected and validated the analytical protocols. Data interpretations are the result of the author but many discussions and valuable feedback from the co-authors helped.

The second manuscript (Chapter 3) is based on the original idea of Gwenaëlle Chaillou and was co-written with Philippe Archambault, Alfonso Mucci, Bjørn Sundby and myself. This manuscript was also submitted to the journal Aquatic Chemistry. Gwenaëlle Chaillou and I performed the laboratory experiments and oxygen concentration determinations carried out in 2007. I retrieved the sediment cores used in the 2007 experiments, carried out the trace metal analyses and actively participated to the data interpretation. Sampling and experiments carried in previous years (i.e. the incubation experiments in 2005 and 2006 with the chemical analyses and pore-water voltammetric micro-electrode profiling) were performed by Gwenaëlle Chaillou. Philippe Archambault contributed his expertise for the statistical analysis.

The third manuscript (Chapter 4) was written by the author and critically reviewed by the four co-authors. It was submitted to the Journal of Geophysical Research-Oceans. Yves Gratton contributed his mathematical expertise for the code development. Alfonso Mucci provided the oxygen data used to construct the climatology. Isabelle Dadou provided the tools (Taylor's diagram and budget) to help the author with data interpretation. Denis Gilbert provided the bathymetric data, as well as the code to plot the Gulf map. The author performed the model runs, analyses, and discussion of the model.

Statement of Originality

Given the complex interactions between processes that lead to oxygen depletion in coastal environments, the study of coastal hypoxia requires the integration of multi-disciplinary studies. The overall originality of this thesis is to emphasize the importance of the multiple interactions between the physics, chemistry, biology and geology of natural aquatic environments in the interpretation of field observations.

Chapter 2 reports on the chemical response of sediment to multi-decadal persistent low bottom-water oxygenation and explains the mechanisms responsible for the re-distribution and speciation of three redox-sensitive elements, Mn, Fe, and As. Original contributions from this chapter include:

- First-time observations of sediment chemical response to persistent hypoxia. This phenomenon has been modeled before, but was never observed in a natural environment.
- Although our observations validate some of previous model results: this chapter provides new and contrasting insights about the fate of some redox-sensitive elements in sediments overlaid by persistently hypoxic water.
- A demonstration that persistent hypoxia in the Lower St. Lawrence Estuary significantly modifies the nature and strength of diagenetic reactions (respiration, precipitation of stable mineral sinks) in the sediments.

Chapter 3 provides insights into the relationship between bottom-water oxygenation and the biogeochemistry and fluxes of nutrients and metabolites in coastal sediments. This Chapter also highlights the effect of benthic chemistry and

transport mechanisms on the exchange of solutes across the sediment-water interface. Original contributions from this chapter include:

- Application of statistical analysis, usually used to show the correlation between biological variables and their environment in ecology study, on chemistry measurement to evaluate the relationship between the chemistry and environmental, including biological, variables.
- Observations that the critical oxygen concentration, below which the sediment oxygen uptake becomes a function of the bottom-water oxygen concentration, has not yet been reached in the Estuary and Gulf of St. Lawrence, in spite of the development and persistence of hypoxic conditions. In other words, the oxygen concentration in the bottom water does not control the benthic flux of solutes under the current, persistent severe hypoxia in the LSLE.
- The exploration of the effects on benthic fluxes of transport mechanisms of solutes, i.e. bioirrigation and bioturbation vs. diffusion, and chemical reactions of solutes with others and the solid phase.

Chapter 4 presents a two-dimensional advection-diffusion model and numerical simulations of the spatial distribution of dissolved oxygen in the deep water of the Laurentian Channel (Estuary and Gulf of St. Lawrence, Eastern Canada) that has been adapted from an earlier model (Benoit et al., 2006; see Chapter 4 for details). Original contributions from this chapter include:

- The inclusion of a realistic bathymetry and a pelagic sink in the earlier model of the deep water of the Laurentian Channel.
- The fine-scale reproduction and explanation of the horizontal and vertical oxygen distribution pattern, including the development of a mid-water oxygen minimum in the bottom water of the Laurentian Channel.

 Suggestion that the content of oxygen advected from the North Atlantic Ocean, where the deep waters originate, is fully responsible for the development of hypoxia in the bottom water of the Lower St. Lawrence Estuary.

Abstract

The dissolved oxygen concentration has progressively decreased in the bottom water of the Lower St. Lawrence Estuary (LSLE) during the last century and reached the severe hypoxic threshold ($[O_2] < 62.5 \mu mol L^{-1}$) in the 1980s where it has hovered ever since. This thesis investigates the causes and impacts of the large-scale persistent hypoxia in the bottom water of the LSLE, using multidisciplinary tools. The causes were identified, by examining the processes governing the oxygen distribution in the water column, using a two-dimensional advection-diffusion model representing the transport of oxygen in the bottom water along the Laurentian Channel (Gulf of St. Lawrence, Canada). The impacts of persistent hypoxia were highlighted on modifications of sediment chemistry, more specifically by the diagenetic response of three redox-sensitive elements, Mn, Fe, and As, as well as on the fluxes of nutrients and metabolites across the sediment-water interface. Results of numerical simulations revealed that the oxygen distribution in the water column is governed by the combination of physical and biogeochemical processes, but its vertical distribution is mostly controlled by the deep-water circulation. In other words, the vertical distribution is much more sensitive to variations in physical than biogeochemical processes, and oxygen conditions at the continental shelf edge, where Laurentian Channel bottom waters originate, are mostly responsible for the establishment of hypoxia in the Lower Estuary. Whereas the concentrations and vertical distributions of sedimentary Mn phases seem to adjust rapidly to the progressive depletion of oxygen in the overlying waters and remained at steady-state since the 1980s, the development and persistence of hypoxia strongly modified the chemistry of Fe and As in LSLE sediments. The lower overlying-water oxygenation increased the proportion of organic matter that is oxidized by anaerobic pathways in the sediments, which contributed to increase the proportion of dissolved and solid

reactive phases of Fe and As. The greater availability of reactive Fe and As phases restricted the formation of pyrite, which, in turn, limited the sequestration of As with pyrite, increasing the availability of this potentially toxic trace element to benthic organisms. Despite the accumulation of Fe and As in sedimentary reactive phases over the past 25 years, it has not significantly modified their fluxes across the sediment-water interface, and their sequestration within the sediment is maintained.

Résumé

La concentration d'oxygène dissous dans l'eau de fond de l'estuaire maritime du Saint-Laurent (EMSL) a progressivement diminué au cours du siècle dernier, pour atteindre, dans les années 1980, le seuil de l'hypoxie sévère ($[O_2] <$ 62.5 umol L⁻¹) autour duquel elle a fluctué depuis. Cette thèse examine, à l'aide d'outils multidisciplinaires, les causes et les impacts de l'hypoxie persistante à grande échelle dans l'EMSL. Les causes sont identifiées à l'aide d'un modèle d'advection-diffusion à deux dimensions représentant le transport d'oxygène dissous dans l'eau de fond le long du Chenal Laurentien (Golfe du Saint-Laurent, Canada). Les impacts de l'hypoxie persistante sont illustrés par les modifications de la chimie du sédiment, notamment par la réponse diagénétique de trois éléments redox-sensibles, le Mn, le Fe et l'As, ainsi que sur les flux de nutriments et métabolites à l'interface eau-sédiment. Les résultats des simulations numériques révèlent que la distribution de l'oxygène dissous dans la colonne d'eau est gouvernée par une combinaison de processus physiques et biogéochimiques, mais sa distribution verticale dépend principalement de la circulation de la masse d'eau de fond. En d'autres termes, la distribution verticale de l'oxygène dissous dans le chenal est beaucoup plus sensible aux variations physiques que biogéochimiques et le niveau d'oxygénation à la limite du plateau continental, d'où la masse d'eau de fond provient, est principalement responsable de l'établissement de l'hypoxie dans l'EMSL. Tandis que les concentrations et distributions verticales des phases sédimentaires du Mn semblent s'être rapidement ajustées à la diminution progressive d'oxygène dans les eaux surnageantes et être restées à l'état stationnaire depuis les années 80, le développement et la persistance de l'hypoxie ont fortement modifié la chimie du Fe et de l'As dans les sédiments de l'EMSL. La diminution de l'oxygénation des eaux surnageantes aurait augmenté la proportion de matière organique métabolisée sous des conditions anaérobiques, contribuant à augmenter la proportion des phases réactives solides et dissoutes du Fe et de l'As. La plus grande disponibilité des phases réactives du Fe et de l'As a restreint la formation de pyrite authigène, qui, par conséquent, a limité la séquestration de l'As avec celle-ci, augmentant la disponibilité de cet élément potentiellement toxique aux organismes benthiques. Malgré l'accumulation du Fe et de l'As dans les phases sédimentaires réactives au cours des dernières 25 années, leur flux à l'interface eau-sédiment n'a pas été modifié significativement, maintenant ainsi l'efficacité de leur puits sédimentaire, pour le moment.

List of Tables

Table 2.1: Characteristics of the sampled stations.	.35
Table 2.2: Measured and certified values for marine sediment reference	
materials PACS I and MESS I from the National Research Council Canada	.36
Table 2.3: Diffusive fluxes of As at the sediment-water interface (out of the	
sediment) calculated from Fick's Law	.37
Table 2.4: Characteristics of the sampled stations.	.45
Table 2.5: Measured and certified values for marine sediment reference	
materials PACS I and MESS I obtained from the National Research Council	
Canada	.46
Table 2.6: Analytical results of sediments recovered at station 24: Field	
measurements, carbon and nitrogen contents and isotopic compositions	.47
Table 2.7: Analytical results of sediments recovered at station 23: Field	
measurements, carbon and nitrogen contents and isotopic compositions	.48
Table 2.8: Analytical results of sediments recovered at station 23S: Field	
measurements, carbon and nitrogen contents and isotopic compositions	.49
Table 2.9: Analytical results of sediments recovered at station 20: Field	
measurements, carbon and nitrogen contents and isotopic compositions	.50
Table 2.10: Analytical results of sediments recovered at station 23S:	
dissolved species concentrations	.51
Table 2.11: Analytical results of sediments recovered at station 20: dissolved	
species concentrations	.52
Table 2.12: Analytical results of sediments recovered at station 23S: solid	
species concentrations of selective extractions	.53
Table 2.13: Analytical results of sediments recovered at station 20: solid	
species concentrations of selective extractions	.54

Table 2.14: Analytical results of sediments recovered at station 20: pyrite and
total solid species concentrations
Table 3.1: Environmental conditions at the date and depth of sediment
recovery at the study stations
Table 3.2: Densities of macrobenthic endofauna at each of the study sites,
averaged across replicates
Table 3.3: Measured fluxes derived from incubation experiments over the
study period
Table 3.4: Comparison of initial $([O_2]_{init})$ and final $([O_2]_{end})$ oxygen
concentration in the sampled overlying water upon experimental
manipulations carried in 2007
Table 3.5: Fluxes of Mn (mmol $m^{-2} d^{-1}$) measured at three different overlying
water dissolved oxygen concentrations in cores recovered in July 2007
Table 3.6: Fluxes of As (μ mol m ⁻² d ⁻¹) measured at three different overlying
water dissolved oxygen concentrations in cores recovered in July 200799
Table 3.7: Fluxes of Se (μ mol m ⁻² d ⁻¹) measured at three different overlying
water dissolved oxygen concentrations in cores recovered in July 2007100
Table 4.1: (a) Model equations, (b) boundary conditions and (c) initial
conditions126
Table 4.2: List of parameters with definitions, values, units and literature
sources
Table 4.3: List of state variables with definitions and units. 128
Table 4.4: Range of physical parameter values tested in model tuning
Table 4.5: Range of parameter values used for the sensitivity analysis. 130
Table 4.6: Range of parameter values used for the sensitivity analysis of
biological parameters131

List of Figures

Figure 1.1: Map of the Laurentian System in Eastern Canada	.13
Figure 2.1: Map of the Lower St. Lawrence Estuary and Gulf showing the	
location of sites 23 and 24 sampled in July 2007	.38
Figure 2.2: Total solid Fe (a, b), reactive solid Fe (c, d), acid-volatile sulfide-	
AVS (FeS) (e, f), pyrite (g, h) and pore-water Fe (i, j) profiles at stations 23	
and 24	.39
Figure 2.3: Total solid (a, b), HA-extractable (c, d), pyritic (e, f) and pore-	
water (g, h) As profiles at stations 23 and 24	.40
Figure 2.4: Total solid (a, b), HA-extractable (c, d) and pore-water (e, f) Mn	
profiles at stations 23 and 24	.41
Figure 2.5: Historical comparison of pore-water [Se(D)] and total solid	
[Se(T)] selenium concentrations	.56
Figure 3.1: Map of the Lower St. Lawrence Estuary and Gulf and location of	
sampling sites	.90
Figure 3.2: Depth profiles of sediment pore-water O ₂ (open symbols) and	
Mn(II) (symbols) at sites 25, 24, 23, 21, 20, 19 and 18	.91
Figure 3.3: Fluxes of O_2 , ΣNO_3 , SRP and dissolved Mn across the sediment-	
water interface at each station, averaged across all dates and replicates	.92
Figure 3.4: Non-metric multi-dimensional scaling (nMDS) plots of depth,	
macrofauna density, bottom water dissolved O2, and measured fluxes of O2,	
ΣNO_3 , SRP and dissolved Mn measured over the study period (2005 to 2007)	
at 6 of the study sites (18, 20, 21, 23, 24, 25)	.93
Figure 3.5: Fluxes of O_2 , ΣNO_3 , and SRP across the sediment-water interface	
upon experimental manipulations of the overlying water oxygen	
concentration during incubations at sediment recovered from stations 23 and	
20, July 2007	.94

Figure 3.6: Measured fluxes of O_2 , ΣNO_3 , SRP, and dissolved Mn across the
sediment-water interface as a function of overlying water oxygen
concentrations
Figure 3.7: Measured fluxes of ΣNO_3 , SRP, and dissolved Mn across the
sediment-water interface as function of the oxygen uptake rate96
Figure 4.1: Map of the Lower Estuary and Gulf of St. Lawrence in Eastern
Canada, showing the sampled stations along the Laurentian Channel132
Figure 4.2: Schematic diagram of the advection-diffusion numerical model
solved by <i>Benoit et al.</i> [2006]133
Figure 4.3: Density, temperature and oxygen concentration measured along
the Laurentian Channel (from Station 23 to Cabot Strait) in July 2010134
Figure 4.4: Schematic diagram of the advection-diffusion numerical model
used in this study135
Figure 4.5: Dissolved oxygen flux at the sediment-water interface measured
from sediment core incubations; derived from the dissolved oxygen isotopic
composition and calculated from the carbon rain rate with a simplified
diagenetic model
Figure 4.6: Dissolved oxygen climatology from 2002 to 2010 in the bottom
water of the Laurentian Channel: (a) mean oxygen concentration in
mmol m ⁻³ , (b) standard deviation and (c) number of measurements
Figure 4.7: Taylor diagram for dissolved oxygen concentrations, showing the
tuning of physical parameters
Figure 4.8: Dissolved oxygen distribution pattern for the reference
simulation with the following parameters: $F_0 = 0.11$ Sv, $W = 97.5$ km and K_z
= 1 cm ² s ⁻¹ , R_{wc} = - 19.6 mmol O ₂ m ⁻³ yr ⁻¹ and R_{sed} = - 3540 mmol O ₂ m ⁻² yr ⁻¹
(see Tables 4.2 and 4.3 for symbol definitions)
Figure 4.9: Taylor diagram for dissolved oxygen concentrations showing
results of the sensitivity study to (a) physical parameters and (b) benthic and
pelagic respiration rates compared to the reference simulation140

Figure 4.10: Dissolved oxygen budget in the bottom water of the Laurentian
Channel separated along the dissolved oxygen minimum at 275 m depth142
Figure 4.11: Schematic representation of the boundary conditions at the
pycnocline and at the sediment-water interface for a bathymetry with a linear
slope

Chapter 1

Introduction

1.1 Hypoxia in the marine environment

When the rate of oxygen consumption in water is greater than the rate of supply, the concentration of oxygen decreases and may reach levels so low that aquatic organisms that respire oxygen may not be able to survive. Waters with such low oxygen levels are termed hypoxic. The threshold level for hypoxia is not a constant but varies among aquatic species (Stramma et al., 2008). In this thesis, hypoxic is defined as concentrations of dissolved oxygen between 1 and 30% saturation (3-90 μ mol L⁻¹), which bracket the threshold for so-called severely hypoxic waters, defined as 20% of saturation or 62.5 μ mol L⁻¹, below which most aquatic species may not survive (Diaz and Rosenberg, 1995).

1.1.1 Distribution and causes

The extent and number of reports of hypoxic aquatic systems have dramatically increased over the last decades (Diaz, 2001; Diaz and Rosenberg, 2008; Gilbert et al., 2010). In 2011, the World Resources Institute identified 479 hypoxic coastal zones around the world, including fjords, estuaries, bays, shelves, as well as enclosed and semi-enclosed seas (see Diaz et al., 2011). These hypoxic environments are mainly found in coastal areas as a result of industrial and agricultural fertilizer discharge (i.e. eutrophication; Rabalais et al., 1999; Diaz and

Breitburg, 2009). The presence of excess nutrients, primarily nitrogen and phosphorus, promote algal growth. As dead algae decompose, oxygen is consumed in the process, reducing its availability in the water (Zhang et al., 2010). Oxygen depletion can be exacerbated by the release of nutrients that accompanies the decomposition of dead algae and promotes additional phytoplankton production (Conley et al., 2007). In eutrophic systems, hypoxia generally develops during summer when the stratification of the water column inhibits the mixing and replenishment of dissolved oxygen from the atmosphere.

Hypoxia may also develop in the absence of anthropogenic waste discharge as the oxygen concentration in aquatic environments is strongly affected by natural forcings (Zhang et al., 2010). Hypoxia develop from enhanced water column stratification, which restricts the exchange between the welloxygenated surface waters and bottom waters (e.g. central basin of the Black Sea, Kideys, 2002), advection of low-oxygen water, prolonged residence times of subsurface water and/or high primary productivity in the surface water (Monteiro 2006, 2008; Czeschel et al., 2010). The combination of high oxygen demand, permanent stratification, sluggish circulation and oxygen-poor source waters, may lead to the development of a mid-water oxygen minimum (Wyrtki, 1962; Kamykowski and Zentara, 1990; Czeschel et al., 2010). The so-called Oxygen Minimum Zones (OMZs) are the largest natural hypoxic areas on Earth and cover about 8 % of the total oceanic area (Paulmier and Ruiz-Pino, 2009).

1.1.2 Reported impacts

Most impacts studies have focused on the effect of hypoxia on benthic and pelagic communities. Severe hypoxia can lead to the migration (Gray et al., 2002) or mortality of aquatic species (Bograd et al., 2008), causing habitat compression, community reorganization, or even ecosystem collapse (Mee, 2006; Bograd et al., 2008; Selman et al., 2008). Thus, hypoxia induces changes in species composition and biomass of the pelagic and benthic communities which results in a loss of biodiversity (Galloway et al., 2003; Selman et al., 2008).

Given their capacity to increase the sediment oxygen penetration depth through bioirrigation and bioturbation, loss or modification of benthic invertebrate communities, through the development of hypoxic conditions, favors a shift to anaerobic metabolic pathways (Aller, 1994; Kristensen et al., 1995; Aller and Aller, 1998; Katsev et al., 2007; Vaquer-Sunyer and Duarte, 2010; Steckbauer et al., 2011). In turn, this may affect the biogeochemical cycles of redox-sensitive elements in the sediments as well as the exchange of solutes with the overlying water column (Sayles et al., 1994; Wijsman et al., 2002; Sell and Morse, 2006; Katsev et al., 2007; Morse and Eldridge, 2007; Pakhomova et al., 2007). Nevertheless, little is known about the effects of biodiversity and faunal interactions on the biogeochemistry of ecosystems (Waldbusser et al., 2004; Bulling et al., 2008), and a better understanding of the response of benthic communities to hypoxia is necessary to further our predictive capabilities on the impacts of oxygen depletion on sediment chemistry (Katsev et al., 2007; Middelburg and Levin, 2009).

The availability of oxygen directly controls the diagenetic cycles of redoxsensitive elements in the sediments. Hypoxia will typically decrease the penetration depth of oxygen in the sediment and bring the oxic-anoxic redox boundary closer to the sediment-water interface (Kristiansen et al., 2002; Kristensen et al., 2003; Katsev et al., 2007; Middelburg and Levin, 2009). It may result enhanced fluxes of the redox-sensitive elements in or out of the sediments (Gobeil et al., 2001; Kristiansen et al., 2002; Kristensen et al., 2003; Sundby et al., 2004; Pakhomova et al., 2007; Chaillou et al., 2008; Morford et al., 2009). For example, Kristiansen et al. (2002) studied the response of manganese, iron and sulfur to hypoxia in sandy coastal sediments. They reported higher fluxes of dissolved manganese, iron and sulfide out of the sediments as overlying water oxygen concentrations decreased. The fluxes of manganese and iron out of the sediments were ascribed to the enhanced reductive dissolution of oxidized manganese and iron close to the sediment-water interface. Within less than a month following the establishment of severe hypoxic conditions (< 15 % saturation = 42 μ mol L⁻¹), the total sedimentary manganese and iron pools were completely exhausted.

In coastal sediment, a consortium of bacteria catalyzes the oxidation of the organic matter. Organic matter is oxidized by the following sequence of oxidants: oxygen, nitrate, manganese (hydr)oxide, iron (hydr)oxide, sulfate (Froelich et al., 1979; Van Cappellen and Wang, 1996). As oxygen is the first oxidant used in the sequence, its limitation will typically increase the demand for other oxidants (Katsev et al., 2007; Middelburg and Levin, 2009). As the contribution of manganese and iron oxides to the pool of alternate electron acceptors is limited by their own availability, sulfate reduction is likely to become the dominant pathway for the oxidation of organic matter under persistent hypoxic conditions (Katsev et al., 2007), but field observations to confirm this hypothesis have not yet been reported.

The diagenetic cycles of many potentially toxic trace elements (Cd, Cu, Hg, As, Se, etc.) are intimately linked with those of manganese, iron or sulfur. When oxic conditions prevail in the water column, these elements are readily sequestered in the sediments. Modification of the sedimentary cycling of manganese, iron and sulfur caused by the development and persistence of hypoxia could thus affect the fate of these potentially toxic trace elements (e.g. Guo et al., 1997). For example, Riedel et al. (1999) showed that an increased arsenic flux accompanied manganese release to the water column during 2 months of bottom water hypoxia following a 162-day core incubation period. The release of potentially toxic trace elements into the water column could ultimately affect the quality of the overlying marine ecosystem. For instance, Tan (2006) showed that, in the northern Gulf of Mexico, the seasonal development of hypoxic conditions promotes mercury methylation by sulfate-reducing bacteria in sediments, a potential source of the methyl mercury that accumulates through the food chain and could explain the increased mercury content in fish in the Gulf and adjacent estuaries and bays.

1.2 The St. Lawrence System: a persistent hypoxic system

The St. Lawrence System is a vast aquatic ecosystem located on the east coast of Canada, a transitional environment between the St. Lawrence River and the northwest North Atlantic Ocean (Dickie and Trites, 1983; Koutitonsky and Bugden, 1991) which are connected through the Lower St. Lawrence Estuary (LSLE) and the Gulf of St. Lawrence (Fig. 1.1). The bathymetry of this system is characterized by three branched, deep (300-550 m) submarine valleys: the Laurentian, the Esquiman and the Anticosti Channels (Fig. 1.1). North Atlantic Central Water (NACW) and Labrador Current Water (LCW) that mix at the edge of the eastern Canadian continental shelf break intrude the Gulf of St. Lawrence at depth (> 500 m) through Cabot Strait (Bugden, 1991). As the mixture flows landward in each channel, dissolved oxygen is consumed by metabolic processes (Lehmann et al., 2009) and can only be replenished by diffusion from the surface water because the water column is strongly and permanently stratified (Bugden, 1991). Persistent hypoxia has been reported in the bottom water at the head of each of these channels (Gilbert et al., 2007), whereas severe hypoxic conditions are only encountered in the bottom water at the head of the Laurentian Channel in the LSLE (Fig. 1.1). As a result, the Laurentian Channel has been the most extensively investigated of the three channels to date (Savenkoff et al, 1995, 1996; Gilbert et al., 2005; Benoit et al., 2006; Thibodeau et al., 2006, 2010a, b; Genovesi et al., 2011; Mucci et al., 2011; Crowe et al., 2011; and many others).

In 2003, an estimated $1300\pm100 \text{ km}^2$ of the LSLE seafloor was covered by severely hypoxic waters (Gilbert et al., 2005). Historical records reveal that, the dissolved oxygen concentration in the bottom waters of the LSLE decreased at an average rate of ~1 µmol L⁻¹ yr⁻¹ since the 1930s (Gilbert et al., 2005). Severe hypoxic conditions were established in the LSLE in the early 1980s, and have persisted since then (Gilbert et al., 2005). The development of severe hypoxia in the LSLE has been mostly attributed to a gradual change in the properties (e.g. temperature, dissolved oxygen concentration) of the bottom water that enter the

Gulf of St. Lawrence (Gilbert et al., 2005). Over the years, the proportion of warm and oxygen-poor NACW has increased at the expense of the cold and oxygen-rich LCW in the mixture (Gilbert et al., 2005). In addition to changes in the properties of the bottom water entering the Gulf, evidence of eutrophication has been reported in the LSLE, possibly increasing the oxygen demand in the water column and sediment (Thibodeau et al., 2006). Increased respiration rates in the bottom water, in response to warming (from 3.3 to 5°C), has also been proposed to explain the increased depletion of oxygen in the Gulf (Genovesi et al., 2011). Nevertheless, whether hypoxia in the bottom water of the Laurentian Channel results from anthropogenic or natural forcings or both remain unclear.

1.3 Objectives: A multidisciplinary study

Understanding environmental changes associated with open ocean and coastal hypoxia require a quantitative understanding of the physics, biogeochemistry and ecology of the marine systems. Hence, the overall objective of this thesis is to identify the main causes and impacts of hypoxia in the Lower St. Lawrence Estuary, as this environment offers a unique opportunity to study persistent hypoxia. One of the objectives of this thesis is to document the impacts of 25 years of persistent hypoxia on sediment chemistry, as the extent, severity and persistence of hypoxia in the LSLE make this environment an ideal laboratory for this type of study. More specifically, we investigate the impact of severe hypoxia on the geochemical behavior three redox-sensitive elements, Fe, Mn, As, in order to gain a better understanding of their fate and evaluate the risks to the health of this environment. A second objective of the thesis is to provide insights on the relationship between bottom-water dissolved oxygen concentrations and the exchange of nutrients and metabolites across the sediment-water interface. Finally, the third objective of this thesis was to identify the processes, among physical and biogeochemical, that govern the spatial distribution of dissolved oxygen in the bottom water of the Laurentian Channel and gain a better understanding of the factors that led to the development of hypoxic conditions.

1.4 Thesis Outline

In the *Chapter 2*, we report results of a study on the geochemical response of redox-sensitive elements, specifically Mn, Fe and As, in sediments of the LSLE over 25 years of persistent low bottom water oxygenation, including a description of the mechanisms that lead to the observed changes. Based on voltammetric micro-electrode profiles and short-term core incubations, in *Chapter* 3, we investigate the relationship between bottom-water oxygenation and the fluxes dissolved oxygen, nitrate, soluble reactive phosphate (SRP), manganese and iron across the sediment-water interface. We also document the effects of bottom-water oxygenation on the benthic community, pore-water chemistry and thus on the benthic elemental fluxes. In Chapter 4, we present a 2D diffusionadvection-reaction model and results of numerical simulations of the concentrations and distribution of dissolved oxygen along the Laurentian Channel. A realistic bathymetry and biogeochemical sinks in the water column and sediment are taken into consideration. Based on the model results and a sensitivity analysis, we identify the physical and biogeochemical processes that are mostly responsible for the distribution pattern of dissolved oxygen in the LSLE. Chapter 5 contains a summary of the findings and their broader implications.

1.5 References

- Aller R. C. (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation, Chem. Geol. 114, 331–345.
- Aller R. C. and J. Y. Aller (1998) The effect of biogenic irrigation intensity and solute exchange on diagenetic reaction rates in marine sediments, J. Mar. Res. 56, 905-936.

- Benoit P., Y. Gratton and A. Mucci (2006) Modeling of dissolved oxygen levels in the bottom waters of the Lower St. Lawrence Estuary: Coupling of benthic and pelagic processes, Mar. Chem. 102, 13–32, doi:10.1016/j.marchem.2005.09.015.
- Bograd S., C. G. Castro, E. Di Lorenzo, D. M. Palacios, H. Bailey, W. Gilly and F. P. Chavez (2008), Oxygen declines and the shoaling of the hypoxic boundary in the California Current, Geophys. Res. Lett. 35, L12607, doi: 10.1029/2008GL034185.
- Bugden G. L. (1991) Changes in the temperature-salinity characteristics of the deeper waters of the Gulf of St. Lawrence over the past several decades, in The Gulf of St. Lawrence: Small sea or big estuary?, Can. Spec. Publ. Fish. Aquat. Sci. 113, edited by J.-C. Therriault, pp. 139–147.
- Bulling M. T., M. Solan, K. E. Dyson, G. Hernandez-Milian, P. Luque, G. J. Pierce, D. Raffaelli and D. M. Paterson (2008) Species effects on ecosystem processes are modified by faunal responses to habitat composition, Oecologia 158, 511–520.
- Chaillou G., J. Schäfer, G. Blanc and P. Anschultz (2008) Mobility of Mo, U, As, and Sb within modern turbidites. Mar. Geol. 254(3/4), 171–179.
- Conley D. J., J. Carstensen, G. A. Ertebjerg, P. B. Christensen, T. Dalsgaard, J. L. S. Hansen, and A. B. Josefon (2007) Long-term changes and impacts of hypoxia in Danish Coastal Waters, Ecol. Appl. 17(5) Suppl., S165–S184.
- Crowe S. A., D. E. Canfield, A. Mucci, B. Sundby and R. Maranger (2011) Anammox, denitrification and fixed-nitrogen removal in sediments of the Lower St. Lawrence Estuary, Biogeosciences Discussion 8, 9503–9534.
- Czeschel R., L. Stramma, F. U. Schwarzkopf, B. S. Giese, A. Funk and J. Karstensen (2011) Mid-depth circulation of the eastern tropical south Pacific and its link to the oxygen minimum zone, J. Geophys. Res. 116, C01015, doi:10.1029/2010JC006565.
- Diaz R. J. (2001) Overview of hypoxia around the world, Environ. Qual. 30, 275–281.
- Diaz R. J. and D. L. Breitburg (2009) The hypoxic environment, in Hypoxia in fishes, edited by J. G. Richards et al., pp. 1–23, Elsevier, San Diego.
- Diaz R. and R. J. Rosenberg (1995) Marine benthic hypoxia: A review of its ecological effects and the behavioural responses of benthic macrofauna, Oceanogr. Mar. Biol. Annu. Rev. 33, 245–303.
- Diaz R. and R. J. Rosenberg (2008) Spreading dead zones and consequences for marine ecosystems, Science 321, 926–929.
- Diaz R., M. Selman. and C. Chique (2011) Global eutrophic and hypoxic coastal systems, World Resources Institute, Eutrophication and hypoxia: Nutrient

pollution in coastal waters, docs.wri.org/wri_eutrophic_hypoxic_dataset_2011-03.xls

- Dickie L. M. and W. Trites (1983) The Gulf of St. Lawrence Estuaries and Enclosed Seas, edited by H. Ketchum, pp. 403–25, Elsevier, Amsterdam.
- Froelich P. N., G. P. Klinkhammer, M. L. Bender, N. A. Luedtkeand, G. R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman and V. Maynard (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis, Geochim. Cosmochim. Acta 43, 1075–1090.
- Galloway J. N., J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling and B. J. Cosby (2003) The nitrogen cascade, Bioscience 53(4), 341–356.
- Genovesi L., A. de Vernal, B. Thibodeau, C. Hillaire-Marcel, A. Mucci and D. Gilbert (2011) Recent changes in bottom water oxygenation and temperature in the Gulf of St. Lawrence: Micropaleontological and geochemical evidence, Limnol. Oceanogr. 56(4), 1319–1329, doi:10.4319/lo.2011.56.4.1319.
- Gilbert D., D. Chabot, P. Archambault, B. Rondeau and S. Hébert (2007) Appauvrissement en oxygène dans les eaux profondes du St-Laurent marin: Causes possibles et impacts écologiques, Nat. Can. 131, 67–75.
- Gilbert D., N. N. Rabalais, R. J. Diaz and J. Zhang (2010) Evidence for greater oxygen decline rates in the coastal ocean than in the open ocean, Biogeosciences 7, 2283–2296.
- Gilbert D., B. Sundby, C. Gobeil, A. Mucci and G. H. Tremblay (2005) A seventy-two-year record of diminishing deep-water oxygen in the St. Lawrence Estuary: The northwest Atlantic connection, Limnol. Oceanogr. 50, 1654–1666, doi:10.4319/lo.2005.50.5.1654.
- Gobeil C., B. Sundby, R. W. Macdonald and J. N. Smith (2001) Recent change in organic carbon flux to Arctic Ocean deep basins' Evidence from acid volatile sulfide manganese and rhenium discord in sediments. Geophys. Res. Lett. 28(9), 1743–1746.
- Gray J. S., R. S. Wu and Y. Y. Or (2002) Effects of hypoxia and organic marine enrichment on the coastal marine environment, Mar. Ecol. Prog. Series 238, 249–279.
- Guo T., R. D. DeLaune and W. H. Patrick Jr. (1997) The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment, Environ. Int. 23(3), 305–316.
- Kamykowski D. Z. and S. J. Zentara (1990) Hypoxia in the world ocean as recorded in the historical data set, Deep-Sea Res. 37, 1861–1874.

- Katsev S., G. Chaillou, B. Sundby and A. Mucci (2007) Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the Lower St. Lawrence Estuary, Limnol. Oceanogr. 52(6), 2555–2568.
- Kideys A.E. (2002) Fall and rise of the Black Sea ecosystem, Science 297, 1482–1484, doi:10.1126/science.1073002.
- Koutitonsky V. G. and G. L. Bugden (1991) The physical oceanography of the Gulf of St. Lawrence: a review with emphasis on the synoptic variability of the motion Can. Spec. Publ. Fish. Aquat. Sci. 113, 57–90.
- Kristensen E., S. Ahmed and A. Devol (1995) Aerobic and anaerobic decomposition of organic matter in marine sediment: Which is fastest?, Limnol. Oceanogr. 40(5), 1430–1437.
- Kristensen E., K. D. Kristiansen and M. H. Jensen (2003) Temporal behavior of manganese and iron in a sandy coastal sediment exposed to water column anoxia, Estuaries 26(3), 690–699.
- Kristiansen K. D., E. Kristensen and M. H. Jensen (2002) The influence of water column hypoxia on the behaviour of manganese and iron in sandy coastal marine sediment, Estuar. Coast. Shelf Sci. 55, 645–654.
- Lehmann M. F., B. Barnett, Y. Gélinas, D. Gilbert, R. J. Maranger, A. Mucci, B. Sundby and B. Thibodeau (2009) Aerobic respiration and hypoxia in the Lower St. Lawrence Estuary: Stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning, Limnol. Oceanogr. 54(6), 2157–2169.
- Mee L. (2006) Reviving dead zones, Scientific American 295(5), 79-85.
- Middelburg J. J. and L. A. Levin (2009) Coastal hypoxia and sediment biogeochemistry, Biogeosciences 6(7), 1273–1293.
- Monteiro P. M. S., A. van der Plas, J.-L. Mélice and P. Florenchie (2008) Interannual hypoxia variability in a coastal upwelling system: Ocean-shelf exchange, climate and ecosystem-state implications, Deep-Sea Res. I 55, 435– 450, doi:10.1016/j.dsr.2007.12.010.
- Monteiro P. M. S., A. van der Plas, V. Mohrholz, E. Mabille, A. Pascall and W. Joubert (2006) Variability of natural hypoxia and methane in a coastal upwelling system: Oceanic physics or shelf biology?, Geophys. Res. Lett. 33, L16614, doi:10.1029/2006GL026234.
- Morford J. L., W. R. Martin, R. François and C. M. Carney (2009) A model for uranium, rhenium, and molybdenum diagenesis in marine sediments based on results from coastal locations. Geochim. Cosmochim. Acta 73(10), 2938– 2960.
- Morse J. and P. Eldridge (2007) A non-steady state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the "dead zone" of the Louisiana shelf, Mar. Chem. 106, 239– 255.

- Mucci A., B. Sundby, D. Gilbert and M. Starr (2011) Acidification of the bottom water of the Lower St-Lawrence Estuary since the 1930s, Atmosphere-Ocean 49(3), 206–213.
- Pakhomova S., P. Hall, M. Kononets, A. Rozanov, A. Tengberg and A. Vershinin (2007) Fluxes of iron and manganese across the sediment-water interface under various redox conditions, Mar. Chem. 107, 319–331.
- Paulmier A. and D. Ruiz-Pino (2009) Oxygen minimum zones (OMZs) in the modern ocean, Progr. Oceanogr. 80, 113–128.
- Rabalais N. N., R. E. Turner, D. Justic, Q. Dortch and W. J. Wiseman Jr. (1999) Characterization of Hypoxia Topic 1 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico, NOAA Coastal Ocean Program, Decision Analysis Series 15.
- Riedel G. F. J. G. Sanders and R. W. Osman (1999) Biogeochemical control on the flux of trace elements from estuarine sediments: effects of seasonal and short-term hypoxia. Mar. Environ. Res. 47, 349–372.
- Savenkoff C., A. F. Vézina, J.-P. Chanut and Y. Gratton (1995) Respiratory activity and CO₂ production rates of microorganisms in the Lower St. Lawrence Estuary, Cont. Shelf Res. 15(6), 613–631.
- Savenkoff C., A. F. Vézina, T. T. Packard, N. Silverberg, J.-C. Therriault, W. Chen, C. Bérubé, A. Mucci, B. Klein, F. Mesplé, J.-E. Tremblay, L. Legendre, J. Wesson and R. G. Ingram (1996) Distributions of oxygen, carbon, and respiratory activity in the deep layer of the Gulf of St. Lawrence and their implications for the carbon cycle, Can. J. Fish. Aquat. Sci. 53, 2451–2465.
- Sayles F., W. Martin and W. Deuser (1994) Response of benthic oxygen demand to particulate organic carbon supply in the deep sea near Bermuda, Nature 371, 686–689.
- Sell K. and J. Morse (2006) Dissolved Fe^{2+} and ΣH_2S behavior in sediments seasonally overlain by hypoxic-to-anoxic waters as determined by CSV microelectrodes, Aquat. Geochem. 12, 179–198.
- Selman M., S. Greenhalgh, R. Diaz and Z. Sugg (2008) Eutrophication and hypoxia in coastal areas: A global assessment of the state of knowledge, WRI policy note, Water quality: Eutrophication and hypoxia 1, 1–6.
- Sundby B., P. Martinez and C. Gobeil (2004) Comparative geochemistry of cadmium, rhenium, uranium, and molybdenum in continental margin sediments. Geochim. Cosmochim. Acta 68, 2485–2493.
- Steckbauer A., C. M. Duarte, J. Carstensen, R. Vaquer-Sunyer and D. J. Conley (2011) Ecosystem impacts of hypoxia: thresholds of hypoxia and pathways to recovery, Environ. Res. Lett. 6, 025033, doi:10.1088/1748-9326/6/2/025003.
- Stramma L., G. C. Johnson, J. Sprintall and V. Mohrholz (2008) Expanding Oxygen-Minimum Zones in the Tropical Oceans, Science 320, 655–658.

- Tan M. H. (2006) The Impact of Hypoxia on Mercury Methylation in Bottom Sediment of Northern Gulf of Mexico, Master's Thesis, Master of Science (M.S.) at Louisiana State University, Department Environmental Studies.
- Thibodeau B., A. de Vernal and A. Mucci (2006) Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleontological and geochemical evidence, Mar. Geol. 231, 37–50, doi:10.1016/j.margeo.2006.05.010.
- Thibodeau B., A. De Vernal, C. Hillaire-Marcel and A. Mucci (2010a) Twentieth century warming in deep waters of the Gulf of St. Lawrence: A unique feature of the last millennium, Geophys. Res. Lett. 37, L17604, doi:10.1029/2010GL044771.
- Thibodeau B., M. Lehmann, J. Kowarzyk, A. Mucci, Y. Gélinas, D. Gilbert, R. Maranger and M. Alkhatib (2010b) Benthic nutrient fluxes along the Laurentian Channel: Environmental controls and impact on the N-budget of the St. Lawrence marine system, Estuar. Coast. Shelf Sci. 90, 195–205, doi 10.1016/j.ecss.2010.08.015.
- Vaquer-Sunyer R. and C. M. Duarte (2010) Sulphide exposure accelerates hypoxia-driven mortality, Limnol. Oceanogr. 55, 1075–82.
- Van Cappellen P. and Y. Wang (1996) Cycling of iron and manganese in surface sediments: a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron and manganese, Am. J. Sci. 296, 197–243.
- Waldbusser G., R. Marinelli, R. Whitlatch and P. Visscher (2004) The effects of infaunal biodiversity on biogeochemistry of coastal marine sediments. Limnol. Oceanogr. 49, 1482–1492.
- Wijsman J., P. Herman, J. Middelburg and K. Soetaert (2002) A model for early diagenetic processes in sediments of the continental shelf of the Black Sea, Estuar. Coast. Shelf Sci. 54, 403–421.
- Wyrtki K. (1962) The oxygen minima in relation to ocean circulation, Deep-Sea Res. 9, 11–23.
- Zhang J., D. Gilbert, A. Gooday, L. Levin, W. Naqvi, J. Middelburg, M. Scranton, W. Ekau, A. Pena, B. Dewitte, T. Oguz, P. M. S. Monteiro, E. Urban, N. Rabalais, V. Ittekkot, W. M. Kemp, O. Ulloa, R. Elmgren, E. Escobar-Briones, and A. Van der Plas (2010) Natural and human-induced hypoxia and consequences for coastal areas: synthesis and future development, Biogeosciences 7, 1443–1467.



Figure 1.1: Map of the Laurentian System in Eastern Canada, showing the Lower Estuary and Gulf of St. Lawrence. The bold grey line represents the 200 m isobath. Modified from Gilbert et al. (2007) and reproduced with permission.
Chapter 2

Sediment response to 25 years of persistent hypoxia

This chapter describes the effect of multi-decadal persistent hypoxia on the redox-sensitive element diagenetic cycles of Fe, Mn, and As in the Lower St. Lawrence Estuary in order to gain a better understanding of their fate and evaluate the risks to the health of this environment.

This chapter is based on a manuscript submitted to the journal Aquatic Geochemistry in December 2011: Lefort S., Mucci A. and Sundby B., Sediment response to 25 years of persistent hypoxia. Aspects of this study were also presented and discussed at several colloquia, including the 24th International Applied Geochemistry Symposium, the international Goldschmidt conference in 2009, and the CMOS-CGU conference in 2010.

Sediment response to 25 years of persistent hypoxia

Lefort S.^{1*}, Mucci A.¹ & Sundby B.^{2,1}

1. Department of Earth & Planetary Sciences, McGill University, 3450 University Street, Montréal (Québec) Canada H3A 2A7

 Institut des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski (UQAR), 310 allée des Ursulines, CP 3300, Rimouski (Québec) Canada G5L 3A1

Submitted to Aquatic Geochemistry, December 2011

2.1 Abstract

We investigated the impact of persistent hypoxia on sediment chemistry by comparing the total, reactive (extractible with 1M hydroxylamine hydrochloride in 25% acetic acid), and dissolved forms of the redox-sensitive elements Mn, Fe, and As in cores recovered between 1982 and 2007 at two sites in the Lower St. Lawrence Estuary (LSLE) where the bottom water has been severely hypoxic since the early 1980's. The data reveal that concentrations and vertical distributions of solid and dissolved Mn, as well as total solid Fe and As, were not significantly affected by the establishment of persistent hypoxia. In contrast, the dissolved Fe and As profiles, as well as the speciation of their respective solid phases, have changed significantly. The relative amounts of solidreactive Fe and As increased, whereas the concentrations of pyrite and pyritic-As decreased in the sediment layer accumulated since 1982. We propose that persistent hypoxic conditions restrict the supply of oxygen to the sediment and increase the relative contribution of alternate electron acceptors -Mn(IV), Fe(III) and sulfate - to the oxidation of organic matter. In marine, iron-rich environments, such as the LSLE sediment, increased sulfate reduction may promote the conversion of less reactive Fe phases to more reactive Fe phases which, in turn, interfere with pyritisation. Consequently, a chalcophile element such as As that would normally be sequestered with authigenic pyrite remains more available for recycling across the oxic-anoxic boundary in the sediment.

2.2 Introduction

Over the last decade, the number of reports of low oxygen bottom waters in the coastal ocean has increased at an alarming rate, as has the extent of the area affected by low oxygen concentrations (Diaz 2001; Gilbert et al. 2010). Many low oxygen environments are considered to be severely hypoxic (Diaz & Rosenberg 2008), defined as dissolved oxygen concentrations below the 62.5 μ mol/L threshold (~20% oxygen saturation) necessary to sustain most aquatic animal life (Diaz & Rosenberg 1995). Until now, most studies of hypoxic environments have focused on the impacts of hypoxia on pelagic and benthic populations (e.g. Phil et al. 1991; Rabalais and Turner 2001; Belley et al. 2010) whereas the impact of hypoxia on sediment chemistry is poorly documented (Morse and Eldridge 2006; Katsev et al. 2007).

Hypoxia is likely to influence the pathways and rates of chemical reactions in sediment (Katsev et al. 2007; Middelburg and Levin 2009). Oxygen is the most energetic oxidant in the sequence of terminal electron acceptors used for organic matter oxidation. Once oxygen is depleted, nitrate, Mn(III/IV), Fe(III), and sulfate are used in this specific order for the oxidation of organic matter that settles to the seafloor (Froelich et al. 1979; Van Cappellen and Wang 1996). If hypoxia restricts the supply of oxygen to the sediment, the depth of the redox boundary may move closer to the sediment-water interface (Park and Jaffé 1996), and the demand for alternate electron acceptors may change (Katsev et al. 2007). Thus, hypoxia may alter the chemistry and the cycles of redox-sensitive metals such as Mn and Fe (Kristiansen et al. 2002) and with the biogeochemical cycles of related elements, such as sulfur and phosphorus, and potentially toxic trace elements such as As (Burdige 1993; Guo et al. 1997; Kristiansen et al. 2002).

The impacts of hypoxia on sediment chemistry are expected to be difficult to observe unless hypoxia persists long enough (~10-100 years) for the sediment to respond measurably to low oxygen conditions (Katsev et al. 2007). Peña et al. (2010) estimated that for a typical coastal sediment burial rate of 0.25 cm/yr, it would take about 80 years for the diagenetically active zone to reach a new steady state following a change in the bottom water oxygen content. Most hypoxic environments are shallow, which allows the water column to be ventilated on seasonal or annual time scales (Gooday et al. 2009). In such environments, persistent changes in sediment chemistry are unlikely to be recorded.

The great depth and the permanent stratification of the water column have allowed the bottom water in the Lower St. Lawrence Estuary (LSLE; Fig. 2.1) to become persistently hypoxic. The dissolved oxygen concentration in the bottom water of the LSLE has decreased progressively at an average rate of about 1 μ mol L⁻¹ yr⁻¹ since the 1930s (Gilbert et al. 2005). Since the 1980s, the concentration has hovered near the threshold value for severe hypoxia (Gilbert et al. 2005), fluctuating between 56 and 69 μ mol L⁻¹ over the 1984-2007 period (Mucci et al. 2011). In this paper, we show that persistent hypoxia has affected the chemistry of LSLE sediments differently, as revealed by the chemistry of the redox-sensitive metals Mn and Fe, and the associated metalloid arsenic.

2.3 Geological setting

The dominant bathymetric feature in the LSLE is a 300-350 m deep glacially-modified submarine trough, known as the Laurentian Channel (or Trough), that extends from Tadoussac all the way to the eastern Canadian continental shelf break (Fig. 2.1). Sediments in the channel are composed of finegrained particulates (pelites) with, on average, 60% clay, 35% silt and 5% sand (Nota and Loring 1964). The clay-size fraction contains amphiboles, feldspars, pyroxenes, chlorite, quartz, illite and kaolinite (Loring and Nota 1968; Ramachandran 1991). These sediments are mainly derived from the mechanical weathering of crystalline rocks, the Quaternary deposits of the Canadian Shield, and from ice-rafting from the shorelines (Nota and Loring 1964). The sediments are dark yellowish-brown in the first 1-3 cm below the sediment-water interface, reflecting the presence of detrital and authigenic ferric iron [Fe(III)] and manganic [Mn(IV)] minerals (Loring and Nota 1968; Lyle 1983; König et al. 1997). Below this oxidized layer, the sediments are dark greenish-grey (Loring and Nota 1968). Ferric iron enters the depositional basin structurally combined to silicate minerals (e.g. chlorite and illite) and resistant iron oxides (e.g. magnetite) (Loring and Nota 1968; Ramachandran 1991) whereas most of the manganese is delivered as oxide coatings on suspended matter (Loring and Nota 1968). Sediment arsenic concentrations in the LSLE are relatively high for a noncontaminated marine environment (80-400 µmol/kg) and reflect the geology of the drainage basin (Edenborn et al. 1986; Tremblay and Gobeil 1990).

2.4 Methods

2.4.1 Sampling

Sediment and water samples were recovered onboard the R/V Coriolis II in July 2007 at stations 23 and 24 located along the latitudinal axis of the Laurentian Channel (Fig. 2.1). Detailed descriptions of each sampled site can be found in Table 2.1.

Undisturbed sediment cores were recovered with an Ocean Instrument Mark II box corer. Immediately upon recovery, each core (0.12 m² x 0.5 m long) was transferred to a specially-designed glove box and sub-sampled under a constant flow of N_2 to limit oxidation (Edenborn et al. 1987). The entire surface area of the core (30 x 40 cm) was used for each subsample, except for the edge of the core which was in contact with the stainless steel box. The core was subsampled at 0.5-cm intervals over the top first centimeter, at 1-cm intervals over the next 4 cm, at 2-cm intervals over the following 10 cm, at 3-cm intervals between 15 and 21 cm depth, at 4-cm intervals down to 25 cm, and at 5-cm intervals thereafter. As the sediment was exposed by step-wise lowering of the front plate, the Eh_(SCE) was measured within each interval with a platinum electrode and solid sediment samples were transferred to pre-weighed plastic scintillation vials. The vials were weighed, freeze-dried, and re-weighed to determine the sediment water content. The sediment water content was used, in combination with the salinity of the corresponding bottom waters, to estimate the sediment porosity. The freeze-dried sediment was then ground with an agate mortar and pestle and stored for later analyses. During sub-sampling, solid sediments were also transferred to Reeburgh-type (Reeburgh 1967) squeezers (250-400 kPa N₂) to extract the pore-waters at near *in-situ* temperature. Porewaters were filtered through a 0.45 μ m Millipore polycarbonate filter (type MA)

as they passed directly into a pre-washed 50-cc plastic syringe. Pore-waters were then transferred to 30 ml acid-washed high-density polyethylene bottles (HDPE), acidified with a 1% equivalent volume of ultrapure, concentrated HNO₃ (Seastar) and kept refrigerated until analyses. Finally, mini-cores (i.e., 13 mL polyethylene screw cap test tubes with their distal ends cut off and 10 cc syringe plunger) were taken at the rate of two per depth interval and frozen immediately in order to maintain the anoxic character of the sediment. These samples were used for acid volatile sulfide (AVS) determinations.

2.4.2 Analytical procedures

2.4.2.1 Pore-water

Total dissolved Fe, Mn, and As were analyzed by flame atomic absorption spectrophotometry (AAS, Perkin-Elmer Analyst 100), with hydride generation for arsenic (FIAS 400). Calibration curves were constructed using diluted, commercial, certified aqueous 1000 mg/L standards in the appropriate matrices. Prior to analysis, arsenic was reduced to arsenite following the addition of hydrochloric acid and a 5% ascorbic acid/5% potassium iodide solution to the samples at a ratio 3:1:10. Detection limits for Mn and Fe are 0.1 mg/L (1.82 and 1.79 μ mol/L, respectively) and 0.17 μ g/L (2.27 nmol/L) for As and the reproducibility was better than 5% for all elements.

2.4.2.2 Solid sediment

AVS were analyzed by the method described by Hsieh and Yang (1989), as modified by Gagnon et al. (1995). The trapped sulfide was titrated iodometrically and the AVS was assumed to have a FeS stoichiometry. The averaged relative standard deviation for 22 replicates was below to 2%. The detection limit was approximately 1.5 mg AVS/kg of dry sediment.

The freeze-dried sediments were subjected to a complete dissolution, two selective extractions, and a pyrite extraction. To determine the total Fe, Mn, and As content of the solid phase, 200 mg of solid freeze-dried sediments were added to a mixture of 4 mL of trace-metal grade HNO₃ (67-70%) and 1 mL of tracemetal grade HF (47-51%), microwave-ramped in sealed Teflon reactors (GEM, Mars 5) from 0 to 200°C over 20 min, and maintained at 200°C for 30 min. The Teflon reactors were then immersed in an ice-water bath until the inner solutions were cooled to ~10°C. Reference sediment materials, MESS-1 and PACS-1, purchased from the National Research Council of Canada, were carried through the same procedure to estimate reproducibility and accuracy (Table 2.2).

The first selective extraction procedure, designed to isolate reactive phases, was carried out in a 1M hydroxylamine-hydrochloride and 25% (v/v) acetic acid (HA) solution (Chester and Hughes, 1967). This extraction is assumed to provide a measure of the amount of Fe, Mn, and As associated with reactive oxide, carbonate and sulfide minerals as well as with organic matter in sediments (Turner 2000). This protocol was chosen so our results could be compared with the historical data of Belzile (1987). The mean relative standard deviation for 23 replicates was 6%.

The second selective extraction was carried out in a buffered ascorbate solution (Ferdelman, 1988), to isolate Mn oxyhydroxides and amorphous Fe oxyhydroxides (Kostka and Luther 1994). As the concentrations of Mn extracted with the ascorbate solution and with HA solution were nearly the same, we only report the concentrations of Mn extracted with the HA solution. The mean relative standard deviation for 9 replicates was 5%.

Pyrite was extracted using the method described by Lord III (1982) to determine the concentrations of Fe and As associated with this mineral. No replicates were performed for the pyrite extraction, but, as estimated by Lord III (1982), we expect the relative standard deviation to be less than 3%. Saulnier and Mucci (2000) reported that the mean relative standard deviation for pyrite extracted from Saguenay Fjord (a tributary of the St. Lawrence) sediments, using the same method, was 1.6% and the detection limit was 0.2 g pyrite/kg of dry sediment.

Element concentrations in the extracts were determined by the methods described above for pore-water analyses, except for the pre-reduction of pyritic As for which the HCl:ascorbic-acid:KI ratio was 1:1:1. The cumulative error of the measurements and reproducibility were better than 5%. Detection limits for Mn and Fe are 0.1 mg/L (1.82 and 1.79 μ mol/L, respectively) and 0.17 μ g/L (2.27 nmol/L) for As.

2.5 Results

2.5.1 Iron

During 25 years of hypoxic conditions in the LSLE, the concentration of total Fe [Fe(T)] did not change (Figs. 2.2a-b), but the reactive component of the total Fe did (Figs. 2.2c-e). The concentration of HA-extractable Fe [Fe(HA)] in the solid sediment at sites 23 and 24, which includes AVS, increased over the same period (Figs. 2.2c-e). Fe(HA) rose from an average of 85 mmol/kg dried sediment in 1982 to 140 mmol/kg in 2007 (Figs. 2.2c-d) and accounted for ~15% of the total solid-phase Fe in 2007. This corresponds to a 50% increase of the Fe(HA):Fe(T) ratio since 1982. Likewise, the concentration of pore-water Fe [Fe(D)] at both sites increased 2-4 fold since 1982, and the peak concentrations migrated closer to the sediment-water interface (Figs. 2.2i-j).

In contrast to the increased proportion of reactive Fe (Figs. 2.2c-e), the pyrite content of the sediment [Fe(P)] at site 23 decreased from \sim 5 mmol/kg in 1982 to \sim 3 mmol/kg in 2007 in the first 13 cm below the sediment-water interface and remained constant below (Fig. 2.2g). Given a sedimentation rate of 0.5 cm/yr at this site (Thibodeau et al. 2006), the pyrite found in the sediment at site 23 in 1982 was buried \sim 12.5 cm deeper by 2007. A comparison of the buried 1982 pyrite profile (grey triangle on Fig. 2.2g) with the 2007 pyrite profile at site 23 shows that the formation of pyrite at depth is similar in 1982 and 2007. At station 24, the pyrite content of the sediment is nearly constant with depth in 2007 (Fig.

2.2h), but temporal comparison is not possible because of the lack of historical data.

2.5.2 Arsenic

Total arsenic concentrations [As(T)] did not change between 1982 and 2007 (Figs. 2.3a-b), but the HA-extractable fraction [As(HA)] increased dramatically (Figs. 2.3c-d). In 2007, As(HA) accounted for 32% and 68% of the total solid-phase arsenic at stations 23 and 24, respectively, whereas it only made up 8% and 9% of total arsenic in 1982 (Figs. 2.3a-d). Between 1982 and 2007, the arsenic content in the pyrite phase [As(P)] decreased by 23% at station 23 (Fig. 2.3e). In addition, the concentration of arsenic in the pore-water [As(D)] increased by factors of 4 and 2.5 between 1982 and 2007 at stations 23 and 24, respectively, and peak concentrations migrated closer to the sediment-water interface (Figs. 2.3g-h). As(D) is removed from pore-water at depth at station 23, but a corresponding sink is not found at station 24.

The vertical distributions of the HA-extractable solid As and Fe phases differ at both stations (Figs. 2.3c-d). Whereas the vertical distribution of Fe(HA) and As(HA) were similar and constant with depth in 1982, the vertical distribution of As(HA) in 2007 displays a narrow peak below the sediment-water interface, and is thus more concentrated at the oxic-anoxic boundary than at depth, where the conditions are sulfidic.

2.5.3 Manganese

In contrast to Fe and As, the concentrations and vertical distributions of solid and pore-water Mn are virtually identical in the cores recovered in 1982 and 2007 at stations 23 and 24 (Fig. 2.4). In 2007, solid-phase HA-extractable Mn [Mn(HA)] accounted for almost 100% of the total solid-phase of Mn [Mn(T)] in the first 4 cm below the sediment-water interface and for ~50% beyond this depth at both stations (Figs. 2.4a-d). Pore-water Mn [Mn(D)] profiles remained nearly the same over the last 25 years of bottom-water hypoxia (Figs. 2.4e-f).

2.6 Discussion

The temporal evolution of pore-water and solid phase profiles of three redox-sensitive elements, Mn, Fe and As illustrated the biogeochemical response of the LSLE sediments to persistent bottom water hypoxia. The speciation of Fe and As phases changed during 25 years of persistently hypoxic bottom water. The relative proportion of reactive-solid (HA-extractible) Fe and As increased and accumulated closer to the sediment-water interface (Figs. 2.2c-d and 2.3c-d) whereas the total concentrations and vertical distributions of Fe and As remained nearly invariant (Figs. 2.2a-b and 2.3a-b). Similarly, pore-water Fe and As concentrations increased and the peak concentrations migrated closer to the sediment-water interface (Figs. 2.2i-j and 2.3g-h). The amount of AVS, which accounts for most of the solid iron sulfides, has increased and accumulated at depth in the anoxic sediment (Fig. 2.2e). In contrast, there is no evidence of pyrite formation in the sediment that accumulated during the 25 years of persistent hypoxia and the amount of As that is sequestrated with pyrite has decreased over this period (Figs. 2.2g and 2.3e). On the other hand, Mn concentrations and vertical distributions show no significant change in 25 years of persistent hypoxia (Fig. 2.4).

Katsev et al. (2007) modeled the response of LSLE sediment to progressive oxygen depletion over decadal timescales. Their model predicted that the relative contribution of sulfate reduction to organic matter respiration would increase as overlying water oxygenation decreased, because the proportion of the organic matter flux that is degraded aerobically decreased. Enhanced sulfate reduction in the anoxic sediment will result in increased sulfide production and, in turn, promote iron sulfide formation at depth. In agreement, our results show enrichment in FeS (AVS) at depth (Fig. 2.2e). Katsev et al. (2007)'s model also predicted that the greater accumulation of FeS would deplete the reactive FeO_x pool and that fluxes of reduced iron out of the sediment would progressively increase with decreasing overlying water oxygen concentration. In contrast, our measurements reveal an increase of the reactive FeO_x pool (Figs. 2.2c-f) and show no evidence that dissolved iron is being released to the water column (Figs. 2.2ij).

Sedimentary Fe(III) minerals display a range of reactivity toward dissolved sulfide. Their relative reactivity is typically characterized in terms of their half-life for the reduction of Fe(III)-bearing solid phases in the presence of dissolved sulfide and these vary from a few days to thousands of years (Canfield et al. 1992; Raiswell et al. 1994). Assuming, as discussed above, that bottomwater hypoxia promoted sulfate reduction rates in LSLE sediments, sedimentary Fe(III)-bearing solid phases in the LSLE would be exposed to higher sulfide concentrations for a longer time. As a result, the reductive dissolution of the less reactive Fe(III) minerals such as crystalline oxides (e.g. uncoated magnetite) and reactive silicates (e.g. chlorite; see Canfield et al. 1992), may be stimulated, leading to both enhanced AVS precipitation (Figs. 2.2e-f) and pore-water Fe(II) accumulation (Figs. 2.2i-j). The LSLE sediments are rich in Fe(III) silicates and contain up to 10-15% wt of chlorite and 33-49% wt of illite (Ramachandran 1991). Fe(II) released to the pore-water upon the reductive dissolution of these minerals will either be precipitated as FeS or diffuse up to the oxic layer, where it will be oxidized and precipitated as authigenic FeO_x , thus adding to the reactive FeO_x pool (Figs. 2.2c-d and 2.2i-j).

In an oxygen-depleted environment, where both recycling of reactive FeO_x and the production of sulfide are increased by burial (sedimentation or bioturbation) of fresher organic matter in the sediment, pyrite formation should increase with depth and time (e.g. Cooper and Brush 1991). In contrast, our data show that little or no authigenic pyrite accumulated in the sediment layer deposited during the 25-year sampling interval at station 23 (Fig. 2.2g). Based on their observation of anomalously high FeS:FeS₂ ratios (as high as 7) in Saguenay Fjord sediment, a marine extension of the LSLE, Gagnon et al. (1995) proposed that the abundance of solid reactive iron in these sediments limits the accumulation of pore-water sulfide by sequestering it as FeS (Pyzik and Sommer, 1981; Rickard, 1995). Because pore-water sulfide cannot accumulate to high

concentrations, a strong concentration gradient cannot be generated, limiting the flux of dissolved sulfide to the oxic-anoxic redox boundary where it would be oxidized to S(0) or polysulfides, both of which promote the conversion of FeS to pyrite (Berner 1970; Gagnon et al. 1995; Butler and Rickard 2000). The increase in reactive iron [Fe(HA) + Fe(D)] (Figs. 2.2c-d and 2.2i-j) availability in the LSLE over the past 25 years further restricted the accumulation and diffusion of pore-water sulfide and the production of S(0) thus preventing authigenic pyrite formation.

A second mechanism that may work independently or in concert with the high reactive iron availability in the inhibition of authigenic pyrite formation is the increased dissolved arsenic concentration over the past 25 years in the LSLE sediment (Figs. 2.3g-h). Indeed, Wolthers et al. (2007) showed that the presence of dissolved arsenic inhibits pyrite formation. Our 2007 data at station 23 reveal that authigenic pyrite only accumulates ~25 cm below the sediment-water interface (Fig. 2.2g), below the dissolved arsenic concentration maximum (i.e. for $As(D) < 0.5 \mu mol/L$, see Fig. 2.3g). At station 24, where the dissolved arsenic concentration remains relatively high (> 1 µmol/L, Fig. 2.3h) throughout the anoxic zone of our core, very little authigenic pyrite formed at depth (Fig. 2.2h). Under sulfidic conditions, As(V) is microbially or abiotically reduced to As(III) (Stolz and Oremland 1999) and As(III) can co-precipitate with iron sulfide or pyrite (Belzile and Lebel 1986; Belzile 1988; Savage et al. 2000; Bostick and Fendorf 2003). The limited or lack of authigenic pyrite formation in the sediment layer accumulated since the 1980s (Fig. 2.3e) reduced the strength of the Aspyritic sink (Fig. 2.2g) and contributed to its own accumulation in reactive phases [As(HA) + As(D)] (Figs. 2.3c-d and 2.3g-h), further inhibiting authigenic pyrite formation (Wolthers et al., 2007).

Like iron, arsenic was redistributed within the dissolved and solid phases of the LSLE sediments over 25 years of persistent hypoxia (Fig. 2.3). In oxic sediments, dissolved arsenic (mostly in the form of As(V); Belzile and Tessier 1990) adsorbs strongly and preferentially to FeO_x (Mucci et al. 2003; Root et al. 2007). Thus, the much higher reactive arsenic content in near surface sediments (Figs. 2.2c-d and 2.3c-d) results from its close association to the iron diagenetic cycle (Mucci et al. 2000; Sracek et al. 2004; Root et al. 2007) and may reflect an enhanced recycling of FeO_x through the oxic-anoxic boundary that has resulted from the limited oxygen availability since 1982.

Arsenic is a potentially toxic trace element, whose retention in the sediments depends, among other processes, on the availability of MnO_x and FeO_x (e.g. Belzile and Tessier 1990; Mucci et al. 2000; Sracek et al 2004; Root et al. 2007). As(III) diffusing up from the sediment anoxic layer is believed to be oxidized by MnO_x that accumulate in the oxic layer (Mucci et al. 2000). Upon oxidation to As(V), arsenic is preferentially adsorbed onto FeO_x that are also abundant in the oxic layer (Figs. 2.2c-d). The efficiency of these reactions is such that, despite the increase in pore-water arsenic near the sediment-water interface (Figs. 2.3g-h), the calculated diffusive flux of arsenic across the sediment-water interface has not increased since 1982 (Table 2.3), and is on the same order than the measured flux (Lefort, 2012), suggesting that the persistence of hypoxia has not significantly affected the exchange of arsenic with the overlying waters. Nevertheless, persistent hypoxia may have increased arsenic availability to benthic organisms that live close to the sediment-water interface.

The invariance in the distribution, concentration and partitioning of manganese phases in the sediment of the LSLE since the 1980s (Fig. 2.4) suggests that manganese was and remained at steady state since 1982, and that the fluxes of Mn in and out of the sediment have been invariant during 25 years of persistent hypoxia. Unlike iron and arsenic, there is no effective sedimentary sulfide sink for manganese (Thamdrup et al. 1994; Arakaki and Morse 1996; Morse and Luther III 1999), a limited carbonate sink at depth (Mucci 2004) and most of the Mn(IV) oxides that accumulate in the oxic sediment layer are reactive (hydroxylamine, ascorbic acid and total acid extractions give nearly the same results; Fig. 2.4a-d and section 2.4.2.2). Sundby and Silverberg (1985) estimated that the manganese contained in the oxic surface layer was turned over every 43-207 days. Hence,

MnO_x are rapidly reduced under anoxic conditions (Magen et al. 2011), and the liberated manganese can freely diffuse back to the oxic layer where it is microbially or autocatalytically oxidized and precipitated or may escape to the overlying water (Katsev et al. 2007; Richard 2011; Chaillou et al. submitted). Since the measured flux of dissolved manganese out of the sediment (0.31 mmol m⁻² d⁻¹; Sundby and Silverberg 1985; 0.17-0.93 mmol m⁻² d⁻¹; Chaillou et al. submitted) is on the same order than the particulate flux into the sediment (0.38 mmol m⁻² d⁻¹; Sundby and Silverberg 1985), there is no net accumulation of manganese in the sediment column. Thus, the MnO_x peak simply migrates with the oxic-anoxic boundary as sediment is accumulated. Mucci et al. (2003) reported that manganese was remobilized to the new sediment-interface within one way and reached a new stordy state within lass then three ways following the

reported that manganese was remobilized to the new sediment-interface within one year and reached a new steady state within less than three years following the catastrophic deposition of more than 30 cm of sediment in the Saguenay Fjord. Given the rapid diagenetic response of manganese to physical or chemical perturbations of the sediment column (Mucci and Edenborn 1992; Mucci et al. 2003) and its limited interaction with reduced sulfur phases (e.g., Thamdrup et al. 1994; Arakaki and Morse 1996; Morse and Luther III 1999), the distribution and partitioning of manganese phases throughout the sedimentary column rapidly reached a new steady-state following the progressive depletion of bottom-water oxygen concentrations and the establishment of persistent hypoxic conditions in the LSLE.

2.7 Conclusions

The development of hypoxic conditions in the bottom waters of the LSLE since the early 1980s differentially affected the geochemical cycles of redoxsensitive elements in the sediments. In contrast to manganese, whose sediment profiles have not been affected by the development and persistence of hypoxia, the solid and dissolved iron and arsenic concentrations changed significantly. Whereas the concentrations and vertical distributions of total solid iron and arsenic remain unchanged over the past 25 years, there has been a redistribution of both elements between solid-reactive and refractory phases as well as with the dissolved phase. Persistent hypoxia resulted in: 1) the transfer of iron from less reactive solid Fe(III) phases (silicates and oxides) to the more reactive solid iron pool (easily reducible oxides and AVS), 2) the inhibition of authigenic pyrite formation and 3) the build-up of pore-water iron. Arsenic concentrations changed concomitantly with those of iron. Pyritic-As concentrations decreased, while both the solid-reactive phase and pore-water arsenic increased and peak concentrations migrated significantly closer to the sediment-water interface. Consequently, the persistence of hypoxia limited the incorporation of arsenic into stable authigenic pyrite and increased its availability to benthic organisms. We expect that other elements, whose geochemical behavior is intimately associated with that of iron (e.g. selenium), will also have been redistributed in response to the establishment of persistent hypoxia in the LSLE sediments.

2.8 Acknowledgements

This research was funded by a NSERC Strategic grant to B.S. and A.M. Additional financial support to S.L. was provided by the Department of Earth and Planetary Sciences/McGill and the GEOTOP-UQAM-McGill research centre. We thank the captain and the crew of R/V Coriolis II for their help during a cruise in July 2007 as well as N. Molnar and C. Guignard for their support in the laboratory. We are very grateful to Prof. Charles Gobeil for providing unpublished historical data. Discussions with G. Chaillou were very helpful. Thanks also go to Dr. Denis Gilbert for providing the data and the Matlab[®] code to generate Fig. 2.1.

2.9 References

- Arakaki T, Morse JW (1996) Coprecipitation and adsorption of Mn(II) with mackinawite (FeS) under conditions similar to those found in anoxic sediments. Geochim Cosmochim Acta 57:9-14.
- Belley R, Archambault P, Sundby B, Gilbert F, Gagnon J-M (2010) Effects of hypoxia on benthic macrofauna and bioturbation in the Estuary and Gulf of St. Lawrence, Canada. Cont Shelf Res 30(12):1302-1313.
- Belzile N (1987) Etude géochimique de l'arsenic et du sélénium dans les sédiments du chenal Laurentien. PhD thesis, Université du Québec à Rimouski, 251 pp.
- Belzile N (1988) The fate of arsenic in sediments of the Laurentian Trough. Geochim Cosmochim Acta 52:2293-2302.
- Belzile N, Lebel J (1986) Capture of arsenic by pyrite in near-shore marine sediments. Chem Geol 54:279-281.
- Belzile N, Tessier A (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim Cosmochim Acta 54:103-109.
- Berner RA (1970) Sedimentary pyrite formation. Am J Sci 268:1-23.
- Bostick BC, Fendorf S (2003) Arsenite sorption on troilite (FeS) and pyrite (FeS₂). Geochim Cosmochim Acta 67(5):909–921.
- Boudreau BP (1996) The diffusive tortuosity of fine-grained unlithified sediments. Geochim Cosmochim Acta 60(16):3139-3142.
- Burdige DJ (1993) The biogeochemistry of manganese and iron reduction in marine sediments. Earth Sci Rev 35:249-284.
- Butler IB, Rickard D (2000) Framboidal pyrite formation via the oxidation of iron (II) monosulfide by hydrogen sulphide. Geochim Cosmochim Acta 64(15):2665-2672.
- Canfield DE, Raiswell R, Bottrell S (1992) The reactivity of sedimentary iron minerals toward sulfide. Am J Sci 202:659-683.
- Chaillou G, Archambault P, Lefort S, Mucci A, Sundby B (submitted) Fluxes and distribution of dissolved oxygen, nitrate, phosphate, iron and manganese in Laurentian Trough sediments exposed to different bottom-water oxygen concentrations. Aquat Geochem.
- Chester R, Hughes MJ (1967) A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem Geol 2:249-262.
- Cooper SR, Brush GS (1991) Long-term history of Chesapeake Bay anoxia. Science 254:992-996.
- Diaz R (2001) Overview of hypoxia around the world. Environ Qual 30:275-281.

- Diaz R, Rosenberg RJ (1995) Marine benthic hypoxia: A review of its ecological effects and the behavioural responses of benthic macrofauna. Oceanogr Mar Biol Annu Rev 33:245-303.
- Diaz R, Rosenberg RJ (2008) Spreading dead zones and consequences for marine ecosystems. Science 321:926-929.
- Edenborn HM, Belzile N, Mucci A, Lebel J, Silverberg N (1986) Observations on the diagenetic behavior of arsenic in a deep coastal sediment. Biogeochem 2(4):359-376.
- Edenborn HM, Silverberg N, Mucci A, Sundby B (1987) Sulfate reduction in the sediments of a deep coastal environment. Mar Chem 21:329-345.
- Ferdelman G (1988) The distribution of sulfur, iron, manganese, copper, and uranium in a salt marsh sediment core as determined by a sequential extraction method. Master thesis, University of Delaware.
- Froelich PN, Klinkhammer GP, Bender ML, Luedtkeand NA, Heath GR, Cullen D, Dauphin P, Hammond D, Hartman B, Maynard V (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim Cosmochim Acta 43:1075-1090.
- Gagnon C, Mucci A, Pelletier E (1995) Anomalous accumulation of acid-volatile sulphides (AVS) in a coastal marine sediment, Saguenay Fjord, Canada. Geochim Cosmochim Acta 59(13):2663-2675.
- Gilbert D, Sundby B, Gobeil C, Mucci A, Tremblay G-H (2005) A seventy-twoyear record of diminishing deep-water oxygen in the St. Lawrence Estuary: The Northwest Atlantic connection. Limnol Oceanogr 50(5):1654-1666.
- Gilbert D, Chabot D, Archambault P, Rondeau B, Hébert S (2007) Appauvrissement en oxygène dans les eaux profondes du Saint-Laurent marin : causes possibles et impacts écologiques. Nat Can 131:67-75.
- Gilbert D, Rabalais NN, Diaz RJ, Zhang J (2010) Evidence for greater oxygen decline rates in the coastal ocean than in the open ocean. Biogeosciences 7:2283-2296.
- Gooday AJ, Jorissen F, Levin LA, Middelburg JJ, Naqvi SWA, Rabalais NN, Scranton M, Zhang J (2009) Historical records of coastal eutrophicationinduced hypoxia. Biogeosciences 6:1707–1745.
- Guo T, DeLaune RD, Patrick WH Jr (1997) The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. Environ Int 23(3):305-316.
- Hsieh Y, Yang C (1989) Diffusion Methods for the Determination of Reduced Inorganic Sulfur Species in Sediments. Limnol Oceanogr 34(6):1126-1130.
- Katsev S, Chaillou G, Sundby B, Mucci A (2007) Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the Lower St. Lawrence Estuary. Limnol Oceanogr 52(6):2555-2568.

- König I, Drodt M, Suess E, Trautwein AX (1997) Iron reduction through the tangreen color transition in deep-sea sediments. Geochim Cosmochim Acta 61(8):1679-1683.
- Kostka JE, Luther III GW (1994) Partitioning and speciation of solid phase iron in saltmarsh sediments. Geochim Cosmochim Acta 58(7):1701-1710.
- Kristiansen KD, Kristensen E, Jensen MH (2002) The influence of water column hypoxia on the behaviour of manganese and iron in sandy coastal marine sediment. Estuar Coast Shelf Sci 55:645–654.
- Lefort S (2012) Multidisciplinary approach to study hypoxia in the Estuary and Gulf of St. Lawrence: Is this ecosystem on borrowed time? PhD thesis, McGill University, 155 pp. Appendix to Chapter 3.
- Li Y-H, Gregory S (1974) Diffusion of ions in sea water and in deep-sea sediments. Geochim Cosmochim Acta 38:703-714.
- Lord III CJ (1982) A selective and precise method for pyrite determination in sedimentary materials. J Sediment Petrol 52:664-666.
- Loring DH, Nota DJG (1968) Occurrence and significance of iron, manganese, and titanium in glacial marine sediments from the Estuary of the St. Lawrence River. J Fish Res Broad Can 25(11):2327-2347.
- Lyle M (1983) The brown-green color transition in marine sediments: A marker of the Fe(III)-Fe(II) redox boundary. Limnol Oceanogr 28(5):1026-1033.
- Magen C, Mucci A, Sundby B (2011) Reduction rates of sedimentary Mn and Fe oxides: An incubation experiment with Arctic Ocean sediments. Aquat Geochem 17:629-643.
- Middelburg JJ, Levin LA (2009) Coastal hypoxia and sediment biogeochemistry. Biogeosciences 6:1273-1293.
- Morse JW, Luther III GW (1999) Chemical influences on trace metal-sulfide interactions in anoxic sediments. Geochim Cosmochim Acta 63:3373-3378.
- Morse JW, Eldridge PM (2006) A non-steady-state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the "dead zone" of the Louisiana shelf. Mar Chem 106:239–255.
- Mucci A, Edenborn H-M (1992) Influence of an organic-poor landslide deposit on the early diagenesis of iron and manganese in a coastal marine sediment. Geochim Cosmochim Acta 56:3909-3921.
- Mucci A, Richard L-F, Lucotte M, Guignard C (2000) The differential geochemical behavior of arsenic and phosphorus in the water column and sediments of the Saguenay Fjord Estuary, Canada. Appl Geochem 6:293-324.
- Mucci A, Boudreau B, Guignard C (2003) Diagenetic mobility of trace elements in sediments covered by a flash flood deposit: Mn, Fe and As. Appl Geochem 18(7):1011-1026.

- Mucci A (2004) The behavior of mixed Ca-Mn carbonates in water and seawater: controls of manganese concentrations in marine pore waters. Aquat Geochem 10:139-169.
- Mucci A, Starr M, Gilbert D, Sundby B (2011) Acidification of Lower St. Lawrence Estuary bottom waters. Atmosphere-Ocean 49(3):206-213.
- Nota DJG, Loring DH (1964) Recent depositional conditions in the St. Lawrence River and Gulf – A reconnaissance survey. Mar Geol 2:198-235.
- Park SS, Jaffé PR (1996) Development of a sediment redox potential model for the assessment of post depositional metal mobility. Ecol Model 91:169-181.
- Peña MA, Katsev S, Oguz T, Gilbert D (2010) Modeling dissolved oxygen dynamics and hypoxia. Biogeosciences 7:933–957.
- Phil L, Baden SP, Diaz JR (1991) Effects of periodic hypoxia on distribution of demersal fish and crustaceans. Mar Biol 108:349-360.
- Pyzik AJ, Sommer SE (1981) Sedimentary iron monosulfides: kinetics and mechanism of formation. Geochim Cosmochim Acta 45:687-698.
- Rabalais N, Turner RE (2001) Coastal and Estuarine studies. Coastal hypoxia: consequences for living resources and ecosystems. Ed. American Geophysical Union.
- Raiswell R, Canfield DE, Berner RA (1994) A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation. Chem Geol 111:101-110.
- Ramachandran R (1991) Geochemical and mineralogical characteristics of some fine post-glacial marine deposits in the St. Lawrence Lowlands. PhD thesis, McGill University, 185 pp.
- Reeburgh WS (1967) An improved interstitial water sampler. Limnol Oceanogr 12:163-165.
- Richard D (2011) Kinetics of Manganese Adsorption, Desorption and Oxidation in Coastal Marine Sediments. Master thesis, McGill University, 81 pp.
- Richard L-F (1997) Comparaison des comportements géochimiques du phosphore et de l'arsenic dans le Fjord du Saguenay et l'estuaire maritime du St. Laurent. Master thesis, Université du Québec à Montréal, 69 pp.
- Rickard D (1995) Kinetics of FeS precipitation: Part 1. Competing reaction mechanisms. Geochim Cosmochim Acta 59(21):4367-4379.
- Roden E (2003) Fe(III) oxide reactivity toward biological versus chemical reduction. Environ Sci Technol 37(7):1319-1324.
- Root RA, Dixit S, Campbell KM, Jew AD, Hering JG, O'Day PA (2007) Arsenic sequestration by sorption processes in high-iron sediments. Geochim Cosmochim Acta 71:5782-5803.
- Saulnier I, Mucci A (2000) Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Appl Geochem 15:191-210.

- Savage KS, Tingle TN, O'Day PA, Waychunas GA, Bird DK (2000) Arsenic speciation in pyrite and secondary weathering phases, Mother Lode gold district, Tuolumne County, California. Appl Geochem 15:1219-1244.
- Sracek O, Bhattacharya P, Jacks G, Gustafsson JP, Von Bromssen M (2004) Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. Appl Geochem 19:169-180.
- Stolz JF, Oremland RS (1999) Bacterial respiration of arsenic and selenium. FEMS Microbiol Rev 23:615-627.
- Sundby B, Martinez P, Gobeil C (2004) Comparative geochemistry of cadmium, rhenium, uranium, and molybdenum in continental margin sediments. Geochim Cosmochim Acta 68:2485-2493.
- Sundby B, Silverberg N. (1985) Manganese fluxes in the benthic boundary layer. Limnol Oceanogr 30(2):372-381.
- Taylor KG, Macquaker HS (2011) Iron minerals in marine sediments record chemical environments. Elements 7:113-118.
- Thamdrup B, Fossing H, Jørgensen BB (1994) Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochim Cosmochim Acta 58:5115-5129.
- Thibodeau B, de Vernal A, Mucci A (2006) Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleolontological and geochemical evidence. Mar Chem 231:37-50.
- Tremblay G-H and Gobeil C (1990) Dissolved arsenic in the St. Lawrence Estuary and the Saguenay Fjord, Canada. Mar Pollut Bull 21(10):465-469.
- Turner A (2000) Trace metal contamination in sediments from U.K. estuaries: An empirical evaluation of the role of hydrous iron and manganese oxides. Estuar Coast Shelf Sci 50, 355–371.
- Van Cappellen P, Wang Y (1996) Cycling of iron and manganese in surface sediments: a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron and manganese. Am J Sci 296:197-243.
- Wolthers M, Butler IB, Rickard D (2007) Influence of arsenic on iron sulfide transformations. Chem Geol 236:217-227.

Date	Station	Water Depth (m)	Latitude (°N)	Longitude (°W)	$[O_2]_{BW}$ (µmol/L)	% sat [O ₂] _{BW}	T _{BW} (°C)	S_{BW}	Sediment depth (cm) at which Eh(mV-SCE) < 0
July 7, 2007	23	350	48.70	-68.65	56.6	18.0	5.20	34.56	3
July 9, 2007	24	321	48.45	-69.11	60.3	19.0	5.04	34.49	2

Table 2.1: Characteristics of the sampled stations. $[O_2]_{BW}$, T_{BW} and S_{BW} are, respectively, the dissolved oxygen concentration, temperature and practical salinity of the bottom waters.

	PACS I			MESS I			
	Averaged	Cartified	Standard	Averaged	Cartified	Standard	
	measured	value	deviation	measured	value	deviation 2σ	
	values $(n = 9)$	value	2σ	values $(n = 8)$	value		
Fe	48511	48660	840	30006	30487	1748	
Mn	464	470	12	502	513	25	
As	203	211	11	11.0	10.6	1.2	

Table 2.2: Measured and certified values for marine sediment reference materials PACS I and MESS I from the National Research Council Canada.

Station	Year	z_1 (cm)	z ₂ (cm)	φ ⁽¹⁾	Δ C (µmol/L) ⁽²⁾	J (nmol/cm ² /yr) $^{(3)}$
23	Aug. 1982	0	0.4	0.88	0.031	8 ± 0.7
	Aug. 1984	0	0.5	0.89	0.017	4 ± 0.5
	July 2003	0	0.5	0.89	0.048	10 ± 1.0
	July 2007	0	0.5	0.92	0.046	11 ± 1.0
24	Aug. 1982	0	0.4	0.86	0.011	3 ± 0.4
	July 2003	0	0.5	0.90	0.025	6 ± 0.6
	July 2007	0	0.5	0.87	0.020	4 ± 0.5

Table 2.3: Diffusive fluxes of As at the sediment-water interface (out of the sediment) calculated from Fick's Law.

⁽¹⁾ Porosity in the sediment layer.

⁽²⁾ Difference in concentration between the bottom (z_2) and the top (z_1) of the layer. Concentration in the overlying water (i.e. at z_1) in 1982: 0.0107 µmol/L (Belzile, 1988); in 2007: 0.0155 µmol/L.

⁽³⁾ Diffusive flux calculated from Fick's Law: $J = \phi D_s(As) \Delta C/\Delta z$, where $D_s(As)$ is the tortuosity corrected diffusion coefficient of arsenate ion (Boudreau, 1996). $D_s(As) \approx \phi^2 D(As)$, where D(As) is the salinity and temperature corrected arsenate ion diffusion coefficient and is equal to 155 cm²/yr (Li and Gregory, 1974). The error was estimated based on a 5 % error on concentration measurements (see Method section 2.4.2.1).



Figure 2.1: Map of the Lower St. Lawrence Estuary and Gulf showing the location of sites 23 and 24 sampled in July 2007. The bold black line represents the 200 m isobath. Modified from Gilbert et al. (2007) and reproduced with permission.



Figure 2.2: Total solid Fe (a, b), reactive solid Fe (c, d), acid-volatile sulfide-AVS (FeS) (e, f), pyrite (g, h) and pore-water Fe (i, j) profiles at stations 23 and 24. HA: Hydroxylamine-hydrochloride and acetic acid extractable. Asc: Ascorbate extractable. The 1982 and 1984 data are from Belzile (1987), the 1987 and 1992 data were provided by C. Gobeil (unpublished), and the 1998 data are from Sundby et al. (2004).



Figure 2.3: Total solid (a, b), HA-extractable (c, d), pyritic (e, f) and pore-water (g, h) As profiles at stations 23 and 24. HA: Hydroxylamine-hydrochloride and acetic acid extractable. The 1982, 1984 and 1985 data are from Belzile (1987). Note the scale change between station 23 and 24.



Figure 2.4: Total solid (a, b), HA-extractable (c, d) and pore-water (e, f) Mn profiles at stations 23 and 24. HA: Hydroxylamine-hydrochloride and acetic acid extractable. The 1980 data are from Sundby and Silverberg (1985), the 1982, 1984 and 1985 data are from Belzile (1987), the 1987 and 1992 data were provided by C. Gobeil (unpublished), and the 1994 data are from Richard (1997).

Here, we report results of all the analyses performed on sediment cores recovered in the LSLE in July 2007, including complementary data for stations 23 and 24 and data from two other study sites (stations 20 and 23S) sampled during the same cruise (Table 2.4). Sediment and water samples were recovered following the sampling protocols described in *section 2.4.1*. If not described in the following section, analyses were performed as described in *section 2.4.2*.

2.10.1 Methods description of complementary analyses

2.10.1.1 Carbon and Nitrogen

Inorganic carbon was measured on homogeneized, freeze-dried ediment by coulometric titration. A weighed amount of solid sediment (typically 0.15 g) as reacted with 2N hydrochloric acid (about 6 ml) under continuous nitrogen gas flow to avoid atmospheric contamination. This step converts inorganic carbon to carbon dioxide CO₂, which is transferred by the nitrogen flow to the colorimetric cell of the coulometer. The cell is composed of separate silver anode and platinum cathode compartments containing a solution of ethanolamine. When CO₂ reaches the cell, it is converted to carbonic acid which, in turn, reacts with the amine to give the color change (CO₂ + HO(CH₂)₂NH₂ \rightarrow O(CH₂)₂NHCOO⁻ (blue)+ H⁺). This change is detected by the photodetector, which initiates the electrochemical production of a base (OH⁻) at the cathode until the acid in neutralized and the solution becomes colorless. The amount of current (coulombs) required to titrate the protons released to solution is a direct measure of the inorganic carbon content of the sample.

The total carbon (TC) and nitrogen (TN) content of the homogeneized, freeze-dried sediment were measured in duplicate with an elemental analyzer (CE Instruments NC 2500TM) at the GEOTOP Research Center (Centre de recherche en géochimie et en géodynamique) on a weighed aliquot (~7 mg) of the solid sample. The standard deviation (1 σ) on TC and TN analyses was determined from replicate measurements of Organic Analytical Standard substances (Acetanilide,

Atropine, Cyclohexanone-2.4-Dinitrophenyl-Hydrazone and Urea). It is estimated at $\pm 0.1\%$ for TC and $\pm 0.3\%$ for TN. The overall analytical reproducibility was 5% ($\pm 1\sigma$). The organic carbon content of the sediment was calculated from the difference between the total and inorganic carbon concentrations.

2.10.1.2 $^{15}N_{tot}$ et $^{13}C_{org}$ stable isotopes

Analyses were performed on a mass spectrometer (Micromass IsoprimeTM) coupled to an elemental analyzer (Carlo Erba NC1500TM) at the GEOTOP Research Center. Prior to analysis, an aliquot of the solid sample was reacted with a 1N HCl solution for 24 hours to remove carbonates. The solution was decanted and the solid rinsed with a small volume of distilled water, decanted, dried at room temperature, ground and homogenized. Data are reported in δ (‰) with reference to Vienna-Pee Dee Belemnite (V-PDB) for carbon and atmospheric N₂ for nitrogen (Coplen 1995). Measurement reproducibility is 0.1‰ for $\delta^{13}C_{org}$ and 0.2‰ for $\delta^{15}N_{org}$, as determined from replicate measurements of standard materials during analytical runs. The international standards IAEA-C6 sucrose and IAEA-N2 were measured several times during the isotopic analyses and yielded, respectively, an average value of $\delta^{13}C = -10.73 \pm 0.02\%$ (n = 4) whereas the reported value is $-10.8 \pm 0.1\%$, and $\delta^{15}N = 20.20 \pm 0.24\%$ (n = 4) whereas the reported value is $20.41 \pm 0.12\%$ (all $\pm 1\sigma$).

2.10.1.3 HCl solid sediment extraction

The HCl extraction was applied because it is one of the most commonly used selective extractions and often operationally defines the reactive iron content of the sediment (Leventhal and Taylor, 1990; Raiswell et al., 1994). A weighed aliquot of the solid freeze-dried sediments was reacted for 24h in 1M HCl (solid:solution ratio = 1:50) and continuously mixed on a wrist shaker. This extraction typically dissolves iron monosulfides, amorphous and crystalline iron oxihydroxides, manganese oxihydroxides, carbonates and hydrous aluminosilicates (Huerta-Diaz and Morse, 1992; Kostka and Luther, 1994).

2.10.1.4 Selenium

The total pore-water Se concentrations were determined by hydride generation-atomic fluorescence spectrometry at the Department of Chemistry and Biochemistry of Laurentian University (Sudbury, Ontario) (Chen et al., 2005). Calibration curves were constructed using diluted, commercial aqueous 1000 mg/L standards in the appropriate matrices. Prior to analysis, selenium was reduced to selenite following the addition of concentrated hydrochloric acid to a final concentration of 4.0M, microwave-ramped from 0 to 110°C for 10 minutes and heated at 110°C for 15 min to accelerate the reduction (Yu-Wei Chen, pers. comm.).

The freeze-dried sediments were also subjected to a total dissolution and pyrite extraction. The procedures are described in detail in *section 2.4.2*. Reference sediment materials, MESS-1 and PACS-1, purchased from the National Research Council of Canada, were carried through the total extraction protocol and provide an estimate of the reproducibility and accuracy of the procedure (Table 2.5). Replicate pyrite extractions were not performed, but, as estimated by Lord III (1982), the relative standard deviation is expected to be less than 3%. Saulnier and Mucci (2000) reported that the mean relative standard deviation for pyrite extracted from Saguenay Fjord (a tributary of the St. Lawrence) sediments, using the same method, was 1.6 % and the detection limit was 0.2 g pyrite/kg of dry sediment. Extracted pyrite Se concentrations were determined by the same instrumental methods described for the pore-water analyses. Total solid Se concentrations were measured by AAS with FIAS. The error of the measurements and reproducibility are better than 5%. The detection limit for Se is 10 ng/L (0.12 nmol/L).

2.10.2 Results

Analytical and field data are presented in the following Tables for each station or core.

Date	Station	Water Depth (m)	Latitude (°N)	Longitude (°W)	$[O_2]_{BW}$ (µmol/L)	% sat [O ₂] _{BW}	T _{BW} (°C)	S_{BW}	Sediment depth (cm) at which Eh(mV-SCE) < 0
July 5, 2007	20	328	49.42	-66.32	99.1	31.4	5.44	34.74	7
July 7, 2007	23	350	48.70	-68.65	56.6	18.0	5.20	34.56	3
July 8, 2007	23 S	308	48.65	-68.56	60.3	18.98	5.07	34.50	1
July 9, 2007	24	321	48.45	-69.11	60.3	19.0	5.04	34.49	2

Table 2.4: Characteristics of the sampled stations. $[O_2]_{BW}$: dissolved oxygen concentration in the bottom waters; T_{BW} : temperature of the bottom waters; S_{BW} : Salinity of the bottom waters.

	PACS I			MESS I		
	Averaged	Cartified	Certified	Averaged	Cartified	Certified
	measured	value	standard	measured	voluo	standard
	values $(n = 9)$	value	deviation 2σ	values $(n = 8)$	value	deviation 2σ
Se	1.00 ± 0.14	1.09	0.11	0.32 ± 0.08	0.34	0.06

Table 2.5: Measured and certified values for marine sediment reference materials PACS I and MESS I obtained from the National Research Council Canada.

30-35

35-40

40-45

-135

-129

-215

0.742

0.738

0.740

1.57

1.49

1.41

0.21

0.19

0.18

Depth	Eh	Porosity	C _{tot}	Cinorg	Corg	N _{tot}	C_{tot}/N_{tot}	C_{org}/N_{tot}	$\delta^{13}C$	$\delta^{15}N$
(cm)	(mV)		(wt%)	(wt%)	(wt%)	(wt%)			(‰)	(‰)
0-0.5	91	0.875	1.82	0.19	1.63	0.16	13.2	11.8	-24.2	
0.5-1	67	0.863	1.83	0.19	1.64	0.16	13.4	12.0	-24.3	5.5
1-2	51	0.843	1.85	0.20	1.65	0.16	13.7	12.2	-24.4	5.6
2-3	-159	0.831	1.76	0.18	1.59	0.15	13.6	12.3	-24.4	4.9
3-4	-168	0.809	1.78	0.19	1.59	0.16	13.3	11.9	-24.4	5.4
4-5	-169	0.779	1.77	0.18	1.59	0.15	13.6	12.3	-24.4	4.9
5-7	-163	0.777	1.75	0.18	1.57	0.15	13.8	12.4	-24.4	4.6
7-9	-165	0.787	1.71	0.18	1.53	0.14	14.2	12.6	-24.6	4.8
9-11	-154	0.783	1.75	0.19	1.56	0.14	14.7	13.2	-24.7	4.7
11-13	-157	0.778	1.79	0.19	1.59	0.14	15.0	13.4	-24.8	4.8
13-15	-152	0.777	1.78	0.20	1.58	0.13	15.5	13.8	-24.9	4.3
15-18	-149	0.774	1.76	0.20	1.56	0.13	15.7	13.9	-25.0	4.7
18-21	-130	0.771	1.76	0.20	1.57	0.13	15.9	14.2	-25.0	4.9
21-25	-162	0.763	1.63	0.20	1.43	0.12	16.2	14.3	-25.0	4.0
25-30	-155	0.756	1.67	0.22	1.45	0.12	16.3	14.1	-25.0	4.2

1.36

1.30

1.23

0.12

0.11

0.11

16.0

16.0

15.0

13.8

13.9

13.0

-25.0

-24.6

-24.7

4.5

4.2

4.6

Table 2.6: Analytical results of sediments recovered at station 24: Field measurements, carbon and nitrogen contents and isotopic compositions.

Depth	Eh	Porosity	C _{tot}	Cinorg	Corg	N _{tot}	Ctot/Ntot	Corg/Ntot	δ ¹³ C	$\delta^{15}N$
(cm)	(mV)		(wt%)	(wt%)	(wt%)	(wt%)		<u> </u>	(‰)	(‰)
0-0.5	155	0.918	1.82	0.18	1.64	0.17	12.3	11.1	-23.7	6.1
0.5-1	194	0.900	1.80	0.17	1.63	0.17	12.4	11.2	-24.0	6.1
1-2	54	0.894	1.83	0.19	1.64	0.17	12.4	11.1	-23.9	6.1
2-3	173	0.877	1.84	0.18	1.66	0.17	12.5	11.3	-23.8	5.9
3-4	-152	0.866	1.80	0.17	1.63	0.16	12.8	11.6	-23.9	5.6
4-5	-153	0.860	1.70	0.17	1.53	0.16	12.6	11.3	-23.9	5.8
5-7	-156	0.849	1.73	0.17	1.56	0.16	12.7	11.4	-23.8	5.4
7-9	-152	0.828	1.72	0.18	1.54	0.16	12.7	11.4	-24.0	5.5
9-11	-140	0.810	1.65	0.18	1.47	0.15	12.9	11.5	-24.2	5.4
11-13	-163	0.803	1.72	0.19	1.53	0.15	13.4	11.9	-24.3	5.4
13-15	-124	0.800	1.69	0.18	1.50	0.14	13.8	12.3	-24.5	5.2
15-18	-159	0.798	1.68	0.17	1.51	0.14	13.6	12.2	-24.4	5.1
18-21	-186	0.796	1.65	0.18	1.46	0.14	14.2	12.6	-24.9	5.1
21-25	-134	0.797	1.57	0.18	1.39	0.13	14.1	12.4	-24.5	5.1
25-30	-145	0.794	1.54	0.18	1.36	0.13	14.1	12.4	-24.5	4.9
30-35	-173	0.780	1.41	0.16	1.26	0.12	13.4	11.9	-24.2	5.0
35-40	-144	0.780	1.37	0.15	1.22	0.12	13.2	11.7	-24.1	4.9
40-45	-164	0.787	1.29	0.16	1.13	0.12	12.9	11.4	-24.2	4.9

Table 2.7: Analytical results of sediments recovered at station 23: Field measurements, carbon and nitrogen contents and isotopic compositions.

49

Depth	Eh	Porosity	C _{tot}	Cinorg	Corg	N _{tot}	C _{tot} /N _{tot}	Corg/Ntot	δ ¹³ C	$\delta^{15}N$
(cm)	(mV)		(wt%)	(wt%)	(wt%)	(wt%)		Ū.	(‰)	(‰)
0-0.5	84	0.902	1.86	0.17	1.69	0.16	13.3	12.1	-24.2	6.1
0.5-1	93	0.879	1.85	0.19	1.67	0.16	13.3	12.0	-24.8	4.9
1-2	-45	0.864	1.82	0.19	1.63	0.16	13.3	11.9	-24.4	5.2
2-3	-80	0.833	1.84	0.19	1.65	0.16	13.3	11.9	-24.3	5.2
3-4	-135	0.832	1.83	0.18	1.65	0.16	13.4	12.1	-24.3	5.1
4-5	-74	0.824	1.84	0.18	1.66	0.16	13.8	12.2	-24.4	5.1
5-7	-79	0.824	1.79	0.18	1.61	0.16	13.3	12.0	-24.3	5.2
7-9	-52	0.810	1.82	0.19	1.63	0.16	13.5	12.1	-24.4	4.2
9-11	-157	0.798	1.79	0.19	1.60	0.15	14.0	12.5	-24.6	4.9
11-13	-136	0.783	1.80	0.19	1.61	0.15	14.0	12.5	-24.7	4.8
13-15	-136	0.775	1.79	0.18	1.61	0.14	15.2	13.6	n.d.	n.d.
15-18	-160	0.771	1.76	0.21	1.55	0.14	15.1	13.4	-24.8	4.7
18-21	-133	0.764	1.73	0.20	1.53	0.13	15.4	13.6	-25.0	4.5
21-25	-137	0.765	1.69	0.28	1.41	0.12	16.2	13.5	-24.9	4.9
25-30	-144	0.759	1.54	0.20	1.34	0.11	15.7	13.7	-24.9	4.7
30-35	-136	0.753	1.57	0.16	1.40	0.12	15.4	13.8	-24.6	4.4
35-40	-303	0.763	1.46	0.16	1.30	0.11	15.2	13.5	-24.8	4.3
40-45	-147	0.776	1.45	0.17	1.27	0.11	14.8	13.0	-24.8	4.4

Table 2.8: Analytical results of sediments recovered at station 23S: Field measurements, carbon and nitrogen contents and isotopic compositions. n.d.: no data.
35-40 -19

0.814

1.84

0.50

Depth	Eh	Porosity	C _{tot}	Cinorg	Corg	N _{tot}	Ctot/Ntot	Corg/Ntot	$\delta^{13}C$	$\delta^{15}N$
(cm)	(mV)		(wt%)	(wt%)	(wt%)	(wt%)		-	(‰)	(‰)
0-0.5	246	0.890	2.04	0.42	1.61	0.20	12.1	9.59	-22.3	7.39
0.5-1	239	0.883	1.99	0.42	1.57	0.19	12.0	9.48	-22.3	7.34
1-2	248	0.873	2.02	0.39	1.62	0.20	12.0	9.67	-22.3	n.d.
2-3	250	0.869	2.04	0.45	1.60	0.20	12.2	9.56	-22.3	7.36
3-4	227	0.856	2.03	0.45	1.59	0.19	12.3	9.59	-22.4	7.11
4-5	178	0.851	2.03	0.45	1.58	0.19	12.2	9.49	-22.4	7.15
5-7	133	0.834	2.03	0.45	1.58	0.19	12.3	9.60	-22.4	7.18
7-9	-58	0.824	1.99	0.47	1.52	0.19	12.5	9.54	-22.5	7.05
9-11	-121	0.823	1.91	0.46	1.44	0.18	12.6	9.52	-22.4	7.1
11-13	-131	0.819	2.02	0.47	1.54	0.19	12.6	9.61	-22.5	7.12
13-15	-93	0.819	1.95	0.49	1.46	0.18	12.4	9.30	-22.5	n.d.
15-18	-84	0.821	1.93	0.49	1.44	0.18	12.5	9.35	-22.6	6.98
18-21	-77	0.820	1.89	0.50	1.39	0.17	12.9	9.50	-22.4	6.92
21-25	-72	0.819	1.88	0.50	1.39	0.17	12.8	9.46	-22.4	5.96
25-30	-34	0.825	1.84	0.49	1.34	0.17	12.8	9.38	-22.3	7.02
30-35	-18	0.826	1.86	0.49	1.37	0.17	12.9	9.48	-22.4	7.01

1.34

0.16

13.3

9.68

-22.4

6.75

Table 2.9: Analytical results of sediments recovered at station 20: Field measurements, carbon and nitrogen contents and isotopic compositions. n.d.: no data.

Depth	Fe(D)	Mn(D)	As(D)	Se(D)
(cm)	(µmol/L)	(µmol/L)	(µmol/L)	(nmol/L)
0-0.5	0	5.1	0.03	12.4
0.5-1	0	8.2	0.04	10.5
1-2	0	22.2	0.07	12.9
2-3	0	104	0.14	12.6
3-4	38	114	0.28	10.2
4-5	68	174	0.29	12.9
5-7	97	109	0.58	14.0
7-9	105	114	0.64	18.3
9-11	131	108	0.88	15.0
11-13	120	166	0.67	11.2
13-15	97	186	0.70	13.6
15-18	70	203	0.74	14.2
18-21	125	207	0.84	15.2
21-25	147	224	1.00	27.8
25-30	137	216	1.04	15.4
30-35	137	219	1.02	18.4
35-40	128	203	0.58	17.0
40-45	111	189	0.41	16.1

Table 2.10: Analytical results of sediments recovered at station 23S: dissolved species concentrations.

Depth	Fe(D)	Mn(D)	As(D)	Se(D)
(cm)	(µmol/L)	(µmol/L)	(µmol/L)	(nmol/L)
0-0.5	0	0	0.04	30.6
0.5-1	0	0	0.05	32.9
1-2	0	30.4	0.08	17.6
2-3	0	26.9	0.11	21.8
3-4	0	119	0.12	25.8
4-5	0	126	0.14	19.8
5-7	0	248	0.15	19.2
7-9	5.5	161	0.11	24.0
9-11	8.4	243	0.11	23.2
11-13	16	287	0.13	23.9
13-15	12	272	0.14	20.2
15-18	9.1	269	0.17	13.2
18-21	5.3	204	0.20	16.8
21-25	5.1	154	0.22	16.4
25-30	0	103	0.24	18.4
30-35	0	68.9	0.26	19.0
35-40	0	57.6	0.37	29.9

Table 2.11: Analytical results of sediments recovered at station 20: dissolved species concentrations.

Depth (cm)	Fe(Asc) (mmol/kg)	Fe(HCl) (mmol/kg)	Fe(HA) (mmol/kg)	Mn(Asc) (mmol/kg)	Mn(HCl) (mmol/kg)	Mn(HA) (mmol/kg)	As(HCl) (umol/kg)	As(HA) (umol/kg)
0-0.5	125	412	154	18.2	50.4	46.7	178	184
0.5-1	131	421	169	29.3	34.4	32.2	204	247
1-2	73.6	435	141	3.1	24.3	21.3	150	176
2-3	105	433	137	6.7	11.9	9.8	146	140
3-4	69.7	399	112	6.3	11.5	9.2	85.9	114
4-5	70.3	416	126	6.5	12.1	9.7	67.7	90.3
5-7	63.5	403	118	3.8	9.0	6.4	40.2	60.3
7-9	69.3	427	124	3.1	8.2	5.6	53.1	81.5
9-11	68.9	419	119	2.9	7.8	5.2	60.1	79.5
11-13	74.8	394	123	3.3	8.2	5.5	49.7	70.8
13-15	84.5	405	134	3.5	8.3	6.1	63.5	94.5
15-18	77.6	414	124	3.6	8.8	6.2	54.9	106
18-21	70.1	422	122	3.2	8.6	6.0	47.4	99.4
21-25	68.5	448	130	3.1	8.7	5.9	45.4	95.2
25-30	72.6	438	134	3.3	8.7	6.1	52.2	70.0
30-35	62.2	393	119	3.1	8.3	5.6	39.2	65.6
35-40	62.1	405	121	3.1	8.4	5.4	32.5	47.0
40-45	58.2	417	122	3.2	8.9	6.1	37.2	68.3

Table 2.12: Analytical results of sediments recovered at station 23S: solid species concentrations of selective extractions.

Denth	Fe(Ase)	E _e (HCl)	E ₂ (HA)	AVS	Mn(Asc)	Mn(HCl)	Mn(HA)	A _c (HCl)	$\Lambda_{c}(\mathbf{H}\Lambda)$
(em)	Fe(ASC)	re(ncl)	$fe(\Pi A)$	Avs	(mm al/lea)	$\operatorname{MII}(\operatorname{HCI})$	$\operatorname{MII}(\Pi A)$	$As(\Pi CI)$	$AS(\Pi A)$
(cm)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(mmoi/kg)	(µmol/kg)	(µmol/kg)
0-0.5	78.0	329	83.9	0.39	88.0	111	127	109	62.4
0.5-1	78.7	335	81.1	0.27	102	121	132	95.4	60.3
1-2	75.7	343	73.1	0.05	84.9	111	98.6	104	58.4
2-3	76.5	378	93.4	0.33	62.4	75.1	70.7	121	76.9
3-4	70.9	366	92.4	0.53	42.7	48.1	51.9	80.5	61.8
4-5	74.3	359	70.2	0.41	55.6	57.8	53.4	93.1	45.6
5-7	54.9	356	73.1	0.46	27.8	33.6	27.9	68.1	40.1
7-9	29.3	347	64.5	0.93	10.4	17.5	14.1	28.4	21.5
9-11	40.6	355	67.4	0.63	21.4	25.1	19.8	34.4	24.6
11-13	29.2	347	57.1	2.30	7.9	16.6	10.7	22.2	17.0
13-15	21.4	326	59.7	0.77	6.0	16.3	13.1	13.2	10.5
15-18	25.9	343	54.4	1.99	7.6	16.7	10.9	16.1	13.5
18-21	16.8	361	47.9	2.22	4.6	13.3	8.5	14.3	11.7
21-25	15.2	352	48.3	1.51	4.1	12.3	7.4	13.4	11.4
25-30	14.4	352	39.1	1.33	3.9	12.8	6.5	16.7	11.4
30-35	11.8	345	41.8	1.80	2.5	10.6	5.8	18.5	12.8
35-40	10.1	342	38.5	0.94	2.2	10.6	5.5	17.0	11.8

Table 2.13: Analytical results of sediments recovered at station 20: solid species concentrations of selective extractions.

35-40 34.4

830

13.9

Depth	Fe(P)	Fe(T)	Mn(T)	As(P)	As(T)	Se(P)	Se(T)
(cm)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(µmol/kg)	(µmol/kg)	(µmol/kg)	(µmol/kg)
0-0.5	0.99	867	111	0.82	111	1.69	n.d.
0.5-1	1.59	874	117	1.25	120	1.81	n.d.
1-2	0.98	891	105	1.32	111	1.94	6.67
2-3	1.15	853	74.7	1.11	128	2.48	7.34
3-4	1.01	952	51.4	1.77	109	2.05	7.66
4-5	1.03	952	59.0	1.21	99.0	2.34	7.75
5-7	1.07	964	33.4	1.33	82.9	2.35	8.61
7-9	1.10	901	20.9	1.94	57.9	2.22	9.14
9-11	1.77	876	27.3	3.05	64.8	2.16	8.16
11-13	1.62	929	20.0	2.87	52.0	1.82	9.26
13-15	2.71	846	18.0	8.43	48.1	2.04	9.37
15-18	6.65	866	20.0	15.8	59.8	2.14	8.55
18-21	13.5	868	16.5	24.8	64.4	2.47	8.69
21-25	20.7	838	15.5	26.9	73.1	3.02	8.26
25-30	28.4	855	16.1	32.5	79.2	3.19	8.08
30-35	35.8	832	14.4	34.6	87.5	3.63	9.24

36.8

75.7

3.36

10.0

Table 2.14: Analytical results of sediments recovered at station 20: pyrite and total solid species concentrations. n.d.: no data.

2.10.3 Short discussion

Like arsenic, the diagenetic cycle of selenium is associated with those of iron and manganese (e.g. Masscheleyn et al., 1991; Aggett & Kriegman, 1998; Takayanagi & Belzile, 1988). Because of the lack of historical data for this element in the LSLE, we did not present the results of our solid sediment and pore-water analyses in the previous manuscript. Nevertheless, it would seem that selenium responded similarly to arsenic as a result of oxygen depletion in the bottom waters of the LSLE since the pore-water Se concentrations increased between 1984 and 2007 (Fig. 2.5) while the total solid Se concentration remained unchanged.



Figure 2.5: Historical comparison of pore-water [Se(D)] and total solid [Se(T)] selenium concentrations. The 1982 and 1984 data are from Belzile (1987).

2.10.4 References

Aggett J, Kriegman MR (1998) The extent formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. Water Resources 22(4):407-411.

- Belzile N (1987) Etude géochimique de l'arsenic et du sélénium dans les sédiments du chenal Laurentien. PhD thesis, Université du Québec à Rimouski, 251 pp.
- Chen Y-W, Zhou XL, Tong J, Truong Y, Belzile N (2005) Photochemical behavior of inorganic and organic selenium compounds in various aqueous solutions. Anal Chim Acta 545(2):142-148.
- Huerta-Diaz M, Morse J (1992) Pyritization of trace metals in anoxic marine sediments. Geochim Cosmochim Acta 56:2681-2702.
- Kostka JE, Luther III GW (1994) Partitioning and speciation of solid phase iron in saltmarsh sediments. Geochim Cosmochim Acta 58(7):1701-1710.
- Leventhal J, Taylor C (1990) Comparison of methods to determine degree of pyritisation. Geochim Cosmochim Acta 54:2621-2625.
- Lord III CJ (1982) A selective and precise method for pyrite determination in sedimentary materials. J Sediment Petrol 52:664-666.
- Masscheleyn PH, Delaune RD, Patrick WH Jr (1991) Biogeochemical behavior of selenium in anoxic soils and sediments: An equilibrium thermodynamics approach. J Environ Sci Health A26(4):555-573.
- Raiswell R, Canfield DE, Berner RA (1994) A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation. Chem Geol 111:101-110.
- Saulnier I, Mucci A (2000) Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Appl Geochem 15:191-210.
- Takayanagi K, Belzile N (1988) Profiles of dissolved and acid-leachable selenium in a sediment core from the Lower St. Lawrence Estuary. Mar Chem 24:307-314.

Chapter 3

Fluxes and distribution of dissolved oxygen, nitrate, phosphate, iron and manganese in Laurentian Trough sediments exposed to different bottomwater oxygen concentrations

In the previous chapter, we showed that the sediment chemistry was modified by the progressive depletion of oxygen and the establishment of hypoxia in the bottom water of the Lower St. Lawrence Estuary. This was reflected in an enhanced recycling of Fe and As, and resulted in greater accumulation of pore-water Fe and As closer to the sediment-water interface. Given the stark modifications in the sediment chemistry, one would think that solute exchange across the sediment-water interface might also be affected. In contrast, despite the build-up of pore-water Fe and As in the past 25 years, the calculated diffusive fluxes (based on Fick's first law and the concentration gradients measured in the overlying water column and over the first 0.5 cm of the sediment) of these two elements across the sediment-water interface have remained statistically the same (see Table 2.3). To confirm these estimates, we investigated the relationship between bottom water oxygenation and the measured fluxes of oxygen, nutrient salts and metabolites in the sediments of the Laurentian Channel.

This chapter is based on a manuscript submitted to the journal Aquatic Geochemistry in September 2011: Chaillou G., Archambault P., Lefort S., Mucci A. and Sundby B., Fluxes and distribution of dissolved oxygen, nitrate, phosphate, iron and manganese in Laurentian Trough sediments exposed to different bottom-water oxygen concentrations.

Fluxes and Distributions of Dissolved Oxygen, Nitrate, Phosphate, Iron, and Manganese in Laurentian Trough Sediments Exposed to Different Bottom-Water Oxygen Concentrations

Gwénaëlle Chaillou¹, Philippe Archambault¹, Stelly Lefort², Alfonso Mucci², and Bjørn Sundby^{1, 2}

 Institut des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski, 310 Allée des Ursulines, CP 3300, Rimouski (Québec) Canada G5L 3A1

2. GEOTOP and Earth & Planetary Sciences, McGill University, 3450 University Street, Montreal (Québec) Canada H3A 2A7

Submitted to Aquatic Geochemistry, September 2011

Accepted with major revisions, January 2012

3.1 Abstract

In order to examine the relationship between bottom-water oxygenation and the biogeochemistry and fluxes of nutrients and metabolites in coastal marine sediments, we measured fluxes of dissolved oxygen, nitrate, soluble reactive phosphate (SRP), and soluble manganese and iron across the sediment-water interface at seven stations in the Lower Estuary and Gulf of St. Lawrence. The bottom water oxygen concentration at these sites ranged from 60 to 155 μ mol O₂ L⁻¹. The measured fluxes were highly variable with intra-station variability being comparable to inter-station variability. Strong variability also characterized the composition of the benthic fauna. No obvious relationship was observed between measured element fluxes and the bottom-water oxygen concentration. Short-term experimental manipulations of the overlying water dissolved O₂ concentration, from in-situ conditions to ~40 and ~20 μ mol O₂ L⁻¹ reveal that nitrate and SRP benthic fluxes were independent on bottom water O₂ concentrations. The lack of a relationship between the sediment oxygen uptake rate and the bottom water oxygenation could imply that a critical oxygen concentration, below which the sediment oxygen uptake becomes a function of the bottom water oxygen concentration, has not yet been reached in the Estuary and Gulf of St. Lawrence in spite of the development and persistence of hypoxic conditions.

3.2 Introduction

Many estuarine and coastal marine environments throughout the world have become hypoxic during the last several decades (Diaz and Rosenberg, 2008; Kemp et al., 2009). Severe hypoxia is the condition that occurs when the dissolved oxygen concentration falls below 62.5 μ mol L⁻¹ (= 2 mg L⁻¹) (Diaz and Rosenberg, 1995). Hypoxia is often a seasonal phenomenon that develops as the water column becomes stratified and is eradicated following annual vertical mixing events (Diaz and Rosenberg, 2008; Rabalais et al., 2010), but hypoxia can be persistent in environments where stratification is permanent. Persistent hypoxia is found throughout the bottom waters of the Lower St. Lawrence Estuary (LSLE), the landward portion of the permanently stratified, Laurentian Trough, a > 300 m deep channel that extends 1240 km from the eastern Canadian continental shelf break to the Saguenay Fjord at Tadoussac (Fig. 3.1).

The bottom water in the Laurentian Trough originates in the Western Atlantic Ocean. As it flows landward towards the head of the channel, the bottom water looses oxygen through pelagic and benthic respiration (Lehmann et al., 2009). The progressive loss of oxygen generates a gradient of decreasing bottom-water oxygen concentrations in the landward direction (Gilbert et al., 2005). Bottom-water oxygen concentrations in the LSLE decreased, on average, by about 1 μ mol L yr⁻¹ between the 1930s and the 1980s, but have since remained relatively stable at 60 (±5) μ mol L⁻¹ (Gilbert et al., 2005).

The bottom water oxygen concentration affects the abundance, diversity, and functions of benthic communities, including bioirrigation and bioturbation (Dauer et al., 1993; Diaz and Rosenberg, 1995; Keister et al., 2000; Levin, 2003). Through its effects on benthic communities, the oxygen concentration impacts the recycling and remineralization efficiency of sedimentary organic matter (Aller, 1994; Aller and Aller, 1998; Kristensen et al., 1995) and the exchange of solutes across the sediment-water interface (Sayles et al., 1994; Sell and Morse, 2006; Katsev et al., 2007; Pakhomova et al., 2007; Wijsman et al., 2002; Morse and Eldridge, 2006). Despite recent efforts to quantify the activity of groups and individual species of benthic organisms (Bulling et al., 2008; Michaud et al., 2005, 2006, 2009; Thrush et al., 2006; Zorn et al., 2006; Weissberger et al., 2009), relatively little is known about the effects of biodiversity and faunal interactions on rates and modes of bioturbation and bioirrigation, and on the biogeochemistry of benthic ecosystems (Bulling et al., 2008; Waldbusser et al., 2004). Most geochemical and ecological models assume a linear relationship between bottom water oxygen concentration, sediment oxygen penetration depth,

and fluxes of oxygen and metabolites at the sediment-water interface (Caï and Sayles, 1996; Pearson and Rosenberg, 1978; Goldbold and Solan, 2009). In contrast, Katsev et al. (2007) applied a non-linear model, taken from Ritter and Montagna (1999), in which benthic activity, represented by bioturbation and bioirrigation coefficients, decreases sharply when the bottom-water oxygen concentration approaches the hypoxic threshold. Moreover, the response of benthic ecosystems to decreasing oxygen concentration may depend on the initial biogeochemical conditions, the history of the water mass, and the temporal persistence of the oxygen depletion (see Middelburg and Levin, 2009).

In this study, we measured the pore-water oxygen, manganese, iron, and sulfide concentrations, the density of macrofauna (expressed as the number of individuals per square meter), as well as the fluxes of dissolved oxygen, nitrate, soluble reactive phosphate (SRP), soluble manganese and iron across the sediment-water interface at seven stations in the Laurentian Channel along which bottom water oxygen concentrations ranged from 60 to 155 μ mol O₂ L⁻¹. Regulation of these fluxes by varying bottom water oxygen concentrations was also studied experimentally. The objective was to provide insight into the relationship between bottom water oxygenation and the biogeochemistry and fluxes of nutrients and metabolites in sediments in a coastal environment.

3.3 Site Description

The sedimentology and lithology of the sediments that cover the Laurentian Trough were described by Loring and Nota (1973). The surficial sediment consists of a brown-coloured layer, 1-3 cm thick, grading downwards to an homogeneous unstratified olive grey mud containing equal parts of clay- and silt-sized particles and 5-10 % sand. The mineralogy of the clay fraction is dominated by quartz, feldspars, amphiboles, pyroxenes and illite, indicating that the sediment is immature. These minerals are principally derived from the

mechanical weathering of the crystalline rocks and the Quaternary deposits of the Canadian Shield. The organic carbon content of the sediment is ~2 % d.w. (Silverberg et al. 1987). It consists of variable fractions of autochtonous and allochtonous particulate material, of which the latter becomes dominant at the boundary between the LSLE and the Gulf (Lucotte et al., 1991, Colombo et al., 1996a,b) (Fig. 3.1). Catabolic processes in the sediment are the most important sinks of oxygen in the LSLE (Lehmann et al., 2009) and play a pivotal role in generating hypoxic conditions in the bottom water (Benoit et al., 2006). In response to the progressive bottom-water oxygen depletion and the accumulation of metabolic CO_2 , a decrease in pH has also been recently reported (Mucci et al., 2011). Details about the sampling stations can be found in Table 3.1.

The diversity, feeding modes, and bioturbation mode and intensity by endofauna and epifauna vary significantly along the length of the Laurentian Trough (Belley et al., 2010; Bourque and Archambault, submitted). An analysis of historical data on macrobenthic endofauna over the last 30 years revealed a decrease in biological richness and diversity in the LSLE sediment, reflected by a decreased density of species with a lower tolerance to low oxygen concentrations, such as the omnivors *Lumbrineris* sp. which were replaced by more tolerant species such as the seafloor surface-dwelling polychaete *Ampharete sp.* (Bourque and Archambault, submitted; Table 3.2). Surface deposit feeders currently dominate the macrofaunal community at stations located at the landward end of the Laurentian Trough. At stations 24 to 21, they make up 40 % to 76 % of the total endofaunal assemblage (Fig. 3.1; Table 3.2). Similar changes are also observed in macrobenthic epifauna (Belley et al., 2010). In the LSLE, surface deposit feeders and low-oxygen tolerant species dominate over suspension feeders and low-oxygen intolerant species. These observations reveal that both the structure and the functionality of the macrofaunal community are being modified along the bottom-water oxygen concentration gradient.

3.4 Materials and Methods

3.4.1 Core collection

Undisturbed, 50-cm long, 10-cm i.d., cylindrical sediment cores, including the overlying water, were recovered in August 2005, August 2006 and July 2007 with a Bowers & Connelly Multicorer (Barnet et al., 1984) (Table 3.1). The multicorer recovers up to eight replicate cores with each cast over a surface area of ~ 1 m². Whereas some of the cores from a same cast were incubated at the in-situ temperature to measure fluxes, others were used to determine the vertical distribution of several electro-active pore-water species.

3.4.2 Flux measurements

In 2005 and 2006, the sediment cores were incubated on-board, as previously reported by Katsev et al. (2007). In 2007, the cores were kept at the *insitu* temperature and transferred to a refrigerated shore-based laboratory where the incubations were carried out on three cores from the same cast under controlled temperature (e.g. 5-6 °C) and oxygen concentration (e.g. 55 to 100 μ mol O₂ L⁻¹) one week upon recovery. The oxygen concentration in the overlying water of the cores collected at sites 23 and 20 was then lowered from *in situ* conditions (Table 3.1) to 40 ±6 μ mol O₂ L⁻¹, and to 20 ±8 μ mol O₂ L⁻¹ by an oxygen regulation system that monitors and regulates oxygen saturation in seawater by injecting nitrogen gas. Incubations were performed again on cores collected at sites 23 and 20 at each overlying O₂ level after three days of equilibration. We assume that three days were sufficient to reach a new steady-state with respect to the oxygen penetration depth (or sediment oxygen gradient) (Rasmussen et al., 1992; Chaillou et al., 2007). Each cycle of re-incubation lasted 6 days total.

Undisturbed cores with approximately 30 cm of sediment and 20 cm of overlying water were maintained at 4°C and incubated in the dark for 60 hours, as described by Hulth et al. (1994). A Plexiglas lid, equipped with a rubber O-ring, a Teflon magnetic stirring bar, and two Teflon valves for sampling, was fitted on

top of each core liner without trapping air bubbles. One of the valves was used for sampling the overlying water at regular time intervals. The other valve was connected to a reservoir of bottom water of known dissolved O₂, SRP, nitrate, manganese, and iron concentrations. In this way, the water samples withdrawn for analysis were immediately replaced by an equivalent volume of bottom water of known composition, keeping the volume of overlying water constant and avoiding air contamination. A 10-ml sample was drawn into a glass syringe for Winkler oxygen analysis, and a second sample was collected with an acid-cleaned plastic syringe and filtered through a Nalgene 0.2 µm cellulose acetate membrane filter. An aliquot of the latter was used for nutrient analyses (SRP, $NO_3^- + NO_2^-$) within a few days of sampling, and a second aliquot was acidified to pH 1.6 with ultrapure Seastar HNO₃ for dissolved metal analyses. Because the replacement water contained oxygen, the oxygen concentration in the overlying water was prevented from decreasing to levels where it interferes with the oxygen supply to the sediment (Hall et al., 1989). The total amount of water withdrawn and replaced during each sampling did not exceed 25% of the total overlying water volume.

The flux, $\frac{\Delta X}{\Delta t \times A}$, of a given solute across the sediment-water interface during the interval between two samplings (Δt), compensated for the amount of solute in the replacement water, is calculated by:

$$\frac{\Delta X}{\Delta t \times A} = \frac{[s_2] - \frac{(V_{tot} - V_{S_1}) \times [s_1] + V_{S_1} \times [replace]}{V_{tot}}}{\Delta t \times A}$$
(1)

where $[s_1]$ and $[s_2]$ are, respectively, the measured solute concentration at the beginning and end of the sampling interval and [*replace*] is the solute concentration in the replacement water. V_{tot} and V_{S_1} are, respectively, the total volume of overlying water and the volume of water withdrawn in the previous sampling, and A is the exposed surface area of the core (78.5 cm²). The flux was

then plotted against time to derive an average value over the incubation period. The fluxes are reported in Table 3.3. Hereafter, we refer to these as measured fluxes.

3.4.3 Pore-water profiling

The vertical distribution of electro-active species in the sediment porewaters was determined with a voltammetric micro-electrode (Brendel and Luther 1995; Luther et al. 1998). The vertical resolution was 1 mm starting 5 mm above the sediment-water interface, 0.5 mm immediately above and below the sedimentwater interface, and 2 mm deeper in the sediment. The location of the sedimentwater interface is within \pm 0.5 mm of the assigned depth (Fig. 3.2). The cores were kept at the in-situ temperature of 4°C throughout the measurements, which were completed within 3 hours of core recovery.

Ex situ voltammetric measurements were obtained with mercury-plated gold (Hg/Au) microelectrodes. A three-electrode system, consisting of a Au/Hg micro-electrode as working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode was use for these measurements, as described by Brendel and Luther (1995) and Luther et al. (1997). Precision, based on multiple replicate analyses of all species at the same depth, was typically better than 5 %. Detection limits for O₂, Mn²⁺, Fe²⁺ and Σ H₂S are 3, 5, 20 and < 0.1 µmol L⁻¹, respectively. Two or three individual elemental profiles were obtained simultaneously using separate micro-electrodes mounted on a support secured to a micro-manipulator, allowing millimeter-scale depth resolution with minimal sediment disturbance. Complete profiles of O₂ and Mn²⁺ are presented in Figure 3.2, where each point is the average of triplicate micro-electrode measurements. The depth at which Σ H₂S was first detected is indicated by an arrow. Electro-active dissolved Fe²⁺ was always below the detection limit of 20 µmol L⁻¹.

The dissolved oxygen concentration gradient across the sediment-water interface (overlying water and 0–1 mm sediment interval) was estimated from the

pore-water profiles, and the flux was calculated using Fick's first law and assuming transport by molecular diffusion (Berner, 1980):

$$J_d = -\Phi D_s \left(\delta C / \delta Z\right) \tag{2}$$

where J_d is the gradient-based flux estimate, Φ is the porosity, and D_s is the bulk sediment diffusion coefficient corrected for tortuosity θ . The diffusion coefficients were corrected for temperature (~4°C) and salinity (34-35) (Berner, 1980; Schulz, 2000) and θ was assumed to be equal to $1 - \ln (\Phi^2)$ (Boudreau, 1996). The porosity of the first centimeter of sediment is 0.85 to 0.90 (Sundby et al., 2004). The concentration gradients are calculated by assuming that the O₂ concentration is linear over the 0–1 mm interval. Diffusive O₂ fluxes are reported in Figure 3.3 as the means ±SD of estimates derived from individual elemental profiles.

3.4.4 Chemical analyses

Soluble reactive phosphate (SRP) was analyzed immediately upon sampling by the spectrophotometic heptamolybdate method of Murphy and Riley (1962). Total dissolved nitrate ($\Sigma NO_3 = NO_3^- + NO_2^-$) was analyzed within two weeks on frozen aliquots, using the flow injection method of Anderson (1979). The detection limits were 0.8 and 0.5 µmol L⁻¹ for SRP and ΣNO_3 , respectively, and the precision of both methods was ±5%. Total dissolved Mn was determined on acidified water samples by flame atomic absorption spectrophotometry using external aqueous standard solutions for calibration. The detection limit was 0.08 µmol L⁻¹ and the precision was better than ±5%. Dissolved Fe was determined using the ferrozine procedure described by Stookey (1970) with a precision of ±5% and a detection limit of 2 µmol L⁻¹ (with a 1-cm cell).

3.4.5 Statistical analysis

To study the influence of abiotic environmental variables on the biotic composition of ecosystems, multivariate statistical analysis techniques have been

used for many years in environmental sciences. Here, we applied these techniques on the measured flux data set. Dissimilarities of measured individual element fluxes between sampled sites are analyzed and related to measured environmental variables such as dissolved oxygen, depth, macrofaunal density and other elemental fluxes. A non-metric multidimensional scaling (nMDS) of the data was applied. It is a multivariate ordination technique used to visualize the clustering of data in a specified number of dimensions or space and reveals hidden patterns that can be difficult to discern in a complex data matrix. Its strength is its ability to find similarities and differences between samples within a large amount of data. Multivariate analysis is a powerful tool for exploratory data analysis of elemental fluxes (e.g., Karle et al., 2007). All data analyses were performed using the software PRIMER 6 (Software from the Plymouth Marine Laboratory, Plymouth, England; <u>http://www.primer-e.com/</u>).

The analysis is carried out in two steps. Firstly, the data were normalized prior to calculation of a Eucledian distance matrix. The Euclidian distance is the ordinary distance between two points that one would measure with a ruler. It is defined as the square root of the sum of the squares of the differences between the corresponding coordinates of the points. For a n-dimensional space, the distance between the point $p(p_1, p_2,..., p_i, p_n)$ and point $q(q_1, q_2,..., q_i, q_n)$ is given by the following relation:

$$d(p,q) = \sqrt{(p_1 - q_1)^2 + (p_2 - q_2)^2 + \dots + (p_i - q_i)^2 + (p_n - q_n)^2}$$
(3)

where d(p,q) is the distance between p and q. Eucledian distance provides an appropriate representation of environmental data (Clarke and Warwick 1994). The normalization step is followed by a validation step, where the goodness of point position is validated. The overall measure of how the distances in the configuration ordinally fit the data is called "stress": it is a measure of the goodness of fit. The nMDS employs an iterative algorithm where initial estimates of the positions of sample are adjusted to minimize the stress until further iterations achieve a sufficient improvement. The nMDS uses the rank order of similarity between samples and tries to place samples in 2 (or 3) dimensional space to represent this rank order. For example, if sample 1 has a higher similarity to sample 2 than it does to sample 3, then sample 1 will be placed closer on the ordination to sample 2 than it is to sample 3. The stress value represents the rank-order agreement between distances and similarities. Ordinations are presented in Figure 3.4 with a stress value < 0.1, indicating an accurate agreement. SIMPER analysis (in PRIMER) was used to determine the contribution of each variable (dissolved oxygen, depth, macrofaunal density and measured flux of O_2 , ΣNO_3 , SRP and dissolved Mn) to the dissimilarity between samples. This method of analysis determines which variables are responsible for any difference that occurs (Clarke 1993; Warwick et al. 1991).

3.5 Results

3.5.1 Fluxes across the sediment-water interface

Values of replicate elemental flux measurements at each sampling site are reported in Table 3.3. As shown in Figure 3.3, the average measured fluxes of O_2 and ΣNO_3 at each site were directed into the sediments, the flux of dissolved Mn was always directed out of the sediment, and the flux of SRP was directed out of the sediment at five of the six sites. Dissolved Fe was not released to the overlying water (detection limit 2 µmol L⁻¹) during any of the incubations. Our results were within the range of sediment net flux estimates previously reported for the St. Lawrence Estuary (Anschutz et al., 2000). The intra-station variability of the measured fluxes was comparable to the inter-station variability (Fig. 3.3, Table 3.3). For example, the ΣNO_3 fluxes at site 23 ranged from 0.12 to 0.57 mmol m⁻² d⁻¹, which encompasses the full range of fluxes (0.03 to 0.65 mmol m⁻² d⁻¹) measured within the study area. The measured fluxes were not related to the bottom-water oxygen concentration (Fig. 3.5). For example, in spite of the lower

overlying water oxygen concentrations at site 23 (63-77 vs. 99 μ mol L⁻¹), the measured O₂ flux at site 23 (core 8) was similar to that at site 20 (core 4).

The pore-water profiles show that the sediment O_2 penetration depths range from 1.5 to 9 mm (Fig. 3.2), in agreement with previous reports (Silverberg et al. 1987, 1990; Anschutz et al. 2000). Nevertheless, the multi-profile approach revealed a high degree of spatial heterogeneity, with the oxygen penetration depth varying between 2 and 5 mm over distances as short as 3 cm at site 20 (Fig. 3.2). Pore-water Mn²⁺ was below the detection limit in the oxic sediment layer, but reached high concentrations (100 to 500 µmol L⁻¹) in the anoxic sediment. Nevertheless, in cores from sites 25, 23, 21, and 19, dissolved Mn was undetectable (< 5 µmol L⁻¹) at and even slightly below the oxygen penetration depth. Pore-water Fe²⁺ concentrations were consistently below the detection limit (< 20 µmol L⁻¹) in all cores. Low Fe²⁺ concentrations (2 to 15 µmol L⁻¹) have been measured previously, by atomic absorption spectrophotometry, in pore-water extracted from the first 10 cm of sediments recovered at LSLE sites (see Katsev et al. 2007 for a compilation). Dissolved sulfide (Σ H₂S) was observed at sites 25, 24, 23, and 20 and was first detected 4 to 6 cm below the sediment-water interface.

3.5.2 Multivariate analysis of measured flux structures

The multivariate analyses show that there is strong spatial variability of measured elemental fluxes in relation to environmental parameters at all sampled scales (Fig. 3.4). For example, measured fluxes at sites 20 and 24 display a significantly smaller spatial heterogeneity than at the hypoxic site 23 in 2007 (black dots on Fig. 3.4). SIMPER analysis confirmed that site 23 displays very high intra-station spatial variability with an average squared distance between samples of 6.95 followed by sites 20 and 24 with, respectively, average squared distances of 0.5 and 0.16. The multivariate analysis reveals that each incubated sediment core had distinct characteristics, resulting in variability in the data that was not related to any of the tested variables. In other words, measured fluxes show no relation to any of the other fluxes or environmental variables, more

specifically with bottom-water oxygenation.

3.5.3 Experimental manipulations of bottom-water O₂ concentrations

Figure 3.5 shows total fluxes of O_2 , ΣNO_3 , and SRP at varying overlying water O₂ concentrations. Fluxes of dissolved Mn were not reported because most were very low or null. The total fluxes are in the same range as those reported in Figure 3.3. Oxygen and ΣNO_3 fluxes were always directed into sediments while SRP was always released from sediments. An ANOVA analysis confirms that there is no significant difference in the elemental fluxes during incubation of a core from site 23 with changing overlying water O₂ concentrations. The elemental benthic fluxes during incubations of a core taken at site 20 tend to decrease at lower overlying water O₂ concentrations, but the ANOVA analyses reveal that none of the manipulated O₂ incubations was significantly different than the others. Table 3.4 reports the difference in the overlying water oxygen concentration at the start and end of each incubation period. The oxygen concentration in the overlying water displays large variations, from a 68% decrease to a 31% increase. Although this artifact does not seem to affect the measured oxygen flux, as the variation of oxygen concentration in the overlying water within a same core can be significantly different from one experiment to the other (e.g. Table 3.4 core #7, $\Delta O2 = -26.3$ and $-1.0 \text{ }\mu\text{mol }L^{-1}$ respectively for the incubation experiments at 40±6 and 20±8 μ mol L⁻¹) but did not resulted in significant variation of the measured oxygen flux (Fig. 3.5 core #7, the flux increases respectively from 1.8 to 1.9 mmol $m^{-2} d^{-1}$). In addition, no relationship could be established between the extent of oxygen concentration decrease (or increase) and the measured flux of nutrients and dissolved metals.

3.6 Discussion

Unlike many shallow hypoxic environments, the more than 300-m deep LSLE has been persistently hypoxic for nearly 30 years. Hypoxia developed slowly as bottom-water dissolved oxygen concentrations decreased at an average rate of 1 μ mol L⁻¹ y⁻¹ over at least the previous 50 years (Gilbert et al. 2005). In other words, both the benthic community and the biogeochemistry of the sediment may have adapted to the decreasing oxygen levels as well as to the changing fluxes of particulate organic matter (Thibodeau et al. 2006) and decreasing pH (Mucci et al. 2011).

3.6.1 Bottom water oxygenation and elemental fluxes across the sediment-water interface.

Experiments with benthic flux chambers have shown that a "critical oxygen concentration" exists below which the sediment oxygen uptake rate becomes a function of the overlying water oxygen concentration (Hall et al. 1989). A similar relationship has also been observed in hypoxic / anoxic coastal environments such as the Louisiana Shelf (Rowe et al. 2008) and the Black Sea (Friedl et al. 1998). In deep-sea sediments, where the oxygen penetration distance may exceed several meters and diffusion is the dominant transport mechanism for O_2 , oxygen consumption rates are also dependent on the overlying water column oxygen concentration (Caï and Reimers 1995). The oxygen uptake regulation by *in-situ* O_2 level has been demonstrated in short-term exposure experiments as well (Rasmussen and Jørgensen 1992). We interpret the apparent lack of a relationship between the bottom-water oxygen concentration and the sediment oxygen uptake rates (Fig. 3.5 and 3.6) in LSLE to mean that a critical oxygen concentration has not yet been reached in the hypoxic bottom water.

Several studies have reported a relationship between the oxygen penetration depth (OPD) in organic-rich sediments and the oxygen concentration in the overlying water (e.g. Caï and Sayles 1996). We observed a good correlation $(r^2 = 0.70; p < 0.05)$ between the OPD and the bottom water oxygen concentration, but, like the bottom-water oxygen concentration, the OPD is not a good predictor of the O₂ uptake rate by Laurentian Channel sediments. One likely explanation is that the OPD in bioturbated sediments can be highly variable on cm-spatial scales, as revealed by two-dimensional optode measurements (Glud 1996). This variability is not readily captured by punctual micro-electrode measurements.

At all stations, measured fluxes of ΣNO_3 , SRP, and dissolved Mn were independent of bottom-water oxygen concentration (Fig. 3.6) as well as of the net O_2 flux (Fig. 3.7). This suggests that the benthic fluxes do not respond linearly to the bottom-water oxygen concentration in the Laurentian Trough despite the persistence of hypoxic water. This is not to say that the low oxygen concentrations have no effect on sediment biogeochemistry or on sediments as a habitat for living organisms. Over 25 years of persistent hypoxia, Lefort et al. (submitted) observed notable changes in sediment particulate and pore-water chemistry. The analysis of historical macrobenthic endofauna data presented by Bourque and Archambault (submitted) revealed a significant change in the feeding mode of the macrobenthic endofauna in the St. Lawrence Estuary sediments over the last 30 years, probably caused by the progressive adaptation of fauna to the bottom water O_2 depletion. Moreover, there is currently a clear shift in the functionality of the epibenthos that parallels the bottom-water oxygen gradient throughout the Laurentian Trough: from high diversity, mixed function populations in the Gulf to lower diversity landward in the LSLE (Belley et al. 2010). In the LSLE, specifically at site 23, a single species (Ophiura sp.) currently dominates the surface detritus feeders. It is unlikely that the benthos responded solely to the decrease in oxygen level, but most likely to multiple stressors including changes in oxygen concentration, pH (Mucci et al. 2011) and organic matter rain rate and composition (Thibodeau et al. 2006; Benoit et al. 2006). The relative importance of these factors is not known and their consequences on benthic fluxes are poorly understood.

A wide range of environmental factors can influence the properties of natural ecosystems. Determining the relative importance of each variable on measured benthic fluxes is difficult because of the multiple biotic and abiotic

interactions (Godbold and Solan 2009). Our multivariate analysis did not reveal a specific pattern in the distribution of samples throughout the Laurentian Trough (Fig. 3.4) and confirmed the strong spatial heterogeneity of the sediments. This heterogeneity is not surprising because the fauna inhabiting the Laurentian Trough vary considerably from site to site (Ouellet 1982; Belley et al. 2010) and the community composition of incubated sediment cores cannot be controlled or identified beforehand. Furthermore, the composition and flux of organic carbon vary considerably from site to site along the Laurentian Trough (Colombo et al. 1996a,b; Lucotte et al. 1991; Muzuka and Hillaire-Marcel 1999; Silverberg et al. 2000; Smith and Schafer 1999; see Table 3 in Benoit et al. (2006) for a compilation of organic carbon accumulation rates). Biotic and abiotic variables, such as organism density, species and functional diversity, organic carbon flux and composition can modify benthic fluxes (Bulling et al., 2008; Goldborg and Solan, 2009; Michaud et al., 2006, 2009). The complexity of the benthic ecosystem and the many feedback loops that take place between macrofauna and surrounding sediment chemistry may be the reason why we could not observe a relationship between the structure and function of the benthos and the individual measured elemental fluxes, as one might have expected in view of the landward shift towards dominance of surface deposit feeders and the decreased abundance of bioirrigating organisms (Belley et al. 2010). If the bottom-water oxygen level continues to decrease beyond the point where species diversity or functionality are further affected, we might see a control of bottom-water oxygen concentrations on benthic fluxes. This would be an acceptable ecological definition of the "critical oxygen concentration".

The progressive decrease of bottom-water oxygen concentrations leads to direct (via chemical reactions) and indirect (via fauna) effects on the sediment chemistry (Middelburg and Levin, 2009; Lefort et al., submitted; Bourque and Archambault, submitted) which are generated on varying time scales (days to decades; Katsev et al., 2007; Lefort et al., submitted). Hence, in the short-term incubation experiments, the sediment and biotic response may be very different than in the field and may explain the lack of relationship between overlying water oxygen concentration and fluxes in the manipulated experiments.

3.6.2 Effects of chemistry and transport mechanisms on fluxes

Each of the solutes, whose fluxes we measured, participates in a web of chemical reactions with other solutes and the solid phase. These reactions ultimately control the pore-water concentration gradients that drive elemental fluxes.

In view of the presence of polychaetes within the first cm of all investigated sediments (Table 3.2) and considering the efficiency of bioirrigation in oxygen transfer through the sediment-water interface (Archer 1992; Wenzhöfer and Glud 2002), the oxygen fluxes derived from sediment incubations were expected to be higher than those calculated from the oxygen concentration gradients. Nevertheless, judging from the close agreement between these two independent estimates of the oxygen fluxes (Fig. 3.3), pore-water irrigation appears to be negligible and molecular diffusion appears to be the predominant O_2 exchange mechanism in these sediments. The rate of bioirrigation is obviously determined by the sediment infauna (Weissberger et al. 2006), but how factors such as burrow geometry, infauna density, and taxonomy influence this rate are far from being well understood.

Measured and diffusive ΣNO_3 flux estimates at five of the six study sites (Fig. 3.3) are within the same narrow range of values (0.1-0.3 mmol m⁻² d⁻¹). Where measured (4 of 6), there is no significant difference between the two independent estimates. Although this is a small sample on which to base such a conclusion, it is consistent with nitrate being consumed close to the sediment-water interface and molecular diffusion being the dominant nitrate transport mechanism.

With the advent of voltammetric micro-electrodes that allow the acquisition of high resolution vertical profiles of manganese and other electro-

active elements in sediment pore-water, it has often been reported (Hulth et al. 1999; Anschutz et al. 2000; Bartlett et al. 2007; Chaillou et al. 2007) that dissolved Mn(II) is only detected at or below the sediment oxygen penetration depth, as illustrated in Figure 3.2. If these profiles are taken at face value, dissolved Mn diffusing up from the anoxic sediment would be trapped and precipitated before it can escape to the overlying water column. Yet, we measured significant fluxes of manganese to the overlying water during our core incubations (Fig. 3.3). One possible explanation for the discrepancy is the relatively high detection limit of the micro-electrodes (~5 μ mol L⁻¹). A second possibility is the presence of a pore-water manganese species (e.g. Mn(III)) that is not detected by the voltammetric micro-electrode. The presence of pore-water Mn(III) in sediment of the St. Lawrence Estuary has recently been demonstrated (Madison et al. 2011).

The pore-water reactive phosphate (SRP) concentration near the sediment surface is controlled by a sorption equilibria with detrital and authigenic hydrous iron oxides that typically accumulate in surface sediments (Sundby et al. 1992). Consequently, all other factors being equal (T, pH, Eh, organic matter flux), the concentration gradient and diffusive flux of SRP across the sediment-water interface will depend mostly on the overlying water SRP concentration. Given that the bottom-water SRP concentrations are nearly identical throughout the Laurentian Trough (Thibodeau et al. 2010), we would expect the concentration gradients and the Fickian fluxes of SRP to be similar throughout the study area. Indeed, Thibodeau et al. (2010) reported that the benthic diffusive fluxes of SRP along the Laurentian Trough are within a factor of two of each other (from 4 to 8 μ mol m⁻² d⁻¹). In contrast, our measured SRP fluxes (Figure 3.3) show slightly more variation and more strikingly, in one case (site 21), a positive rather than a negative flux of SRP at the sediment-water interface.

The capacity of the sediment to retain phosphate depends on the thickness of the iron oxide-rich layer, which, in turn, depends on the oxygen penetration

depth. Hence, one would expect that, as the overlying water dissolved oxygen concentration decreases beyond a threshold value, the iron oxide layer will thin, reduce the capacity of the sediment to retain phosphate and increase the flux of phosphate to the overlying water column. In the modeled predictions of Katsev et al. (2007), the flux of phosphorus out of the sediment remains almost constant down to a critical overlying water oxygen concentration of 20 μ mol L⁻¹. Below this value, the model predicts a progressive release of SRP until anoxia sets in. With a single exception, the SRP fluxes we measured during core incubations agree with each other within a factor of three, consistent with the concept described above. The SRP fluxes derived from our core incubations are 7 to 20 times larger than the diffusive fluxes calculated by Anschutz et al. (1998) and Thibodeau et al. (2010) at the same sites. Given that the pore-water SRP concentration in the near-surface sediment is controlled by sorption equilibria (Sundby et al. 1992), the difference in our measured fluxes and published data may reflect different methodologies. An alternate explanation would be that, during our core incubations, much of the mobilized phosphate was rapidly produced by decomposition of reactive organic matter near the sediment-water interface, from where it can readily escape to the water column and that SRP concentration gradients across the sediment-water interface would not record this phenomenon.

3.7 Acknowledgments

We thank the captain and crew of the R/V Coriolis II as well as Stéphanie Ringuet, Emmanuelle Hélias, Mylène Bourque, and Constance Guignard for their valuable help at sea and in the laboratory. The study was funded by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada to B. Sundby, A. Mucci and P. Archambault and by contributions from the Department of Fisheries and Oceans Canada.

3.8 References

- Aller RC (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. Chemical Geology 114: 331-345.
- Aller RC, Aller JY (1998) The effect of biogenic irrigation intensity and solute exchange on diagenetic reaction rates in marine sediments. Journal of Marine Research 56: 905-936.
- Anderson L (1979) Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. Analytica Chimica Acta 110: 123-128.
- Anschutz P, Zhong S, Sundby B, Mucci A, Gobeil C (1998) Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. Limnology and Oceanography 43(1): 53–64.
- Anschutz P, Sundby B, Lefrançois L, Luther G, Mucci A (2000) Interactions between metal oxides and species of nitrogen and iodine in bioturbated marine sediments. Geochimica et Cosmochimica Acta 64: 2751-2763.
- Archer D (1992) Benthic oxygen fluxes on the Washington shelf and slope: A comparison of in situ microelectrode and chamber flux measurements. Limnology and Oceanography 37 (3): 614-629.
- Bartlett R, Mortimer R, Morris K (2007) The biogeochemistry of a manganeserich Scottish sea loch: Implications for the study of anoxic nitrification. Continental Shelf Research 27(10-11): 1501–1509.
- Barnett PRO, Watson J, Connelly D (1984) A multiple corer for taking virtually undisturbed samples from shelf, bathyal and abyssal sediments. Oceanologica Acta 7: 399-408.
- Belley R, Archambault P, Sundby B, Gilbert F, Gagnon JM (2010) Environmental variables influencing macrobenthic diversity and bioturbation in the Estuary and Gulf of St. Lawrence, Canada. Continental Shelf Research30: 1302-1313.

- Benoit P, Gratton Y, Mucci A (2006) Modelling of dissolved oxygen level in the bottom waters of the Lower St-Lawrence Estuary: Coupling of benthic and pelagic processes. Marine Chemistry 102: 13-32.
- Berelson W, McManus J, Coale K, Johnson K, Kilgore T, Burdige D, Pilskaln C (1996) Biogenic matter diagenesis on the sea floor: A comparison between two continental margin transects. Journal of Marine Research 54: 731-762.
- Berner R (1980) Early diagenesis: a theoretical approach. Princeton, NY. 241 pp.
- Boudreau BP (1996) The diffusive tortuosity of fine-grained unlithified sediments. Geochimica et Cosmochimica Acta 60: 3139-3142.
- Bourque M (2009) Variabilité spatio-temporelle de la macrofaune endobenthique profonde du Saint-Laurent (Québec, Canada) au cours d'un évênement hypoxique. Ph.D. Thesis, Université du Québec à Rimouski, 106 pp.
- Bourque M, Archambault P (submitted) Spatio-temporal patterns of infaunal community structure in the deep estuary and gulf of St. Lawrence (Quebec, Canada) in relation to environmental conditions. Marine Ecology.
- Brendel PJ, Luther III GW (1995) Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O₂, and S(-II) in porewaters of marine and fresh-water sediments. Environmental Science and Technology 29: 751-761.
- Bulling MT, Solan M, Dyson KE, Hernandez-Milian G, Luque P, Pierce GJ, Raffaelli D, Paterson DM (2008) Species effects on ecosystem processes are modified by faunal responses to habitat composition. Oecologia 158: 511-520.
- Cai W-J, Sayles F (1996) Oxygen penetration depths and fluxes in marine sediments. Marine Chemistry 52: 123-131.
- Caï WJ, Reimers CE (1995) Benthic oxygen flux, bottom water oxygen concentration and core top organic carbon content in the deep northeast Pacific Ocean. Deep-Sea Research Part I-Oceanographic Research Papers 42 (10): 1681-1699.
- Chaillou G, Anschutz P, Dubrulle C (2007) Transient states in diagenesis following the deposition of a gravity layer: Dynamics of O₂, Mn, Fe and N-species in experimental units. Aquatic Geochemistry 13(2) : 157-172.
- Clarke KM (1993) Nonparametric multivariate analyses of changes in community. Australian Journal of Ecology 18: 117-143.
- Clarke KR, Warwick RM (1994) Similarity-based testing for community pattern: the two-way layout with no replication. Marine Biology 118: 167–176.
- Colombo JC, Silverberg N, Gearing JN (1996a) Biogeochemistry of organic matter in the laurentian trough .1. Composition and vertical fluxes of rapidly settling particles. Marine Chemistry 51: 277-293.

- Colombo JC, Silverberg N, Gearing JN (1996b) Biogeochemistry of organic matter in the Laurentian Trough .2. Bulk composition of the sediments and relative reactivity of major components during early diagenesis. Marine Chemistry 51: 295-314.
- Dauer DM (1993) Biological criteria, environmental health and estuarine macrobenthic community structure. Marine Pollution Bulletin 26: 249-257.
- Diaz R, Rosenberg R (1995) Marine benthic hypoxia: a review of its ecological effects and the behavioral responses of benthic macrofauna. Oceanography and Marine Biology: Annual Review 33: 245-303.
- Diaz R, Rosenberg R (2008) Spreading dead zones and consequences for marine ecosystems. Science 321: 926-929.
- Friedl G, Dinkel C, Wehrli B (1998) Benthic fluxes of nutrients in the northwestern Black Sea. Marine Chemistry 62 (1-2): 77-88.
- Gilbert D, Sundby B, Gobeil C, Mucci A, Tremblay G (2005) A seventy-two-year record of diminishing deep-water oxygen in the St. Lawrence Estuary: The northwest Atlantic connection Limnology and Oceanography 50: 1654–1666.
- Glud RN, Ramsing NB, Gundersen JK, Klimant I (1996) Planar optrodes: a new tool for fine scale measurements of two-dimensional O₂ distribution in benthic communities. Marine Ecology Progress Series 140:217–226.
- Godbold JA, Solan M (2009) Relative importance of biodiversity and the abiotic environment in mediating an ecosystem process. Marine Ecology Progress Series 396: 273-282.
- Hall POJ, Anderson LG, Rutgers van der Loeff MM, Sundby B, Westerlund SFG (1989) Oxygen uptake kinetics in the benthic boundary layer. Limnology and Oceanography 34: 734-746.
- Hulth S, Blackburn T, Hall P (1994) Arctic sediments (Svalbard): consumption and microdistribution of oxygen. Marine Chemistry 46: 293-316.
- Hulth S, Aller R, Gibert F (1999) Coupled anoxic nitrification/manganese reduction in marine sediments. Geochimica et Cosmochimica Acta 63 : 49–66.
- Karle IM, Hall POJ, Dahllöf I (2007) Biogeochemical response of an intact coastal sediment to organic matter input: a multivariate approach. Marine Ecology Progress Series 342: 15-25.
- Katsev S, Chaillou G, Sundby B, Mucci A (2007) Impact of progressive oxygen depletion on sediment diagenesis and fluxes: a model for the Lower St-Lawrence Estuary. Limnology and Oceanography 52: 2555-2568.
- Keister J, Houde E, Breitburg D (2000) Effects of bottom-layer hypoxia on abundances and depth distributions of organisms in Patuxent River, Chesapeake Bay. Marine Ecology Progress Series 205: 43-59.

- Kemp WM, Testa JM, Conley DJ, Gilbert D, Hagy JD (2009) Coastal hypoxia responses to remediation. Biogeosciences Discussions 6: 6889-6948.
- Kristensen E, Ahmed S, Devol A (1995) Aerobic and anaerobic decomposition of organic matter in marine sediment: Which is fastest. Limnology and Oceanography 40(5): 1430–1437.
- Lefort S, Mucci A, Sundby B. (submitted) Sediment response to 25 years of persistent hypoxia. Aquatic Geochemistry.
- Lehmann MF, Barnett B, Gelinas Y, Gilbert D, Maranger RJ, Mucci A, Sundby B, Thibodeau B (2009) Aerobic respiration and hypoxia in the Lower St. Lawrence Estuary: Stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning. Limnology and Oceanography 54: 2157-2169.
- Levin L (2003) Oxygen minimum zone benthos: Adaptation and community response to hypoxia. Oceanography and Marine Biology 41: 1-45.
- Loring DH, Nota DJG (1973) Morphology and sediments of the Gulf of St. Lawrence. Bulletin of the Fisheries Research Board of Canada. 183: 147.
- Lucotte M, Hillaire-Marcel C, Louchouarn P (1991) First order organic carbon budget in the St Lawrence Lower Estuary from 13C data. Estuarine, Coastal and Shelf Science 32: 297-312.
- Luther III GW, Sundby B, Lewis B, Brendel P, Silverberg N (1997) Interactions of manganese with nitrogen cycle: Alternative pathways to dinitrogen. Geochimica et Cosmochimica Acta 61: 4043-4052.
- Luther III GW, Brendel P, Lewis B, Sundby B, Lefrançois L, Silverberg N, Nuzzio D (1998) Simultaneous measurement of O₂, Mn, Fe, I-, and S(-II) in marine pore waters with a solid-state voltammetric microelectrode. Limnology and Oceanography 43: 325-333.
- Madison AS, Tebo BM, Luther III GW (2011) Simultaneous determination of soluble Mn(III), manganese (II) and total manganese in natural (pore)waters. Talanta 84: 374-381.
- Michaud E, Desrosiers G, Aller RC, Mermillod-Blondin F, Sundby B, Stora G (2009) Spatial interactions in the Macoma balthica community control biogeochemical fluxes at the sediment-water interface and microbial abundances. Journal of Marine Research 67: 43-70.
- Michaud E, Desrosiers G, Mermillod-Blondin F, Sundby B, Stora G (2005) The functional group approach to bioturbation: The effects of biodiffusers and gallery-diffusers of the Macoma balthica community on sediment oxygen uptake. Journal of Experimental Marine Biology and Ecology 326: 77-88.
- Michaud E, Desrosiers G, Mermillod-Blondin F, Sundby B, Stora G (2006) The functional group approach to bioturbation: II. The effects of the *Macoma balthica* community on fluxes of nutrients and dissolved organic carbon

across the sediment-water interface. Journal of Experimental Marine Biology and Ecology 337: 178-189.

- Middelburg JJ, Levin LA (2009) Coastal hypoxia and sediment biogeochemistry. Biogeosciences 6(7): 1273–1293.
- Morse J, Eldridge P (2007) A non-steady state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the "dead zone" of the Louisiana shelf. Marine Chemistry 106: 239-255.
- Mucci A, Sundby B, Gilbert D, Starr M (2011) Acidification of the bottom water of the Lower St-Lawrence Estuary since the 1930s. Atmosphere-Ocean.
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36.
- Muzuka ANN, Hillaire-Marcel C. (1999) Burial rates of organic matter along the eastern Canadian margin and stable isotope constraints on its origin and diagenetic evolution. Marine Geology, 160: 251–270.
- Ouellet G (1982) Étude de l'interaction des animaux benthiques avec les sédiments du chenal Laurentien. M.Sc. thesis, Université du Québec à Rimouski, 177 pp.
- Pakhomova S, Hall P, Kononets M, Rozanov A, Tengberg A, Vershinin A (2007) Fluxes of iron and manganese across the sediment–water interface under various redox conditions. Marine Chemistry 107: 319-331.
- Pearson TH, Rosenberg R (1978) Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. Oceanography and Marine Biology: Annual Review 16: 229-311.
- Rabalais NN, Diaz RJ, Levin LA, Turner RE, Gilbert D, Zhang J (2010) Dynamics and distribution of natural and human-caused hypoxia. Biogeosciences 7: 585-619.
- Rasmussen H, Jørgensen B (1992) Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion Marine Ecology Progress Series 81(3): 289–303.
- Ritter, C., Montagna P.A. (1999) Seasonal hypoxia and models of benthic response in a Texas bay. Estuaries 22: 7-20.
- Rowe GT, Morse J, Nunnally C, Boland GS (2008) Sediment community oxygen consumption in the deep Gulf of Mexico. Deep-Sea Research Part II 55 (24-26): 2686-2691.
- Sayles F, Martin W, Deuser W (1994) Response of benthic oxygen demand to particulate organic carbon supply in the deep sea near Bermuda. Nature 371: 686-689.

- Schulz H, Zabel M (2000) Quantification of early diagenesis: Dissolved constituents in marine pore water. In: Schulz H, Zabel M (ed) Marine Geochemistry, 2nd edition. Berlin, Heidelberg, New York, pp 85-128.
- Sell K, Morse J (2006) Dissolved Fe²⁺ and sigma H₂S behavior in sediments seasonally overlain by hypoxic-to-anoxic waters as determined by CSV microelectrodes. Aquatic Geochemistry 12: 179-198.
- Silverberg N, Bakker J, Edenborn H, Sundby B (1987) Oxygen profiles and organic carbon fluxes in Laurentian Trough sediments. Netherlands Journal for Sea Research 21: 95-105.
- Silverberg N, Sundby B, El-Sabh MI (1990) Early diagenesis and sediment–water interaction in the Laurentian Trough. In: El-Sabh M.,Silverberg N. (ed) Oceanography of a Large-Scale Estuarine System: The St. Lawrence. Coastal and Estuarine Studies. Springer-Verlag, New York, pp 202–238.
- Silverberg N, Sundby B, Mucci A, Zhong S, Arakaki T, Per Hall P, Landén A, Tengberg A (2000) Remineralization of organic carbon in eastern Canadian continental margin sediments. Deep-Sea Res. I, 47: 699–731.
- Smith JN, Schafer CT (1999) Sedimentation, bioturbation, and Hg uptake in the sediments of the Estuary and Gulf of St. Lawrence. Limnology and Oceanography 44: 207–219.
- Stookey L (1970) Ferrozine-a new spectrophotometric reagent for iron. Analytical Chemistry 42: 779-781.
- Sundby B, Martinez P, Gobeil C (2004) Comparative geochemistry of cadmium, rhenium, uranium, and molybdenum in continental margin sediments. Geochimica et Cosmochimica Acta 68(11): 2485–2493.
- Thibodeau B, Lehmann M, Gilbert D, Mucci A, Maranger R, Kowarzyk J, Gélinas Y, Sundby B, Alkhatib M (2010) Benthic nutrient fluxes along the Laurentian Channel: Environmental controls and impact on N-deficiency in the water column of the lower St. Lawrence Estuary. Estuarine, Coastal and Shelf Science 90: 195-205.
- Thibodeau B, de Vernal A, Mucci A (2006) Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleontological and geochemical evidence. Marine Geology 231(1-4): 37–50.
- Thrush SF, Hewitt JE, Gibbs M, Lundquist C, Norkko A (2006) Functional role of large organisms in intertidal communities: Community effects and ecosystem function. Ecosystems 9: 1029-1040.
- Waldbusser G, Marinelli R, Whitlatch R, Visscher P (2004) The effects of infaunal biodiversity on biogeochemistry of coastal marine sediments. Limnology and Oceanography 49: 1482-1492.

- Warwick RM, Goss-Custard JD, Kirby R, George CL, Pope ND, Rowden AA (1991) Static and Dynamic Environmental Factors Determining the Community Structure of Estuarine Macrobenthos in SW Britain: Why is the Severn Estuary Different? Journal of Applied Ecology 28: 329-345.
- Weissberger EJ, Coiro LL, Davey EW (2009) Effects of hypoxia on animal burrow construction and consequent effects on sediment redox profiles. Journal of Experimental Marine Biology and Ecology 371: 60-67.
- Wenzhöfer F, Glud R (2004). Small-Scale Spatial and Temporal Variability in Coastal Benthic O₂ Dynamics: Effects of Fauna Activity. Limnology and Oceanography 49(5): 1471–1481.
- Wijsman J, Herman P, Middelburg J, Soetaert K (2002) A model for early diagenetic processes in sediments of the continental shelf of the Black Sea. Estuarine, Coastal and Shelf Science 54: 403-421.
- Zorn ME, Lalonde SV, Gingra MK, Pemberton SG, Konhauser KO (2006) Microscale oxygen distribution in various invertebrate burrow walls. Geobiology 4: 137-145.
Table 3.1: Environmental conditions at the date and depth of sediment recovery at the study stations. Multiple sediment cores were collected simultaneously at the same station from a single multi-corer deployment and, thus, were separated by at most 1 m. All sediments cores were incubated (Inc) under *in situ* bottom-water O_2 concentrations. Micro-electrode profiles (Prof) were only measured in 2005.

Station	Data	Core	Depth	Т	S	DO	DO	Inc	Drof
Station	Date	index	(m)	(°C)		$(\mu mol L^{-1})$	(%sat)	me	1101
St. 25	08 21 2005	1	285	4.8	34.4	67.1	21.0	×	×
St. 24	08 27 2005	1	315	5.1	34.5	69.3	21.9	×	×
	07 09 2007	2	320	5.0	34.5	60.3	19.0	×	
	07 09 2007	3	320	5.0	34.5	60.3	19.0	×	
	07 09 2007	4	320	5.0	34.5	60.3	19.0	×	
St. 23	08 20 2005	1	350	5.2	34.4	63	19.9	×	×
	08 15 2006	2	347	5.2	34.6	76.7	24.4	×	
	08 15 2006	3	347	5.2	34.6	76.7	24.4	×	
	08 15 2006	4	347	5.2	34.6	76.7	24.4	×	
	07 07 2007	5	342	5.2	34.6	56.6	17.9	×	
	07 07 2007	6	342	5.2	34.6	56.6	17.9	×	
	07 07 2007	7	342	5.2	34.6	56.6	17.9	×	
	07 07 2007	8	342	5.2	34.6	56.6	17.9	×	
St. 21	08 23 2005	1	332	5.4	34.6	80.7	25.6		×
St. 20	08 24 2005	1	331	5.4	34.7	90.7	28.9	×	×
	07 05 2007	2	320	5.4	34.7	99.1	31.5	×	
	07 05 2007	3	320	5.4	34.7	99.1	31.5	×	
	07 05 2007	4	320	5.4	34.7	99.1	31.5	×	
St. 19	08 25 2005	1		5.5	34.8	123.6	39.5		×
St. 18	08 24 2005	1	370	5.4	34.8	155.3	49.5	×	×

Station	Density ±SD (ind. m ⁻²)	Dominant organisms / traits	Functional groups
St. 25	859 ± 104	Spiophanes kroyeri (Spionidae /polychaeta) Maldanidae (polychaeta)	Surface deposit feeder Subsurface deposit feeder
St. 24	267 ± 136	Ampharete lindstroemi (Ampharetidae/polychaeta) Spiophanes kroyeri (Spionidae /polychaeta)	Surface deposit feeder Surface deposit feeder
St. 23	315 ± 72	Ampharete lindstroemi (Ampharetidae/polychaeta) Ceratocephale loveni (Nereidae/Polychaeta)	Surface deposit feeder Omnivores
St. 21	304 ± 111	Ampharete lindstroemi (Ampharetidae/polychaeta) Ceratocephale loveni (Nereidae/Polychaeta)	Surface deposit feeder Omnivores
St. 20	320 ± 28	Ceratocephale loveni (Nereidae/Polychaeta) Heteromastus filiformis (Capitellidae/Polychaeta)	Omnivores Subsurface deposit feeder
St. 19	331 ± 106	Ceratocephale loveni (Nereidae/Polychaeta) Amphiura sundevalli (Amphiuridae/Echinodermata)	Omnivores Omnivores
St.18	392 ± 29	<i>Ceratocephale loveni</i> (Nereidae/Polychaeta) <i>Amphiura sundevalli</i> (Amphiuridae/Echinodermata)	Omnivores Omnivores

Table 3.2: Densities of macrobenthic endofauna (individual m^{-2} ; mean \pm SD, n = 3) at each of the study sites, averaged across replicates. Functional attributes of dominant species are given as indications (from Bourque, 2009).

Table 3.3: Measured fluxes derived from incubation experiments over the study period (e.g. Table 3.1 for details). Fluxes are given in mmol $m^{-2} d^{-1}$. The positive fluxes are directed into the sediment and negative fluxes are from the sediment to the overlying water. The notation n.d. indicates that data are unavailable and < dl that fluxes were below the detection limit (0.5, 0.8, and 0.08 μ mol L⁻¹ for Σ NO₃, SRP, and dissolved Mn respectively).

Station	Core index	O ₂	ΣNO_3	SRP	Mn
St. 25	1	6.35	0.65	-0.09	-0.12
St. 24	1	6.50	0.32	-0.07	-0.19
	2	3.41	0.08	-0.04	-0.13
	3	3.02	0.07	-0.04	-0.11
	4	3.10	0.03	-0.04	<dl< td=""></dl<>
St. 23	1	4.29	0.57	-0.10	-0.42
	2	4.34	0.40	-0.03	<dl< td=""></dl<>
	3	1.45	0.28	-0.06	<dl< td=""></dl<>
	4	2.58	0.34	-0.10	<dl< td=""></dl<>
	5	1.49	0.32	-0.08	-0.93
	6	4.66	0.26	-0.07	-0.31
	7	0.94	0.24	-0.05	<dl< td=""></dl<>
	8	n.d.	0.12	-0.04	-0.17
St. 21	1	3.01	0.19	-0.03	-0.07
St. 20	1	n.d.	n.d.	n.d.	n.d.
	2	1.96	0.40	-0.03	<dl< td=""></dl<>
	3	2.23	0.11	-0.04	<dl< td=""></dl<>
	4	2.47	0.17	-0.06	-0.13
St. 18	1	4.95	n.d	-0.08	<dl< td=""></dl<>

Experiment	Station	Core	[O ₂] _{end}	[O ₂] _{init}	ΔO_2	ΔO_2
		index	$(\mu mol L^{-1})$	$(\mu mol L^{-1})$	$(\mu mol L^{-1})$	(%)
<i>in situ</i> [O ₂]	St. 20	2	57	82.4	-25.4	-30.8
		3	56.9	84.4	-27.5	-32.6
		4	61.9	89.9	-28	-31.1
	St. 23	6	34.8	91.9	-57.1	-62.1
		7	40.9	45.8	-4.9	-10.7
		8	n.d.	n.d.	n.d.	n.d.
$40\pm6 \ \mu mol \ L^{-1}$	St. 20	2	34.6	50.5	-15.9	-31.5
		3	20.7	47.4	-26.7	-56.3
		4	31.6	48	-16.4	-34.2
	St. 23	6	25.5	80	-54.5	-68.1
		7	24.7	51	-26.3	-51.6
		8	32	46.9	-14.9	-31.8
20±8 μmol L ⁻¹	St. 20	2	32.5	27.5	5.0	18.2
		3	32.8	25.2	7.6	30.2
		4	19.8	27.3	-7.5	-27.5
	St. 23	6	25.9	29	-3.1	-10.7
		7	16.4	17.4	-1.0	-5.7
		8	32.2	44.3	-12.1	-27.3

Table 3.4: Comparison of initial ($[O_2]_{init}$) and final ($[O_2]_{end}$) oxygen concentration in the sampled overlying water upon experimental manipulations carried in 2007. $\Delta O_2 = [O_2]_{init} - [O_2]_{end}$. Corresponding fluxes are reported in figure 3.5.



Figure 3.1: Map of the Lower St. Lawrence Estuary and Gulf and location of sampling sites. Environmental characteristics are given in Table 3.1.



Figure 3.2: Depth profiles of sediment pore-water O_2 (open symbols) and Mn(II) (symbols) at sites 25, 24, 23, 21, 20, 19 and 18. Each point is the average of triplicate, independent micro-electrode measurements at a given depth. Arrows indicate the depth where dissolved sulfide was first detected. Sulfide was undetectable at sites 21 and 19. For site 18, we report only the O_2 profile because of analytical problems.



Figure 3.3: Fluxes of O_2 , ΣNO_3 , SRP and dissolved Mn across the sediment-water interface at each station, averaged across all dates and replicates. The hatched blue bars are measured fluxes derived from sediment incubations. The grey bars represent gradient-based fluxes, calculated from Fick's first law and measured linear concentration gradients of O_2 and ΣNO_3 across the sediment-water interface. The pore-water nitrate data were collected by B. Thibodeau during one of our cruises (Thibodeau et al. 2010). The positive fluxes are directed into the sediment and negative fluxes are from the sediment to the overlying water. Error bars are standard deviations. Details about replicates are given in Table 3.3.

	Normalise Resemblance: D1 Euclidean distance	
	2D Stress: 0.09	Station-Date ♦ 25-05 ■ 24-05 ■ 24-07 ● 23-05 ■ 23-06 ● 23-07 ▲ 21-05 ♥ 20-07 × 18-05
0		
•	\$	

Figure 3.4: Non-metric multi-dimensional scaling (nMDS) plots of depth, macrofauna density, bottom water dissolved O_2 , and measured fluxes of O_2 , ΣNO_3 , SRP and dissolved Mn measured over the study period (2005 to 2007) at 6 of the study sites (18, 20, 21, 23, 24, 25).



Figure 3.5: Fluxes of O_2 , ΣNO_3 , and SRP across the sediment-water interface upon experimental manipulations of the overlying water oxygen concentration during incubations of sediment cores recovered from stations 23 and 20, July 2007. The oxygen concentration was changed stepwise from in-situ conditions (grey bars) to $40 \pm 6 \mu mol O_2 L^{-1}$ (stripped bars), and to $20 \pm 8 \mu mol O_2 L^{-1}$ (black bars) over a periods a 9 days.



Figure 3.6: Measured fluxes of O_2 , ΣNO_3 , SRP, and dissolved Mn across the sediment-water interface as a function of overlying water oxygen concentrations.



Figure 3.7: Measured fluxes of ΣNO_3 , SRP, and dissolved Mn across the sediment-water interface as function of the oxygen uptake rate.

3.9 Appendix: Supplementary information on manganese, arsenic and selenium fluxes

In 2007, three series of core incubations were performed at three different overlying water dissolved oxygen saturations: 30%, 15% and 6.5%. At these low oxygen saturations, most of the benthic species died during the incubations, and since the activity of organisms (bioturbation) was not followed over time, we could not correlate this variable to the measured elemental fluxes across the sediment-water interface. In addition, based on the results of *Chapter 2*, we realized that the incubations were performed over too short a period of time to significantly modify the sediment chemistry and the resulting fluxes at the sediment-water interface. Since the experimental results could not readily be exploited for a scientific paper, I report them here in the appendix.

3.9.1 Methods

The recovery of sediment cores is described in *section 3.4.1*. The incubation protocol and flux measurements are described in *section 3.4.2*. In 2007, in addition to O_2 , ΣNO_3 and SRP fluxes, Mn, As and Se were measured. Filtered overlying water dissolved Mn and As concentrations were determined as described in *section 2.4.2.1*, whereas dissolved Se analyses were carried out as described in *section 2.10.1.4*. The uncertainty on measured concentrations is 5%, and the error on the estimated flux is 30%.

3.9.2 Results

The measured fluxes at different overlying dissolved oxygen concentrations are presented in the following tables. Uptake fluxes (i.e. from the water into the sediment) are positive and fluxes out of the sediment are negative. The magnitude of the flux is on the same order for a given solute, whatever the sampled station or the overlying water oxygen concentration.

Table 3.5: Fluxes of Mn (mmol $m^{-2} d^{-1}$) measured at three different overlying water dissolved oxygen concentrations in cores recovered in July 2007. Uptake fluxes (i.e. from the water into the sediment) are positive wehereas fluxes out of the sediment are negative. The notation n.d. indicates that data are unavailable and < dl that the sample concentrations were below the detection limit (1.8 μ mol L⁻¹).

	Flux of Mn (mmol $m^{-2} d^{-1}$)				
Site	$[O_2]_{BW} \sim 29\%$ sat (<i>in-situ</i>)	$[O_2]_{BW} \sim 15\%$ sat	$[O_2]_{BW} \sim 6.5\%$ sat		
24 A	-0.1	n.d	n.d		
24 B	-0.1	n.d	n.d		
24 C	n.d.	n.d	n.d		
23S A	-0.9	n.d	n.d		
23S B	-0.3	n.d	-0.2		
23 B	< dl	n.d	n.d		
23 C	-0.2	n.d	-0.5		
23 D	-0.1	n.d	-0.1		
20 B	< d1	n.d	< dl		
20 C	< d1	-0.2	-0.01		
20 D	-0.1	n.d	n.d		

	Flux o	of As (μ mol m ⁻² d ⁻¹)		
Site	$[O_2]_{BW} \sim 29\%$ sat (in-situ)	$[O_2]_{BW} \sim 15\%$ sat	$[O_2]_{BW} \sim 6.5\%$ sat	
24 A	-0.1	n.d	n.d	
24 B	-0.09	n.d	n.d	
24 C	-0.05	n.d	n.d	
23S A	-0.5	n.d	n.d	
23S B	-0.5	-0.4	n.d	
23 B	n.d	n.d	n.d	
23 C	-0.4	n.d	-0.6	
23 D	-0.5	n.d	-0.5	
20 B	-0.3	-0.2	$-0.09 \ (R^2 = 0.38)$	
20 C	-0.3	$0.08 (R^2 = 0.12)$	0.4	
20 D	-0.4	-0.1	0.4	

Table 3.6: Fluxes of As (μ mol m⁻² d⁻¹) measured at three different overlying water dissolved oxygen concentrations in cores recovered in July 2007. Uptake fluxes (i.e. from the water into the sediment) are positive whereas fluxes out of the sediment are negative. The notation n.d. indicates that data are unavailable.

	Flux	of Se (nmol $m^{-2} d^{-1}$)	
Site	$[O_2]_{BW} \sim 29\%$ sat (<i>in-situ</i>)	$[O_2]_{BW} \sim 15\%$ sat	$[O_2]_{BW} \sim 6.5\%$ sat
24 A	n.d	n.d	n.d
24 B	n.d	n.d	n.d
24 C	n.d	n.d	n.d
23S A	n.d	n.d	n.d
23S B	n.d	n.d	n.d
23 B	n.d	n.d	n.d
23 C	0.04	n.d	-0.01
23 D	n.d	n.d	n.d
20 B	n.d	n.d	n.d
20 C	n.d	n.d	n.d
20 D	n.d	n.d	n.d

Table 3.7: Fluxes of Se (μ mol m⁻² d⁻¹) measured at three different overlying water dissolved oxygen concentrations in cores recovered in July 2007. Uptake fluxes (i.e. from the water into the sediment) are positive whereas fluxes out of the sediment are negative. The notation n.d. indicates that data are unavailable.

Chapter 4

Hypoxia in the Lower St. Lawrence Estuary: How physics controls spatial patterns

The previous chapter reveals that the "critical threshold" of bottom-water dissolved oxygen concentration below which the benthic species diversity or functionality are affected to the point that we see a control of the bottom-water oxygen concentration on benthic fluxes has not yet been reached in the LSLE. The benthic fluxes of oxygen, derived from short-term incubations of sediment cores recovered along the Laurentian Channel, are independent of the bottom water dissolved oxygen concentration and organic carbon rain rate, despite a recent report of eutrophication in the LSLE (Thibodeau et al., 2006). Yet, there is a strong horizontal gradient in oxygen concentration along the Laurentian Channel and this gradient appears to have increased over the last 80 years. Based on the results of Chapter 3 and other field observations, and building from a previous model (Benoit et al., 2006), we numerically simulated the spatial distribution of oxygen in the bottom water of the Laurentian Channel and identified the processes (physical and biogeochemical) that are mostly responsible for the vertical and horizontal oxygen distribution in the bottom water of the LSLE, including the presence of a mid-water oxygen minimum.

This chapter consists of a paper submitted to Journal of Geophysical Research Oceans in November 2011: Lefort S., Gratton Y., Mucci A., Dadou I. and Gilbert D., Hypoxia in the Lower St. Lawrence Estuary (LSLE): Physics or shelf biogeochemistry? Aspects of this study were also presented at the ASLO meeting in February 2011.

Hypoxia in the Lower St. Lawrence Estuary: How physics controls spatial patterns

Lefort S.¹, Gratton Y.², Mucci A.¹, Dadou I.³ and Gilbert D.⁴

 GEOTOP and Department of Earth & Planetary Sciences, McGill University, 3450 University Street, Montréal, QC, H3A 2A7, Canada.

2. Institut National de la Recherche Scientifique, Eau Terre & Environnement (INRS-ETE), 490 rue de la Couronne, Québec, QC, G1K 9A9, Canada.

 Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (UMR5566/CNRS /UPS), 14 Avenue Edouard Belin, 31400 Toulouse Cedex, France.

4. Maurice Lamontagne Institute, Fisheries and Oceans Canada, P.O. Box 1000, Mont-Joli, QC, G5H 3Z4, Canada.

Submitted to JGR-Oceans, November 2011 Accepted with minor revisions, January 2012 Re-submitted to JGR-Oceans, April 2012

4.1 Abstract

A laterally-integrated advection-diffusion two-dimensional model was implemented to simulate the spatial distribution of dissolved oxygen and the development of hypoxic conditions in the deep waters of the Laurentian Channel (Estuary and Gulf of St. Lawrence, Eastern Canada). Our simulations reveal that the horizontal distribution of dissolved oxygen in the bottom waters of the Laurentian Channel is determined by a combination of physical and biogeochemical processes, whereas its vertical distribution is governed by the deep water circulation. This result strongly suggests that the physics of the system and the source water properties are mostly responsible for the generation of a mid-water column oxygen minimum and the oxygen distribution pattern in the deep water column.

4.2 Introduction

Hypoxia ($[O_2] < 62.5 \mu mol L^{-1}$) results from complex interactions between physical and biogeochemical processes [*Peña et al.*, 2010]. In coastal environments, eutrophication is often identified as the main cause of hypoxia. Nutrient discharge by rivers sustains high surface water primary production which, in turn, is exported to deep waters and serves as a sink for dissolved oxygen [*Cloern*, 2001]. Nevertheless, physical conditions limiting water ventilation (e.g., stratification) or remote advection of oxygen-poor water under a persistent pycnocline are also necessary for the development of hypoxia [*Diaz and Breitburg*, 2009]. Hypoxic conditions are reported in numerous fjords (e.g., Framvaren Fjord, Saanich Inlet) and semi-enclosed seas (e.g. Baltic Sea) where persistent stratification prevents the ventilation of deep waters [*Özsoy and Ünlüata*, 1997]. Given the global spread of hypoxia and its impacts in coastal ecosystems [*Diaz*, 2001; *Gilbert et al.*, 2010], we need to understand processes controlling hypoxic conditions, especially the relative contribution of physical and biogeochemical processes that regulate the development of hypoxic bottom waters.

The deep waters (> 250 m) of the Lower St. Lawrence Estuary (LSLE; Fig. 4.1) have been hypoxic since the mid-1980s [Gilbert et al., 2005]. The bathymetry of the LSLE is marked by the presence of a deep channel, the Laurentian Channel, that extends from Tadoussac to the edge of the eastern Canadian continental shelf. The persistence of hypoxic conditions in the LSLE results from the year-round stratification of the water column and the estuarine circulation pattern. Throughout most of the year, the water column in the Laurentian Channel is characterized by three distinct layers [Dickie and Trites, 1983]: (1) a 25-50 m deep surface layer of low salinity (27-32) flowing seaward, (2) a 50 to 100 m thick intermediate layer of cold (-1 to 2° C) and saline (31.5-33) water flowing landward, and (3) a deep layer that extends to depths of 350 m or more with warmer $(4-6^{\circ}C)$ and saltier (34-34.6) water flowing landward. The surface layer displays large seasonal variations in temperature and salinity due to atmospheric and buoyancy forcing. In winter, as tributary flow decreases and ice is formed, this layer becomes progressively colder and denser until it merges with the cold intermediate layer (CIL) [Galbraith, 2006; Gilbert and Pettigrew, 1997]. The CIL is separated from the bottom water by a permanent pycnocline that inhibits the ventilation of deep waters [Bugden, 1991; Craig and Gilbert, 2008; *Tee*, 1989]. The deep waters originate from the edge of the continental shelf, enter the Gulf through Cabot Strait and travel landward to Tadoussac (Fig. 4.1) where they are tidally upwelled due to an abrupt change in bathymetry (from 350 to \sim 35 m) [Gratton et al., 1988]. They are a mixture of cold and oxygen-rich Labrador Current Water (LCW) and warm oxygen-poor North Atlantic Central Water (NACW) whose proportions vary on a decadal or secular time scales [Bugden, 1991; Gilbert et al., 2005]. Given that the bottom waters are isolated from the surface waters and atmosphere by a permanent pycnocline, dissolved oxygen in the bottom waters can only be replenished by diffusion from the oxygenated surface layer and by landward advection from the oxygenated Atlantic waters [Bugden, 1991].

The transport of a tracer in the bottom water of the Laurentian Channel can be described by a simple advection-diffusion equation [Bugden, 1991]. Thus, variations of the bottom water dissolved oxygen concentration along the Laurentian Channel can be modeled as a laterally averaged 2-D fluid influenced by horizontal and vertical diffusion as well as horizontal advection [Benoit et al., 2006; see Fig. 4.2 for a description of their model]. With this simple model, Benoit et al. [2006] successfully generated hypoxia in the LSLE but could not reproduce the tongue of oxygen minimum water that is observed between 250 and 275 m depth or along the $\sigma_t \approx 27.25$ kg m⁻³ isopycnal (Fig. 4.3). They made two major simplifications which could explain the lack of fine-scale vertical structure in their model simulations: (1) they applied a constant advection velocity (i.e., flat bathymetry) and (2) assumed that the only significant oxygen sink was the sediment (benthic respiration), i.e. they neglected pelagic (water column) respiration (Fig. 4.2). In a recent study, Lehmann et al. [2009] reported that pelagic respiration may account for up to 40% of the oxygen consumption in the deep waters of the Laurentian Channel. Hence, to reproduce the distribution of dissolved oxygen concentrations throughout the LSLE as well as identify and determine the relative contributions of the processes responsible for the generation of this mid-water column oxygen minimum, we developed a simple 2-D numerical model that includes both pelagic and benthic oxygen respiration and in which we implemented a more realistic bathymetry of the Laurentian Channel.

4.3 Model description

Our numerical model is a 2-D representation of oxygen transport in the bottom waters of the Laurentian Channel, where the advection and diffusion of dissolved oxygen, respectively from the Atlantic Ocean and the surface waters, are counterbalanced by benthic and pelagic respiration (Fig. 4.4). The bottom waters flow landward from Cabot Strait and upwell at the head of the Laurentian Channel (Fig. 4.1). Cabot Strait and Station 25, respectively, correspond to the

eastern and western boundaries of the model, where the bottom water extends from the permanent pycnocline at 150 m to the seafloor. Station 25 was set as the western boundary because of its location before the abrupt change in bathymetry, allowing us to neglect the influence of upwelling in the water circulation landward of this station.

4.3.1 Oxygen transport

As proposed by *Bugden* [1991] and applied by *Benoit et al.* [2006], the transport of oxygen in the bottom water of the Laurentian Channel was represented by a 2-D advection-diffusion equation:

$$\frac{\partial O_2}{\partial t} = -\vec{\nabla}.(\vec{u}O_2) + K\nabla^2 O_2 + SMS(O_2)$$
(1)

where *K* is a diagonal matrix of eddy diffusivity coefficients, \vec{u} is the velocity vector and *SMS* is the source minus sink term due to the biogeochemical processes. The solution to Eq. (1) is simplified by making the following assumptions about the flow:

(1) The system is assumed stationary since the properties of the bottom waters vary mainly on decadal to secular time scales [*Benoit et al.*, 2006; *Gilbert et al.*, 2005; *Koutitonsky and Bugden*, 1991].

(2) The deep waters of the Laurentian Channel are considered as a laterallyaveraged 2-D uniform fluid [*Bugden*, 1991], with a vanishing cross-channel velocity. We also assume that the funnel effect (slowly changing depth) will only affect the vertical and along-channel velocity components.

(3) The upper boundary of the model (at 150 m depth) is considered rigid so that the advection velocity depends on the flow at Cabot Strait, the water column height, and the width of the channel. The horizontal velocity was calculated from the flow with a variable depth and constant width (Table 4.1, Eq. (a1)). The Laurentian Channel width was assumed constant with depth: the V-channel is approximated as a U-channel [*Bugden*, 1991]. The width of the Laurentian Channel was also assumed constant between Cabot Strait and Station 25 since it is nearly constant over four fifths of its length (from Cabot Strait to the mouth of the LSLE). The bathymetry follows the maximum depth along the central axis of the Laurentian Channel from Station 25 (300 m) to Cabot Strait (525 m) at a 1-km spatial resolution. The bottom topography data were provided by the Canadian Hydrographic Service of Fisheries and Oceans Canada. The vertical velocity was computed from the continuity equation (Table 4.1, Eq. (a2)) and satisfies the boundary conditions at the pycnocline and the sediment-water interface (Table 4.1, Eq. (b1) and Eq. (b3)), so that the component of the total velocity (u, w) perpendicular to the boundary is zero at the bottom [*LeBlond and Mysak*, 1978].

(4) The horizontal diffusion coefficient K_x is enhanced to reflect the impact of the cross-channel flow [*Benoit et al.*, 2006; *Bugden*, 1991]. This coefficient is assumed constant in the bottom water and is calculated from the mean advection velocity and the channel width, as proposed by *Bugden* [1991] (Table 4.1, Eq. (a3) and Eq. (a4)).

Under these assumptions, Eq. (1) simplifies to:

$$u(x)\frac{\partial[O_2]}{\partial x} + w(x,z)\frac{\partial[O_2]}{\partial z} = K_x \frac{\partial^2[O_2]}{\partial x^2} + K_z \frac{\partial^2[O_2]}{\partial z^2} + R_{wc}$$
(2)

Note that the *SMS* term from Eq. (1) was replaced by R_{wc} , which corresponds to the sink induced by pelagic respiration; the benthic sink does not appear in the transport equation since it is included in the model as a boundary condition at the sediment-water interface (see Table 4.1, Eq. (b4) and sections 4.3.2.2 and 4.3.3). K_z represents the constant vertical diffusion coefficient (Table 4.2). The variables (x, u) and (z, w) are used for the horizontal and vertical positions and velocity components, respectively. For other parameter and variable descriptions, see Tables 4.1, 4.2 and 4.3.

4.3.2 Oxygen sinks

4.3.2.1 Pelagic respiration

Based on modeling of the dissolved oxygen isotope compositions, Lehmann et al. [2009] calculated that 1960 mmol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$ are consumed in the 100 m water layer above the sediment-water interface between Stations 23 and 16 (Fig. 4.1). The respiration rate was assumed equally distributed in this water layer $(19.6 \text{ mmol m}^{-3} \text{ yr}^{-1})$ and the latter value was assigned to the pelagic sink value R_{wc} (Eq. (2)) over the entire model domain. R_{wc} is assumed to be invariant with depth (z) and distance (x), as implemented in previous studies [Savenkoff et al., 1995, 1996]. The latter authors showed that the pelagic respiration rate is constant with depth from 150 m to the sediment-water interface throughout the Lower Estuary and the Gulf of St. Lawrence. Based on ETS (electron transport system) measurements, they estimated that about 40 mmol $O_2 \text{ m}^{-3} \text{ yr}^{-1}$ are consumed in the Lower Estuary whereas between 35 and 55 mmol $O_2 \text{ m}^{-3} \text{ yr}^{-1}$ are consumed in the Gulf at depths below 150 m. ETS measurements are known to overestimate respiration in marine water [Packard, 1985; Vosjan and Newland, 1987; Vosjan et al., 1990], but Packard [1985] empirically demonstrated that the R:ETS (respiration to ETS) ratio is equal to 0.75 for bacteria. Accordingly, we applied this ratio to correct the measurements of Savenkoff et al. [1995, 1996] and derived an averaged respiration rate of $32.5\pm7.8 \text{ mmol } O_2 \text{ m}^{-3} \text{ yr}^{-1}$, within a factor of two of the rate (19.6 \pm 5.6 mmol O₂ m⁻³ yr⁻¹) derived by *Lehmann et al.* [2009].

4.3.2.2 Benthic respiration

Benthic oxygen fluxes measured along the Laurentian Channel [*Anschutz* et al., 2000; *Katsev et al.*, 2007; *Silverberg et al.*, 2000] display as much spatial variations at the small-scale (1 m; within the sampling diameter of a multi-corer) than at larger spatial scales (50-100 km; i.e., between stations) and show no clear trend from Station 25 to Cabot Strait (Fig. 4.5; for details see G. Chaillou, P. Archambault, S. Lefort, M. Bourque, A. Mucci and B. Sundby, Fluxes and distributions of dissolved oxygen, nitrate, phosphate, iron, and manganese in

Laurentian Trough sediments exposed to different bottom-water oxygen concentrations, submitted to *Aquatic Geochemistry*, 2011), despite documented variations in the nature (terrestrial:marine) and accumulation rates of organic matter along the Laurentian Channel [*Colombo et al.*, 1996a,b; *Lucotte et al.*, 1991; *Muzuka and Hillaire-Marcel*, 1999; *Silverberg et al.*, 2000; *Smith and Schafer*, 1999; see Table 3 in *Benoit et al.* [2006] for a compilation of organic carbon accumulation rates]. Hence, we assumed that the oxygen uptake rate from the sediment is constant along the Laurentian Channel (Table 4.1, Eq. (b4)).

The spatially-averaged oxygen flux derived from sediment core incubations (1374 \pm 624 mmol O₂ m⁻² yr⁻¹) is 2.5 times smaller than the benthic respiration estimated by Lehmann et al. [2009] (3540±560 mmol O₂ m⁻² yr⁻¹). We believe that benthic oxygen fluxes measured from sediment core incubations might underestimate the sediment oxygen demand because of sampling artifacts. *Glud et al.* [1994] showed that total O_2 uptake rates measured in the laboratory were lower than those measured in-situ because of underrepresentation and disturbance of the macrofauna. Variability of macrofauna density in incubation experiments, carried out on multiple sediment cores recovered from the same station, might also explain the high intra-site variability in oxygen uptake rates (G. Chaillou, P. Archambault, S. Lefort, M. Bourgue, A. Mucci and B. Sundby, Fluxes and distributions of dissolved oxygen, nitrate, phosphate, iron, and manganese in Laurentian Trough sediments exposed to different bottom-water oxygen concentrations, submitted to Aquatic Geochemistry, 2011). Consequently, we chose the benthic respiration rate estimated by Lehmann et al. [2009] as a boundary condition for the benthic oxygen flux. Hence, both the pelagic and benthic respiration rates used in our model were estimated by the same method (i.e. modeling of the dissolved oxygen isotope compositions).

4.3.3 Initial and boundary conditions

The vertical oxygen concentration at Cabot Strait is nearly invariant with depth below 150 m (169 \pm 18 mmol O₂ m⁻³), and, with the exception of a few small scale variations, the oxygen concentration at 150 m depth between Station 25 and

Cabot Strait does not vary significantly (168±34 mmol O₂ m⁻³; Fig. 4.6; D. Gilbert and E. Nault, Oxygen Atlas for the Gulf of St. Lawrence, unpublished data, 2007). Consequently, the oxygen concentration at these boundaries was set at 170 mmol m⁻³ (Table 4.1, Eq. (b2) and Eq. (b7)). Since the system is stationary, these boundary conditions were applied as initial conditions within the model domain for all variables (Table 4.1, Eq. (c1)). At the head of the estuary (Station 25), the boundary is open as the numerical grid ends but fluid motion remains unrestricted [*Chapman*, 1985]. We impose a no-gradient Neumann condition: $\frac{\partial [O_2]_{x=0}}{\partial x} = 0$.

Dirichlet conditions were imposed at the three other boundaries (at Cabot Strait, along the pycnocline and at the sediment-water interface).

4.3.4 Tuning of physical parameters

In order to tune the physical model parameters, simulation runs were performed with physical parameters (F_{0} , \overline{u} , W, K_x , K_z) whose assigned values covered the range reported in the literature (Table 4.4). The outputs of these simulations were compared statistically to a reference state chosen to be the 2002-2010 oxygen climatology (Fig. 4.6). The climatology was preferred to a specific-year transect to neglect small seasonal and inter-annual variabilities since temporal variations are not represented in our steady-state model. The similarity between the model output and the climatology is quantified in terms of the mean (M), the bias $(M_{model} - M_{data})$, the root mean square (RMS) difference, the centered pattern RMS difference ($E' = \sqrt{(RMS^2 - bias^2)}$), the standard deviation (σ) and the correlation (R). The statistical information (σ , R, E') is summarized on a Taylor diagram [Taylor, 2001], which graphically summarizes how closely a pattern (or a set of patterns) matches observations (Fig. 4.7). Using the benthic and pelagic respiration rates estimated by *Lehmann et al.* [2009], the model best fit (simulated dissolved oxygen concentrations) to the observations (identified as model-ref in Fig. 4.7) is given for the parameter values listed in Table 4.2. The chosen modelref presents the best combination of high correlation (R = 0.899), low

bias (2.07 mmol O₂ m⁻³), small centered RMS difference (E' = 0.438) and low standard deviation ($\sigma = -3.10 \text{ mmol O}_2 \text{ m}^{-3}$).

If the spatially-averaged benthic oxygen uptake rate derived from sediment core incubation experiments is substituted for the value derived by *Lehmann et al.* [2009], the best fit to the data is given for a flow $F_0 = 0.035$ Sv (1 Sv = 10^6 m³ s⁻¹), corresponding to an averaged along-channel advection velocity of 0.17 cm.s⁻¹ (not shown). This advection velocity is much smaller than the values computed by *Bugden* [1991] (0.5 cm s⁻¹) and *Gilbert* [2004] (1.0 cm s⁻¹) from the temperature field, further supporting the hypothesis that oxygen fluxes derived from sediment core incubations might be underestimated.

4.3.5 Model implementation

The model was implemented within the Matlab[®] programming environment using the finite element code for elliptic equations from their Partial Differential Equations Toolbox [*MathWorks*, 2006]. The toolbox has also a function for global, uniform mesh refinement. The refinement ends when each triangle contributes less than 10^{-3} , the preset tolerance. More details on the finite element method may be found in *Johnson* [1987].

4.4 Model-data comparison

Our model properly reproduces the spatial distribution of dissolved oxygen in the bottom water of the Laurentian Channel (Figs. 4.6 and 4.8). The simulated oxygen concentration decreases as the bottom water travels landward and reaches the hypoxic threshold in the LSLE. The vertical modeled-profiles of oxygen reproduce the observed oxygen minimum between 250 and 275 m depth (Fig. 4.8). In agreement with the climatology (Fig. 4.6), the oxygen minimum depth increases with the water column thickness (Fig. 4.8). Nevertheless, from Station 17 to Cabot Strait, the simulated oxygen concentration is underestimated in the first tens of meters below the pycnocline. This small discrepancy is caused by our choice of boundary conditions, i.e., setting the dissolved oxygen concentration at a fixed value of 170 mmol O_2 m⁻³ along the pycnocline while, in reality, it is ~ 215 mmol O_2 m⁻³ between Station 17 and Cabot Strait (Fig. 4.6). Despite the simplified representation of the deep water circulation, the compatibility of the modeled and observed oxygen concentrations confirms that dissolved oxygen is only provided to the bottom waters of the Laurentian Channel through advective and diffusive processes, as proposed by *Bugden* [1991].

4.5 Sensitivity analysis

We performed a sensitivity analysis to assess the impact of physical (advection and diffusion) and biogeochemical processes (benthic and pelagic respiration) on the distribution of dissolved oxygen in the deep waters of the Laurentian Channel. Physical and biogeochemical parameters of the model were modified individually over the range of values reported in the literature (Tables 4.4, 4.5 and 4.6). The simulated dissolved oxygen concentrations from each run are compared with the reference run, referred to as model-ref (Fig. 4.8). Sensitivity analysis results are presented on Taylor diagrams (Fig. 4.9) [*Taylor*, 2001].

4.5.1 Physical parameters

Tested physical parameters included the flow (F_0), the coefficient of vertical diffusion (K_z) and the channel width (W), since a modification of any of these values can potentially change the oxygen transport mode. Indeed, the alongchannel advection rate of oxygen varies with the water advection velocity, which changes if either F_0 or W is modified (Table 4.1, Eq. (a1) and Eq. (a2)). The horizontal diffusion rate of dissolved oxygen varies with the horizontal diffusion coefficient (K_x), which changes with F_0 (Table 4.1, Eq. (a4)). Finally, the vertical diffusion of dissolved oxygen varies with K_z . The vertical diffusion coefficient was varied between 0.1 cm² s⁻¹, a typical value for the deep ocean [*Ledwell et al.*, 1993], and 5 cm² s⁻¹, a value that reflects intense vertical mixing [*Large et al.*, 1994]. The reference flow value was varied from 0% to 100% in order to include the range of horizontal advection velocities estimated by *Bugden* [1991] and *Gilbert* [2004], respectively. The channel width was varied from 50 km to ~ 105 km to encompass the true range from the Lower Estuary to Cabot Strait. Refer to Table 4.5 for the range of parameter values.

An increase of the horizontal diffusion coefficient (represented on Fig. 4.9a by the distance between the yellow and green symbols at a same advection velocity, i.e. compare yellow triangle with green square and yellow diamond with green triangle) enhances the oxygenation of the bottom water but has the smallest impact of the three tested physical parameters (i.e. advection velocity, horizontal and vertical diffusion coefficients) on the oxygen distribution. As variations in the flow (Fig. 4.9a, green symbols) embrace variations of the advection velocity and the horizontal diffusion coefficient, they have a greater influence on the oxygen distribution than variations of the advection velocity (yellow symbols) or horizontal diffusion alone. The linear variation of the three statistic metrics (σ , R, *E'*), combined to high correlation coefficients (> 0.977) and high bias (Fig. 4.9a) between model simulations and model reference, reveal that variations in the flow slightly modify the shape of the oxygen profile (i.e. vertical distribution) but greatly impact the oxygen concentrations throughout the Channel (i.e. horizontal distribution): the higher the flow, the higher the advection velocity, the higher the dissolved oxygen renewal rate and concentrations. In contrast, variations of the vertical diffusion coefficient (Fig. 4.9a, black symbols) modify both the shape of the profiles (high variations of the three statistic metrics (σ , R, E')) and the dissolved oxygen concentrations (high variations of the bias). Hence, the vertical diffusion seems to be the physical parameter that influences most the dissolved oxygen distribution. Results of our sensitivity analysis agree with those of *Benoit* et al. [2006] who showed that, in the LSLE, the dissolved oxygen concentration is very sensitive to vertical mixing when the vertical eddy diffusivity, K_z, is smaller than 3 cm² s⁻¹. Consequently, the vertical diffusion coefficient, K_z , needs to be better constrained. For reasonable variations of the physical parameter values (i.e.

-55 to 120 % for vertical diffusivity, 0 to 20 % for the flow and -20 to + 5 % for the channel width), the discrepancies between the spatially-averaged modeled and observed oxygen concentrations are less than 15 %.

4.5.2 Biogeochemical parameters

Benthic and pelagic respiration rates were varied in order to estimate their impact on the dissolved oxygen distribution. This is equivalent to modifying the location and strength of the oxygen sinks. In our simulations, the pelagic and benthic respiration rates were varied either independently or simultaneously. The benthic respiration rate was varied between 750 and 3960 mmol O₂ m⁻² yr⁻¹ (i.e. - 80 to +12 % from the reference) whereas the pelagic respiration rate was varied between 15.4 and 40.3 mmol $O_2 \text{ m}^{-3} \text{ yr}^{-1}$ (i.e. - 21 % and +105 % from the reference). The chosen ranges cover realistic variations estimated by *Lehmann et* al. [2009] (green symbols on Fig. 4.9b), the range of estimated benthic and pelagic respiration measurements (black open symbol on Fig. 4.9b), as well as the influence of a spatially-variable benthic respiration (filled yellow symbols on Fig. 4.9b; the function $F_{O2} = f(x)$ is plotted on Fig. 4.5 (blue dots) and has a spatiallyaveraged value of 4365 mmol O_2 m⁻² yr⁻¹). The range of respiration rates estimated from direct measurements (incubations and ETS) is shown to give the best possible representation of the impact of biogeochemistry on the oxygen distribution even though it yields improbable, much smaller benthic:pelagic respiration rate ratios (< 1) than the value (1.5) estimated by Lehmann et al. [2009]. The simulations with either benthic or pelagic respiration alone are presented for information (filled black symbols on Fig. 4.9b). Refer to Table 4.6 for the range of respiration values.

Within the range investigated, the respiration rates have little impact on the spatial dissolved oxygen distribution pattern, but mostly affect the absolute oxygen concentrations. With the more realistic bathymetry, the oxygen minimum is always generated regardless of the location or the strength of the oxygen sink (excepted when benthic and pelagic sinks are null), and its location within the water column varies at most by 15 m. The greatest variation in the depth of the

oxygen minimum occurs when either benthic or pelagic respiration are null (respectively filled black triangle and filled black circle and diamond on Fig. 4.9b), and although such a situation is unrealistic, the correlation coefficient between the simulated and reference oxygen distribution patterns remain above 0.956. Variations of the benthic:pelagic respiration rate ratio (filled green symbols, open black symbols and yellow symbols on Figure 4.9b), from the reference value of 3:2 estimated by *Lehmann et al.* [2009], induce small changes in the spatial distribution of oxygen, as reflected by the high correlation coefficient (> 0.974). The largest deviations from the modeled reference values are observed when the total respiration rate (i.e. spatially-integrated pelagic + benthic rates) is either minimal (3220 mmol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$, open black triangle on Fig. 4.9b) or maximal (7015 mmol O_2 m⁻² yr⁻¹, filled yellow diamond on Fig. 4.9b). The minimal total respiration rate is smaller than the estimated benthic respiration rate (3540 mmol O_2 m⁻² yr⁻¹, filled black circle on Fig. 4.9b) and, thus, too low to be considered as a plausible situation. Variations of the benthic respiration rate along the channel do not significantly affect the distribution and concentration of dissolved oxygen in the bottom water (filled yellow symbols on Fig. 4.9b). The modeled dissolved oxygen concentrations mostly depend on the strength of the total oxygen sink, and for reasonable values of the oxygen sinks (i.e. between 4390 and 7015 mmol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$), the discrepancy between the spatially-averaged modeled and observed oxygen concentrations is less than 11%.

4.6 Interpretation and implication of the oxygen minimum

In order to explain the generation of a mid-water column oxygen minimum, we examined the mechanisms governing the spatial distribution of dissolved oxygen in the deep water of the Laurentian Channel by establishing an oxygen mass budget in two sub-domains divided by the 275 m depth (Fig. 4.10), corresponding approximately to the oxygen minimum (Fig. 4.8). The budget allows us to identify which process drives the oxygen supply, sink and transport, and thus improves our understanding of the role of each physical process on the spatial distribution of dissolved oxygen. We focus on the role of physical processes in the bottom water of the Laurentian Channel because results of our sensitivity analysis (see section 4.5) show that the dissolved oxygen concentrations and distribution pattern are much more sensitive to variations of physical than biogeochemical parameters, and that the latter only slightly modify the position of the oxygen minimum.

Apart from the horizontal diffusion, which makes a small contribution to the oxygen budget regardless of the location along the channel, the transport modes above and below the oxygen minimum change considerably (Fig. 4.10). Above the oxygen minimum, dissolved oxygen is supplied by both vertical diffusion and vertical advection, and is lost by horizontal advection. Below the oxygen minimum, it is the opposite: oxygen is mainly supplied by horizontal advection while it is lost by vertical advection to the upper layer because of the reduction of the water column height and by vertical diffusion across the sediment-water interface because of benthic respiration. Oxygen concentration isopleths along the Laurentian Channel (from Station 25 to Cabot Strait) have a negative (positive) slope when oxygen is supplied (lost) by vertical processes and lost (supplied) by horizontal processes, and the balance between vertical advection and vertical diffusion determines the depth of the oxygen minimum. Hence, vertical diffusion as well as horizontal and vertical advection govern the vertical distribution of dissolved oxygen. This finding implies that the physics of the system is mostly responsible for the generation of the dissolved oxygen minimum, and probably for its general geographical distribution pattern.

A vertical distribution of dissolved oxygen similar to that observed along the Laurentian Channel has been reported in a coastal upwelling system off Namibia [*Gutknecht et al.*, 2011], where the physical processes are known to control the development and intensification of subsurface oxygen-depleted water [e.g. *Monteiro et al.*, 2008, 2011]. Physical processes can affect the dissolved oxygen concentration through either weak ventilation [*Czeschel et al.*, 2011] or remote advection of oxygen-depleted water masses [*Bograd et al.*, 2008]. Physical

processes, such as wind forcing, can also influence the biogeochemical oxygen demand through the intensification of the upwelling of nutrient-rich water [Monteiro et al., 2006] which promotes primary production [Mohrholz et al., 2008] and, in turn, can lead to eutrophication [Monteiro and Largier, 1999]. Although upwelling at the head of the Laurentian Channel is not physically represented in our model, it is an intrinsic part of the St. Lawrence estuarine circulation system and strongly influences primary production in the surface waters of the LSLE, which, in turn, is ultimately exported to the bottom waters and modifies the strength of the pelagic and benthic oxygen sinks. In contrast to coastal upwelling systems, intensification of upwelling at the head of the Laurentian Channel has been mostly observed in winter [Smith et al., 2006] when the temperature, the ice cover and the low light conditions hinder phytoplankton growth. Thus, we believe that the establishment of hypoxia in the bottom waters of the LSLE results mostly from the weak ventilation and the low initial dissolved oxygen concentration in the advected water rather than from an intensification of the biogeochemical oxygen demand, as our model reproduces the hypoxia observed in the LSLE (Fig. 4.8) with constant benthic and pelagic respiration rates throughout the Laurentian Channel.

Dissolved oxygen concentrations in the bottom waters of the LSLE have decreased by 50% over the last century [*Gilbert et al.*, 2005]. A concurrent warming of these waters [*Thibodeau et al.*, 2010; *Genovesi et al.*, 2011; *Sherwood et al.*, 2011] suggests that changes in the relative proportions of the cold oxygen-rich LCW and the warm oxygen-poor NACW, whose mixture makes up the bottom waters feeding the Laurentian Channel, modified their properties and played a determining role in the progressive depletion of dissolved oxygen and ultimate establishment of hypoxic conditions in the LSLE [*Gilbert et al.*, 2005]. *Gilbert et al.* [2005] estimated that one half to two thirds of the oxygen loss in the LSLE could be attributed to modifications of the water circulation pattern on the remaining third was tentatively ascribed to eutrophication [*Gilbert et al.*, 2005]. Whereas *Thibodeau et al.* [2006] demonstrated, using geochemical and

micropaleontological tracers in the sediment, that primary productivity and the flux of marine organic matter to the seafloor might have increased over the last 30-40 years in the LSLE, Genovesi et al. [2011], using the same tracers, showed that the organic matter input to the seafloor in the Gulf of St. Lawrence has been nearly constant for the last two centuries while the bottom water dissolved oxygen gradient between Cabot Strait and the LSLE has increased since the turn of the century (~ 1880-1910). Genovesi et al. [2011] proposed that the nearly 1.7°C increase in temperature of the waters entering the Laurentian Channel and the resulting increased respiration rates may be responsible for the increasing oxygen gradient in the Gulf of St. Lawrence since the early 1930s [Gilbert et al., 2005]. Likewise, our model results suggest that the horizontal advection of water with lower dissolved oxygen concentration is mostly responsible for the establishment of hypoxic conditions in the Lower Estuary. Since climate models predict the expansion of oxygen minimum zones under global warming conditions [Matear and Hirst, 2003], the hypoxic zone in the Laurentian Channel may spread from the LSLE to the Gulf. Only long-term monitoring of the LSLE and Gulf of St. Lawrence will allow us to elucidate how the St. Lawrence ecosystem will respond to climate change.

4.7 Conclusions

This study examined the role of physical and biogeochemical processes and their relative contributions on the spatial distribution of dissolved oxygen in the bottom waters of the Laurentian Channel, using a simple 2-D advectiondiffusion model. The inclusion of a realistic bathymetry to an earlier model [*Benoit et al.*, 2006], combined with independently-derived benthic and pelagic respiration rates, reproduced the observed geographical distribution of dissolved oxygen concentrations. Spatial changes in the flow velocity of bottom waters, induced by the inclusion of a realistic bathymetry, are mostly responsible for generating the fine-scale vertical distribution pattern of dissolved oxygen and, more importantly, the presence of a mid-water column oxygen minimum, while benthic and pelagic sinks only influence the intensity of the oxygen minimum. Our simulations of bottom water oxygen concentrations and distribution pattern along the Laurentian Channel show that the system is much more sensitive to physical than biogeochemical processes and demonstrate that the oceanographic conditions at the continental shelf edge, where Laurentian Channel bottom waters originate, and the circulation within the Channel are mostly responsible for the establishment of hypoxic conditions in the Lower Estuary.

4.8 Acknowledgments

This research was funded by a NSERC Strategic grant to A.M., D.G. and Y.G, and a DFO CCSI (Climate Change Science Initiative) grant to D.G. Additional financial support to S.L. was provided by the Department of Earth and Planetary Sciences/McGill, the GEOTOP-UQAM-McGill research centre, the LEGOS laboratory and the University of Toulouse (Paul Sabatier, France). We thank the captains and crew of R/V Alcide C. Horth and R/V Coriolis II for their help during the numerous cruises between 2002 and 2011.

4.9 References

- Anschutz, P., B. Sundby, L. LeFrançois, G. W. Luther III and A. Mucci (2000), High resolution profiles and fluxes of redox species in continental margin sediments: implication for the cycles of nitrogen, iodide, manganese, and iron, *Geochim. Cosmochim. Acta*, 64, 2751–2763.
- Benoit, P., Y. Gratton and A. Mucci (2006), Modeling of dissolved oxygen levels in the bottom waters of the Lower St. Lawrence Estuary: Coupling of benthic and pelagic processes, *Mar. Chem.*, 102, 13–32, doi:10.1016/j.marchem.2005.09.015.
- Bograd, S., C. G. Castro, E. Di Lorenzo, D. M. Palacios, H. Bailey, W. Gilly and F. P. Chavez (2008), Oxygen declines and the shoaling of the hypoxic boundary in the California Current, *Geophys. Res. Lett.*, 35, L12607, doi: 10.1029/2008GL034185.

- Bugden, G. L. (1991), Changes in the temperature-salinity characteristics of the deeper waters of the Gulf of St. Lawrence over the past several decades, in *The Gulf of St. Lawrence: Small sea or big estuary? Can. Spec. Publ. Fish. Aquat. Sci.*, vol. 113, edited by J.-C. Therriault, pp. 139–147.
- Chapman, D. C. (1985), Numerical treatment of cross-shelf open boundaries in a barotropic coastal ocean model, *J. Phys. Oceanogr.* 15, 1060–1075.
- Cloern, J. E. (2001), Our evolving conceptual model of the coastal eutrophication problem, *Mar. Ecol. Prog. Ser.*, *210*, 223–253, doi:10.3354/meps210223.
- Colombo, J. C., N. Silverberg and J. N. Gearing (1996a), Biogeochemistry of organic matter in the Laurentian Trough. I. Composition and vertical fluxes of rapidly settling particles, *Mar. Chem.*, *51*, 277–293.
- Colombo, J. C., N. Silverberg and J. N. Gearing (1996b), Biogeochemistry of organic matter in the Laurentian Trough. II. Bulk components during early diagenesis, *Mar. Chem.*, *51*, 295–314.
- Craig, J., and D. Gilbert (2008), Estimation of mixed layer depth at the AZMP fixed stations. *AZMP Bulletin*, 7, 37–42.
- Czeschel, R., L. Stramma, F. U. Schwarzkopf, B. S. Giese, A. Funk and J. Karstensen (2011), Mid-depth circulation of the eastern tropical south Pacific and its link to the oxygen minimum zone, J. Geophys. Res., 116, C01015, doi:10.1029/2010JC006565.
- Diaz, R. J. (2001), Overview of hypoxia around the world, *Environ. Qual.*, 30, 275–281.
- Diaz, R. J., and D. L. Breitburg (2009), The hypoxic environment, in *Hypoxia in fishes*, edited by J. G. Richards et al., pp. 1–23, Elsevier, San Diego.
- Dickie, L. M., and R. W. Trites (1983), The Gulf of St. Lawrence, in *Estuaries and enclosed seas*, edited by B. H. Ketchum, Elsevier, Amsterdam.
- Dufour, R., and P. Ouellet (2007), Estuary and Gulf of St. Lawrence Marine Ecosystem, *Rep. 2744E*, Overview and Assessment Report Canadian Technical Report of Fisheries and Aquatic Sciences.
- Galbraith, P. S. (2006), Winter water masses in the Gulf of St. Lawrence, J. *Geophys. Res.*, 111, C06022, doi:10.1029/2005JC003159.
- Genovesi, L., A. de Vernal, B. Thibodeau, C. Hillaire-Marcel, A. Mucci and D. Gilbert (2011), Recent changes in bottom water oxygenation and temperature in the Gulf of St. Lawrence: Micropaleontological and geochemical evidence, *Limnol. Oceanogr.*, 56(4), 1319–1329, doi:10.4319/lo.2011.56.4.1319.
- Gilbert, D. (2004), Propagation of temperature signals along the north-west Atlantic continental shelf edge and into the Laurentian Channel, paper presented at the ICES Annual Science Conference, Vigo, Spain.
- Gilbert, D., and B. Pettigrew (1997), Interannual variability (1948–1994) of the CIL core temperature in the Gulf of St. Lawrence, *Can. J. Fish. Aquat. Sci.*, *54*, 57–67.
- Gilbert, D., D. Chabot, P. Archambault, B. Rondeau and S. Hébert (2007), Appauvrissement en oxygène dans les eaux profondes du St-Laurent marin: Causes possibles et impacts écologiques, *Nat. Can.*, *131*, 67–75.
- Gilbert, D., N. N. Rabalais, R. J. Diaz and J. Zhang (2010), Evidence for greater oxygen decline rates in the coastal ocean than in the open ocean, *Biogeosciences*, 7, 2283–2296, doi:10.5194/bg-7-2283-2010.
- Gilbert, D., B. Sundby, C. Gobeil, A. Mucci and G. H. Tremblay (2005), A seventy-two-year record of diminishing deep-water oxygen in the St. Lawrence Estuary: The northwest Atlantic connection, *Limnol. Oceanogr.*, 50, 1654– 1666, doi:10.4319/lo.2005.50.5.1654.
- Glud, R., J. Gundersen, B. B. Jorgensen, N. P. Revsbech and H. Schulz (1994), Diffusive total oxygen uptake of deep-sea sediments in the eastern South Atlantic Ocean: in situ and laboratory measurements, *Deep-Sea Res. I*, 41(11/12), 1767–1788.
- Grasshoff, K., K. Kremling and M. Ehrhardt (1999), *Methods of Seawater Analysis*, 3rd edition Wiley-VCH, Weinheim, Germany.
- Gratton, Y., G. Mertz and J. A. Gagné (1988), Satellite observations of tidal upwelling and mixing in the St. Lawrence Estuary. *J. Geophys. Res.* 93, 6947–6954.
- Gutknecht, E., I. Dadou, B. Le Vu, G. Cambon, J. Sudre, V. Garçon, E. Machu, T. Rixen, A. Kock, A. Flohr, A. Paulmier and G. Lavik (2011), Nitrogen transfers and air-sea N₂O fluxes in the upwelling off Namibia within the oxygen minimum zone: a 3-D model approach, *Biogeosciences Discuss.*, 8, 3537–3618, doi:10.5194/bgd-8-3537-2011.
- Han, G., J. W. Loder and P. C. Smith (1999), Seasonal-mean hydrography and circulation in the Gulf of St. Lawrence and on the eastern Scotian and southern Newfoundland shelves, *J. Phys. Oceanogr.*, 29, 1279–1301.
- Johnson, C. (1987), Numerical Solution of Partial Differential Equations by the *Finite Element Method*, Student litteratur, Lund, Sweden.
- Katsev, S., G. Chaillou, B. Sundby and A. Mucci (2007), Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the Lower St. Lawrence River Estuary, *Limnol. Oceanogr.*, 52(6), 2555–2568.
- Koutitonsky, V.G., and G. L. Bugden (1991), The physical oceanography of the Gulf of St. Lawrence: A review with emphasis on the synoptic variability of the motion, in *The Gulf of St. Lawrence: Small sea or big estuary? Can. Spec. Publ. Fish. Aquat. Sci.*, vol. 113, edited by J.-C. Therriault, pp. 139–147.
- Large, W. G., J. C. McWilliams and S. C. Doney (1994), Oceanic vertical mixing: A review and a model with nonlocal boundary layer parametrization, *Rev. Geophys.*, *32*(4), 363–403.
- LeBlond, P. H., and L. A. Mysak (1978), *Waves in the ocean*, Elsevier, New York.

- Ledwell, J. R., A. J. Wilson and C. S. Low (1993), Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment, *Nature*, *364*, 701–703.
- Lehmann, M. F., B. Barnett, Y. Gélinas, D. Gilbert, R. J. Maranger, A. Mucci, B. Sundby and B. Thibodeau (2009), Aerobic respiration and hypoxia in the Lower St. Lawrence Estuary: Stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning, *Limnol. Oceanogr.*, 54(6), 2157–2169.
- Levasseur, M. E., and J.-C. Therriault (1987), Phytoplankton biomass and nutrient dynamics in a tidally induced upwelling: the role of the NO₃:SiO₄ ratio, *Mar. Ecol. Prog. Ser.*, *39*, 87–97.
- Lucotte, M., C. Hillaire-Marcel and P. Louchouarn (1991) First-order organic carbon budget in the St. Lawrence Lower Estuary from ¹³C data, *Estuar. Coast. Shelf Sci.*, *32*, 297–312.
- Matear, R. J., and A. C. Hirst (2003), Long-term changes in dissolved oxygen concentrations in the ocean caused by protracted global warming, *Glob. Biogeochem. Cycles*, 17(4), 1125, doi:10.1029/2002GB001997.
- Matworks (2006), *Partial Differential Equation Toolbox User's Guide*, The Mathworks Inc., Natick, MA.
- Mohrholz, V., C. H. Bartholomae, A. K. van der Plas and H. U. Lass (2008), The seasonal variability of the northern Benguela undercurrent and its relation to the oxygen budget on the shelf, *Cont. Shelf Res.*, 28, 424–441, doi:10.1016/j.csr.2007.10.001.
- Monteiro, P. M. S., and J. L. Largier (1999), Thermal stratification in Saldanha Bay (South Africa) and subtidal, density-driven exchange with the coastal waters of the Benguela upwelling system, *Estuar. Coast. Shelf Sci.*, 49(6), 877–890, doi:10.1006/ecss.1999.0550.
- Monteiro, P. M. S., B. Dewitte, M. I. Scranton, A. Paulmier and A. van der Plas, A. (2011), The role of open ocean boundary forcing on seasonal to decadalscale variability and long-term change of natural shelf hypoxia, *Environ. Res. Letters*, 6, doi:10.1088/1748-9326/6/2/025002.
- Monteiro, P. M. S., A. van der Plas, J.-L. Mélice and P. Florenchie (2008), Interannual hypoxia variability in a coastal upwelling system: Ocean-shelf exchange, climate and ecosystem-state implications, *Deep-Sea Research I*, 55, 435–450, doi:10.1016/j.dsr.2007.12.010.
- Monteiro, P. M. S., A. van der Plas, V. Mohrholz, E. Mabille, A. Pascall and W. Joubert (2006), Variability of natural hypoxia and methane in a coastal upwelling system: Oceanic physics or shelf biology?, *Geophys. Res. Letters*, 33, L16614, doi:10.1029/2006GL026234.
- Muzuka, A. N. N., and C. Hillaire-Marcel (1999), Burial rates of organic matter along the eastern Canadian margin and stable isotope constraints on its origin and diagenetic evolution, *Mar. Geol.*, 160, 251–270.

- Özsoy, E., and Ü. Ünlüata (1997), Oceanography of the Black Sea: a review of some recent results, *Earth Sci. Rev.*, 42, 231–272.
- Packard, T. T. (1985), Measurement of electron transport activity of microplankton, *Adv. Aquat. Microbio.*, *3*, 207–261.
- Peña, M. A., S. Katsev, T. Oguz and D. Gilbert (2010), Modeling dissolved oxygen dynamics and hypoxia, *Biogeosciences*, 7, 933–957, doi:10.5194/bg-7-933-2010.
- Saucier, F. J., F. Roy, D. Gilbert, P. Pellerin and H. Ritchie (2003), Modeling the formation and circulation processes of water masses and sea ice in the Gulf of St. Lawrence, Canada, J. Geophys. Res., 108, 3269–3289, doi:10.1029/2000JC000686.
- Savenkoff, C., A. F. Vézina, J.-P. Chanut and Y. Gratton (1995), Respiratory activity and CO₂ production rates of microorganisms in the Lower St. Lawrence Estuary, *Cont. Shelf Res.*, 15(6), 613–631.
- Savenkoff, C., A. F. Vézina, T. T. Packard, N. Silverberg, J.-C. Therriault, W. Chen, C. Bérubé, A. Mucci, B. Klein, F. Mesplé, J.-E. Tremblay, L. Legendre, J. Wesson and R. G. Ingram (1996), Distributions of oxygen, carbon, and respiratory activity in the deep layer of the Gulf of St. Lawrence and their implications for the carbon cycle, *Can. J. Fish. Aquat. Sci.*, 53, 2451–2465.
- Savenkoff, C., A. F. Vézina, P. C. Smith and G. Han (2001), Summer transports of nutrients in the Gulf of St. Lawrence estimated by inverse modeling, *Estuar*. *Coast. Shelf Sci.*, 52, 565–587.
- Silverberg, N., B. Sundby, A. Mucci, S, Zhong, T. Arakaki, P. Per Hall, A. Landén and A. Tengberg (2000), Remineralization of organic carbon in eastern Canadian continental margin sediments, *Deep-Sea Res. I*, 47, 699–731.
- Sherwood, O. A., M. F. Lehmann, C. J. Schubert, D. B. Scott and M. D. McCarthy (2011), Nutrient regime shift in the western North Atlantic indicated by compound-specific δ^{15} N of deep-sea gorgonian corals, *Proc. Natl. Acad. Sci. USA*, 108, 1011–1015, doi:10.1073/pnas.1004904108.
- Smith, J. N., and C. T. Schafer (1999), Sedimentation, bioturbation, and Hg uptake in the sediments of the Estuary and Gulf of St. Lawrence, *Limnol. Oceanogr.*, 44, 207–219.
- Taylor, K. E. (2001) Summarizing multiple aspects of model performance in a single diagram, J. Geophys. Res., 106, 7183–7192.
- Tee, K.-T. (1989), Subtidal salinity and velocity variations in the St. Lawrence Estuary, J. Geophys. Res., 94, 8075–8090.
- Thibodeau, B., A. de Vernal and A. Mucci (2006), Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleontological and geochemical evidence, *Mar. Geol.*, 231, 37–50, doi:10.1016/j.margeo.2006.05.010.

- Thibodeau, B., A. De Vernal, C. Hillaire-Marcel and A. Mucci (2010), Twentieth century warming in deep waters of the Gulf of St. Lawrence: A unique feature of the last millennium, *Geophys. Res. Letters*, *37*, L17604, doi:10.1029/2010GL044771.
- Vosjan, J. H., and G. Nieuwland (1987), Microbial biomass and respiratory activity in surface waters of the East Banda Sea and North West Arafura Sea (Indonesia) at the time of the South East Monsoon, *Limnol. Oceanogr.*, *32*, 767–775.
- Vosjan, J. H., S. B. Tijssen, G. Nieuwland and F. J. Wetsteyn (1990), Oxygen regime, respiratory activity and biomass of microorganisms, and the carbon budget in the Fladen Ground area (Northern North Sea) during spring, *Neth. J. Sea Res.*, 25, 89–99.

Table 4.1: (a) Model equations, (b) boundary conditions and (c) initial conditions. x stands for the seaward distance from Station 25 along the central axis of the Laurentian Channel and z stands for the depth, upward. See Tables 4.2 and 4.3 for undefined parameters and variables.

(a) **Transport** *Advection*

(a1)
$$u(x) = \frac{F_0}{H(x) \times W}$$
, where W is the channel width.

(a2)
$$w(x,z) = (H_{\text{max}} - z)\frac{\partial u(x)}{\partial x}$$
; deduced from $\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$

Diffusion

(a3)
$$K_x = \frac{\overline{u}^2 W^2}{120 K_l}$$
, where \overline{u} is the mean advection velocity along the Laurentian Channel

and K_l is the lateral diffusion coefficient [see *Bugden*, 1991]. Substituting Eq. (a1) into Eq. (a3), we obtain:

(a4)
$$K_x = \frac{(F_0/H)^2}{120 K_l}$$
, where \overline{H} is the averaged deep water column height along the

Laurentian Channel

(b) Boundary conditions

At
$$z = 150 m$$

(b1) $w = 0$
(b2) $[O_2]_{150m} = 170 mmol m^{-3}$

At the sediment-water interface z = h(x)

(b3)
$$w(x) = u(x)\frac{\partial h(x)}{\partial x}$$

(b4)
$$R_{sed} = -3540 \text{ mmol } m^{-2} \text{ yr}^{-1}$$

At Station 25 (x = 0 km)

(b5)
$$u(0) = \frac{F_0}{H(0) \times W}$$

At Cabot Strait (x = L = 825 km)

(b6)
$$u(L) = \frac{F_0}{H(L) \times W}$$

(b7) $[O_2]_L = 170 \text{ mmol } m^{-3}$

(c) Initial conditions

Oxygen

(c1)
$$[O_2]_{init} = 170 \text{ mmol } m^{-3}$$
, assumed to be the same over the entire domain.

Parameter	Definition	Value	Unit	Reference		
Physics						
F_0	Flow below the 150 m depth at	$0.11 \cdot 10^{6}$	$m^3 s^{-1}$	Bugden [1991]		
\overline{u}	Cabot Strait Averaged horizontal velocity along the Laurentian Channel	0.53.10-2	m s ⁻¹	Bugden [1991]		
K_x	Horizontal diffusion coefficient	$16 \cdot 10^2$	$m^2 s^{-1}$	Bugden [1991]		
K_z	Vertical diffusion coefficient	$1.0 \cdot 10^{-4}$	$m^2 s^{-1}$	Bugden [1991]		
W	Width of the Laurentian Channel	$97.5 \cdot 10^3$	m	Fig. 4.1; section 4.3.1		
D: 1						
Biogeochemistry						
R_{WC}	Respiration in the water column, i.e. pelagic respiration	-19.6	mmol $O_2 \text{ m}^{-3} \text{ yr}^{-1}$	Lehmann et al. [2009]		
R _{sed}	Sediment oxygen demand, i.e. benthic respiration	-3540	mmol $O_2 m^{-2} yr^{-1}$	Lehmann et al. [2009]		

Table 4.2: List of parameters with definitions, values, units and literature sources.

Variable	Definition	Unit
$[O_2]$	Dissolved oxygen concentration	mol m ⁻³
$[O_2]_{init}$	Initial dissolved oxygen concentration	mol m ⁻³
$u(x^*)$	Horizontal velocity along the Laurentian Channel	$m s^{-1}$
$w(x^*)$	Vertical velocity along the Laurentian Channel	$m s^{-1}$
$H(x^*)$	Deep water column height	m
$h(x^*)$	Superficial sediment height from water column maximal depth	m

Table 4.3: List of state variables with definitions and units.

* x represents the seaward distance from Station 25 along the LC.

Parameter	Range of values tested	Unit	Reference
F_0	0.11 - 0.22	$10^6 \text{ m}^3 \text{ s}^{-1}$	Bugden [1991]; Gilbert [2004]; Han et al. [1999];
			Saucier and Chassé [2003]
1	0.47 - 2.06	10^{-2} m s^{-1}	Bugden [1991]; Gilbert [2004]; Han et al. [1999];
и			Saucier and Chassé [2003]
K_x	4.27 - 81	$10^2 \text{ m}^2 \text{ s}^{-1}$	Bugden [1991]
K_z	0.45 - 2.2	$10^{-4} \text{ m}^2 \text{ s}^{-1}$	Bugden [1991]; Savenkoff et al. [2001]
W	50 - 110	$10^3 \mathrm{m}$	Fig. 4.1

Table 4.4: Range of physical parameter values tested in model tuning.

Table 4.5: Range of parameter values used for the sensitivity analysis. ref stands for reference: $F_0 = 0.11$ Sv, W = 97.5 km and $K_z = 1$ cm² s⁻¹. u, u_{min} and u_{max} are, respectively, the spatially-averaged, the minimum and the maximum advection velocities. Refer to Table 4.2 for other parameters values.

Parameter	Variation	Parameter value	$\frac{-}{u}$	u_{\min}	$u_{\rm max}$	K_x
	(70)	value	$(\mathrm{cm}\mathrm{s}^{-1})$	$(cm s^{-1})$	$(cm s^{+})$	$(10^{2} \text{ m}^{2} \text{ s}^{-1})$
F_0 (Sv or $10^6 m^3 s^{-1}$)	ref	0.11	0.53	0.30	0.76	$16 \sim \text{ref}$
for W = 97.5 km	+10	0.12	0.58	0.33	0.84	$19 \sim +20 \%$
	+20	0.13	0.63	0.36	0.91	$23 \sim +45 \%$
	+50	0.17	0.79	0.45	1.14	$36 \sim +125 \%$
	+100	0.22	1.05	0.60	1.52	$64 \sim +300 \%$
W (km)	-50	48.75	1.05	0.60	1.52	16
for $F_0 = 0.11$ Sv	-20	78	0.66	0.38	0.95	16
-	-10	87.75	0.59	0.33	0.85	16
	ref	97.5	0.53	0.30	0.76	16
	+ 5	103	0.50	0.28	0.72	16
$K_z(cm^2 s^{-1})$	-90	0.1	-	-	-	-
	-55	0.45	-	-	-	-
	ref	1	-	-	-	-
	+ 120	2.2	-	-	-	-
	+400	5	-	-	-	-

Tested respiration	Pelagic respiration	Benthic respiration	Total respiration	R_{sed} : R_{wc}			
(R_{wc}, R_{sed})	$(\text{mmol } \text{m}^{-3})$	$(\text{mmol } \text{m}^{-2} \text{ yr}^{-1})$	$(\text{mmol } \text{m}^{-2} \text{ yr}^{-1})$				
Lehmann et al. [2009]							
Ref	19.6	3450	5410	1.8			
(-21%, Ref)	15.4	3450	4990	2.2			
(+35%, Ref)	26.5	3450	6100	1.3			
(Ref, +12%)	19.6	3960	5920	2.0			
(Ref, -20%)	19.6	2850	4810	1.5			
(-21%, +12%)	15.4	3960	5500	2.6			
(+35%, -20%)	26.5	2850	5500	1.1			
(-21%, -20%)	15.4	2850	4390	1.9			
(+35%, +12%)	26.5	3960	6610	1.5			
ETS + Incubations							
(+26%, -80%)	24.7	750	3220	0.3			
(+105%, -44%)	40.3	1998	6028	0.5			
(+105%, -80%)	40.3	750	4780	0.2			
(+26%, -44%)	24.7	1998	4468	0.8			
Lehmann et al. [2009	9] + Benoit et al. [2006]					
$(-20\%, F_{O2} = f(x))$	15.4	772 - 4946	5905	2.8			
(Ref, $F_{O2} = f(x)$)	19.6	772 - 4946	6325	2.2			
$(+12\%, F_{O2} = f(x))$	26.5	772 - 4946	7015	1.6			
Benthic or pelagic respiration alone							
(Ref, -100%)	19.6	0	1960	0			
(-100%, Ref)	0	3540	3540	-			
$(-100\%, F_{O2} = f(x))$	0	772 - 4946	4365	-			



Figure 4.1: Map of the Lower Estuary and Gulf of St. Lawrence in Eastern Canada, showing the sampled stations along the Laurentian Channel.



Figure 4.2: Schematic diagram of the advection-diffusion numerical model solved by *Benoit et al.* [2006]. The bold line represents the model boundaries. The gray area represents the benthic (sediment) oxygen sink. The strength of the sediment oxygen sink was calculated from a diagenetic model (see Fig. 4.5 for the value of the benthic sink and *Benoit et al.* [2006] for a detailed model description).



Figure 4.3: Density, temperature and oxygen concentration measured along the Laurentian Channel (from Station 23 to Cabot Strait) in July 2010.



Figure 4.4: Schematic diagram of the advection-diffusion numerical model used in this study. The bold line represents the model boundaries. The gray area represents the benthic (sediment) oxygen sink. The variables h(x) and H(x) are defined in Table 4.3.



Figure 4.5: Dissolved oxygen flux at the sediment-water interface measured from sediment core incubations (black symbols); derived from the dissolved oxygen isotopic composition (green lines) and calculated from the carbon rain rate with a simplified diagenetic model (blue dots).



Figure 4.6: Dissolved oxygen climatology from 2002 to 2010 in the bottom water of the Laurentian Channel: (a) mean oxygen concentration in mmol $O_2 \text{ m}^{-3}$, (b) standard deviation in mmol $O_2 \text{ m}^{-3}$ and (c) number of measurements. The dashed lines follow the 150 m depth. Dissolved oxygen concentrations were determined by Winkler titrations [*Grasshoff et al.*, 1999].



Figure 4.7: Taylor's diagram for dissolved oxygen concentrations, showing the tuning of physical parameters. Filled symbols are for $F_0 = 0.11$ Sv and open symbols for $F_0 = 0.22$ Sv. Pelagic and benthic respiration rates are fixed to the mean values given by *Lehmann et al.* [2009]: $R_{wc} = -19.6$ mmol $O_2 \text{ m}^{-3} \text{ yr}^{-1}$ and $R_{sed} = -3540$ mmol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$. The radial distance from the origin is proportional to the standard deviation (STD) of a pattern (normalized by the standard deviation of the climatology). The bold dotted line represents a STD = 1. The green lines are the distances from the reference point and indicate the centered pattern RMS difference E' (i.e. the RMS error once overall bias has been removed; see the mathematical expression in section 4.3.4 for more details). The correlation between the climatology data and the model output is given by the azimuthal position of the model output. The model output giving the best fit to the data is labeled model-ref. For this simulation, the bias (M_{model} - M_{data}) is 2.07 mmol $O_2 \text{ m}^{-3}$.



Figure 4.8: Dissolved oxygen distribution pattern for the reference simulation with the following parameters: $F_{\theta} = 0.11$ Sv, W = 97.5 km and $K_z = 1$ cm² s⁻¹, $R_{wc} = -19.6$ mmol O₂ m⁻³ yr⁻¹ and $R_{sed} = -3540$ mmol O₂ m⁻² yr⁻¹ (see Tables 4.2 and 4.3 for symbol definitions). Top: colored circles for the climatology are overlaid on the simulated dissolved oxygen field using the same color bar. Bottom: comparison of simulated dissolved oxygen vertical profiles with data at Stations 23, 19 and 17.



Figure 4.9: Taylor's diagrams for dissolved oxygen concentrations showing results of the sensitivity study to (a) physical parameters and (b) benthic and pelagic respiration rates compared to the reference simulation. The percentages represent deviations from the reference (see Table 4.5 and 4.6 for corresponding values) within the possible ranges of parameters. The bias ($M_{model} - M_{data}$) is expressed in mmol O₂ m⁻³. (a) The flow variations are represented in green; the vertical diffusion coefficient variations are represented in black; the channel width variations, impacting the horizontal advection velocity (see text for more details), are represented in yellow. Benthic and pelagic respiration rates are fixed to their reference values at - 3540 mmol O₂ m⁻² yr⁻¹ and - 19.6 mmol O₂ m⁻³ yr⁻¹, respectively. (b) The pair of numbers in brackets represents variations of the pelagic and benthic respiration rates from the reference values. Physical parameters are fixed to their reference values. Physical parameters are fixed to their reference values. $F_0 = 0.11$ Sv, W = 97.5 km and $K_z = 1$ cm² s⁻¹. Filled green symbols

represent variations of the R_{sed} : R_{wc} ratio from the reference value of 3:2 [*Lehmann et al.*, 2009]; open green symbols represent the maximal and minimal variations of the total respiration at a fixed R_{sed} : R_{wc} ratio of 3:2 [*Lehmann et al.*, 2009]; open black symbols encompass the range of measured values by incubations for benthic respiration and ETS for pelagic respiration; filled yellow symbols represent the sensitivity for an along channel variable benthic respiration ($F_{O2} = f(x)$ defined from the diagenetic model of *Benoit et al.* [2006], the function is plotted on Fig. 4.5); and filled black symbols represent simulations with either pelagic or benthic respiration alone.



Figure 4.10: Dissolved oxygen budget in the bottom water of the Laurentian Channel, separated along the dissolved oxygen minimum at 275 m depth. The dissolved oxygen budget is calculated using the reference simulation parameters. Integrated fluxes are in 10^{10} mol O₂ yr⁻¹. The vertical diffusion at the sediment-water interface was calculated from R_{sed} and integrated over the whole sediment surface area. The error is $\pm 1 \times 10^{10}$ mol O₂ yr⁻¹.

4.10 Appendix

4.10.1 Verification of boundary conditions for advective velocities in the case of a variable bathymetry

The Matlab[®] PDE Toolbox can solve the following general elliptic equation:

(A1) $-\nabla \cdot (c\nabla O) + aO = f$

where O is the variable, in this case the dissolved oxygen concentration, and c, a, and f are the coefficients (or functions) that have to be determined and must satisfy the boundary conditions. The coefficients (or functions) c, a, and f cannot be directly identified to the coefficient in the general advection-diffusion equation (see Eq. A2). Thus, we manipulated the general advection-diffusion equation in order to define c, a, and f so that it can be solved with Matlab[®]. The following derivations lead to the proper formulation and ensure that the boundary conditions are satisfied.

The stationary case of the advection-diffusion equation for variable advection velocities (u and w) is written:

(A2)

$$K_{x} \quad \frac{\partial^{2}O}{\partial x^{2}} + K_{z} \quad \frac{\partial^{2}O}{\partial z^{2}} + u \frac{\partial O}{\partial x} + w \frac{\partial O}{\partial z} + O \frac{\partial u}{\partial x} + O \frac{\partial w}{\partial z} = 0$$

where K_x et K_z are, respectively, the horizontal and vertical diffusivity coefficients, and u and w are, respectively, the horizontal and vertical advection velocities.

The horizontal (u) and vertical (w) advection velocities must satisfy the continuity equation

(A3)
$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$

By integrating Eq. (A3) into Eq. (A2), the last two terms of Eq. (A2) cancel each other out. In addition, we used the continuity equation to introduce the following stream function φ :

(A4)
$$u = -\frac{\partial \varphi}{\partial z} et w = \frac{\partial \varphi}{\partial x}$$

Equation (A2) thus simplifies to:

(A5)
$$K_x \quad \frac{\partial^2 O}{\partial x^2} + K_z \quad \frac{\partial^2 O}{\partial z^2} + u \frac{\partial O}{\partial x} + w \frac{\partial O}{\partial z} = 0$$

We assume a constant flow at Cabot Strait. The advection velocity u(x) can thus be defined as a function of the flow F_0 , the channel width, assumed constant from Cabot Strait to Tadoussac (Fig. 4.1), and the height of the water column, from the sediment-water interface to the permanent pychocline at 150 m depth: $F_0 = H(x) \cdot$ u(x), where H(x) is the deep water thickness, i.e. [400 – h(x)] (see Fig. 4.11).

(A6)
$$u = \frac{F_0}{H(x)} = \frac{F_0}{H_1 - h(x)} = \frac{F_0}{400 - 150 - ax}$$
, for a linear slope.

For clarity, validations of the boundary conditions are illustrated for a bathymetry with a negative linear slope, but they were also validated for a bathymetry with a positive linear slope and for the general case, independent of the formulation of H(x), as the real slope of the seafloor along Laurentian Channel is not linear.

The boundary conditions are as follow:

At z = 400 m:

 $(A7) \quad w = 0$

This hypothesis allows us consider the bottom water independently from the surface layer and not represent the surface layer in our model.

At the sediment-water interface:

(A8)
$$w = u \bullet \frac{\partial h}{\partial x} = \frac{F_0}{H} \bullet \frac{\partial h}{\partial x}$$

Given this formulation, the perpendicular components of u and w cancel each other out. In the case of a linear slope, there are four combinations of sign for the slope a and the horizontal velocity u: a > 0, a < 0, u > 0, and u < 0. Each case was verified and satisfies the boundary conditions.



Figure 4.11: Schematic representation of the boundary conditions at the pycnocline and at the sediment-water interface for a bathymetry with a linear slope. The nomenclature used is the same as defined in Table 4.1 (see paper), H stands for the water column height between the pycnocline and the sediment-water interface, and h stands for the sediment height from the reference (i.e. z=0). Note that along the abscise: H(x) + h(x) = 400 for any x.

The Matlab[®] PDE Toolbox handles equations of the form:

(A9)
$$\nabla \cdot (c\nabla O) = \begin{pmatrix} \frac{\partial}{\partial x}, \frac{\partial}{\partial z} \end{pmatrix} \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{pmatrix} \frac{\partial O}{\partial x} \\ \frac{\partial O}{\partial z} \end{pmatrix}$$

Once developed, they convert to the form:

$$A\frac{\partial^2 O}{\partial x^2} + D\frac{\partial^2 O}{\partial z^2} + (B+C)\frac{\partial^2 O}{\partial x \partial z} + \left(\frac{\partial A}{\partial x} + \frac{\partial C}{\partial z}\right)\frac{\partial O}{\partial x} + \left(\frac{\partial B}{\partial x} + \frac{\partial D}{\partial z}\right)\frac{\partial O}{\partial z} = 0$$

The coefficients A, B, C and D of Eq. (A10) are determined by comparison with Eq. (A5) and we obtain:

- B + C = 0
- $A = K_x$ and $D = K_z$
- $\frac{\partial A}{\partial x} = 0$ and $\frac{\partial D}{\partial z} = 0$ since the diffusivity coefficients are constant.

•
$$\frac{\partial C}{\partial z} = u$$
 and $\frac{\partial B}{\partial x} = w$.

By comparing with Eq. (A4), we obtain: $B = -C = \varphi$, but φ must be shown to satisfy the boundary conditions.

We assume that the vertical velocity is null at z = 400 (i.e. at 150 m from the ocean-atmosphere interface). The components of u and w perpendicular to the bottom must cancel each other out at the sediment-water interface, i.e. at z = h(x).

(A11)
$$u = -\frac{\partial \varphi}{\partial z} = \frac{F_0}{H(x)}$$
 integrating, we find that:

(A12)
$$\varphi = -\int \frac{F_0}{H(x)} dz = \frac{-F_0}{H(x)} (z - z_0) + f(x)$$

At z = 400 m:

w = 0, which implies that f(x) = 0 and $z_0 = 400$.

At the sediment-water interface:

We must have $w = u \cdot \frac{\partial h}{\partial x}$

The deep-water thickness H can be written as: H(x) = 400 - h(x).

The vertical velocity is:
$$w = \frac{\partial \varphi}{\partial x} = -(z - 400) \frac{\partial}{\partial x} \left[\frac{F_0}{H(x)}\right]$$

Along the sediment-water interface, i.e. at z = h(x), the vertical velocity becomes:

$$w = -(z - 400) \frac{\partial}{\partial x} \left[\frac{F_0}{H(x)}\right] = -(-)(h - 400) \frac{F_0}{H^2} \frac{\partial H}{\partial x}$$

But
$$\frac{\partial H}{\partial x} = \frac{\partial}{\partial x} [400 - h(x)] = -\frac{\partial h}{\partial x}$$
 and $-(h - 400) = H$

Consequently, along the bottom boundary condition, w can be expressed as:

$$w = \frac{F_0}{H} \frac{\partial h}{\partial x} = u \frac{\partial h}{\partial x} \qquad \text{CQFD}$$

4.10.2 Recommendations for future work

Although our simplified model closely reproduces the bottom water dissolved oxygen distribution in the Laurentian Channel, because of software limitations, the development of a more sophisticated model that would include more flexible boundary conditions (e.g., variable channel width) will have to be carried out outside the Matlab[®] environment.

Chapter 5

Conclusions

5.1 Summary and suggestions for future work

A set of physical and biogeochemical conditions have lead to the development of persistent and severe hypoxic conditions in the Lower St. Lawrence Estuary. Lack of ventilation due to stable and permanent water column stratification and a constant supply of metabolizable organic matter throughout the Laurentian Channel (Bugden, 1991) promote oxygen depletion in the LSLE. In addition, spatial changes in the flow velocity, induced by the variable bathymetry between Cabot Strait and the head of the Laurentian Channel, generate the presence of a mid-water column oxygen minimum (Chapter 4). Nevertheless, this oxygen minimum would not have reached the severe hypoxic threshold in the Lower Estuary if the properties (temperature, dissolved oxygen level) of the water that enter the Channel at depth had not changed over time.

According to Gilbert et al. (2005), since the early 1930's, the proportion of warm, oxygen-depleted North Atlantic Central Water (NACW), relative to the cold oxygen-saturated Labrador Current Water (LCW), has increased in the mixture entering the Laurentian Channel. Consequently, the bottom water currently entering the Channel through Cabot Strait is warmer (~1.7°C) and poorer in dissolved oxygen (~50 μ M) than 75 years ago. In response to warming, it was proposed that an increase in the metabolic respiration rate in the bottom water and sediment further contributed to the observed oxygen depletion

(Genovesi et al., 2011). It has also been proposed that an increase of the organic carbon flux to the seafloor, resulting from eutrophication caused by increased nutrient discharge from the St. Lawrence River (Gilbert et al., 2007), could account for the development of severe hypoxic conditions in the LSLE (Thibodeau et al., 2006). Using a 2-D diffusion-advection model (Chapter 4), we showed that the oceanic circulation in the northwestern Atlantic (i.e. the proportion of NACW vs. LCW that make up the water flowing along the bottom of the Laurentian Channel) controls the concentration of dissolved oxygen and the ultimate development of bottom-water hypoxia in the LSLE (Chapter 4). In other words, the progressive development of persistent, severe hypoxia in the bottom

words, the progressive development of persistent, severe hypoxia in the bottom water of the LSLE can be solely accounted for by changes in the northwestern North Atlantic Ocean circulation pattern rather than by local anthropogenic forcings (e.g. nutrient discharge and eutrophication) (Chapter 4). This would also explain why bottom water at the head of the Anticosti and Esquiman Channels, far from anthropogenic influences, are also hypoxic. Whether modifications of the oceanic circulation pattern in the northwestern Atlantic Ocean result from natural or anthropogenic forcings (i.e. global warming and a northern drift of NACW or the Gulf Stream) remains to be determined. Documenting past hypoxic events in the LSLE and Gulf of St. Lawrence, based on sedimentary proxy studies, might resolve this issue and, ultimately, allow us to forecast the evolution of hypoxia in the bottom water.

Future modeling efforts should be directed towards adding a third spatial dimension and time-dependency, but because of software limitations, the development of a 3-D numerical model will have to be carried out outside the Matlab[®] environment. The improved model should include the three-layer circulation in the Estuary and a realistic morphology of the Channel (variable width and the bathymetric sill at Tadoussac to generate the upwelling). Such improvements would more closely represent the physical processes in the Estuary, a critical step to properly simulate the biological processes (Keeling et al., 2010), such as local productivity. Thus, coupled to a sophisticated diagenetic model such as the one developed by Katsev et al. (2007) and to a planktonic ecosystem model

such as the NPZD (Nitrogen Phytoplankton Zooplankton Detritus) model, this improved model should be a good tool to predict the levels of oxygen in the bottom waters that will result from various scenarios of external forcing. For example, this model could evaluate the seasonal variations of the primary productivity and the impact of the latter on the oxygen levels; the impact of bottom-water hypoxia on the nutrient cycles and their feedback on the bottomwater hypoxia; the relative impacts of anthropogenic (i.e. river discharge) vs. natural (i.e. upwelling) forcings on the nutrient cycle; and other boundary conditions. In addition, our simple 2-D advection-diffusion model of the bottom water could be expanded to the other two channels (Anticosti and Esquiman), but more data (e.g. oxygen concentration, hydrographic measurements, organic carbon flux) would be required to better constrain the parameters and variables.

The relatively slow and progressive dissolved oxygen depletion (average rate of 1 μ mol O₂ L⁻¹ yr⁻¹ between the 1930s and 1980s; Gilbert et al., 2005) and concomitant acidification (Mucci et al., 2011) of the bottom waters may have allowed the benthic community to adapt to these changing conditions (Belley et al., 2010; Bourque and Archambault, submitted). Bourque and Archambault (submitted) recently documented that the benthic assemblage has been modified since the establishment of severe hypoxia in the 1980s in the LSLE, but the sediments remain bioturbated and bioirrigated albeit to shallower depths (Belley et al., 2010; Bourque and Archambault, submitted; Chapter 3). Consequently, the sediment surface layer has remained sufficiently oxygenated to ensure the partial or complete sequestration of manganese, iron and arsenic within the sediment (Chapter 2 and Chapter 3).

As the oxygen levels in the overlying water decreased, the relative contribution of alternate electron acceptors (Fe(III) and Mn(VI) minerals, pore-water sulfate) to the oxidation of organic matter likely increased (Katsev et al., 2007; Chapter 2) and sulfate reduction may have progressively replaced oxic respiration as the dominant, integrated respiratory pathway (Middelburg et al., 1996; Katsev et al., 2007). In the iron-rich sediments of the LSLE, increased

sulfate reduction appears to have promoted iron recycling (greater relative proportion of the total iron was found as reactive iron) which, in turn, limited the formation of pyrite. As arsenic is typically sequestered with pyrite upon burial in organic-rich coastal sediments (Belzile and Lebel, 1986), the limited formation of pyrite in the LSLE sediments increased the proportion of arsenic in the dissolved and solid reactive phases in the LSLE sediments, increasing its availability to benthic organisms (Chapter 2). Nevertheless, as mentioned above, the benthic flux of this potentially toxic element remained nearly invariant since the 1980's (Chapter 2). These observations raise new questions, for example: Could the fate of other trace elements (e.g. Se, Mo, Cu), whose diagenetic behavior is closely associated to that of iron and sulfur, also have changed in response to persistent hypoxia? Could arsenic compete with other solutes that adsorb on iron oxihydroxides and affect their fluxes across the sediment-water interface? What is the threshold overlying water oxygen concentration below which the adsorption efficiency of Mn(IV) and Fe(III) oxides will no longer be sufficient to kept metabolites such as phosphate and metals/metalloids such as As from being released to the overlying waters? Will the migration of the oxic-anoxic redox boundary closer to the sediment-water interface promote the diffusion and sequestration of other redox-sensitive elements such as Re, Mo, U and V into the sediment?

The resilience of a system is defined as its capacity to respond a disturbance without shifting into an alternate regime (Walker et al., 2006). Despite modifications to the benthic assemblage (Bourque and Archambault, submitted) and the chemistry of the sediments (Chapter 2), fluxes of measured solutes (oxygen, nitrate, manganese, iron and soluble reactive phosphate) at the sediment-water interface remained independent of the bottom-water oxygen concentration (Chapter 3). The critical oxygen level at which species diversity or functionality are affected to the point that bottom-water oxygen concentrations control benthic fluxes has not yet been reached (Chapter 3). We can thus consider that the St. Lawrence System has not yet shifted to an alternate regime and is still resilient. A shift to an alternate regime could be considered as a definition of the

ecosystem collapse. Katsev et al. (2007) estimated that the LSLE ecosystem would collapse when the dissolved oxygen concentration will reach the 20 μ mol O₂ L⁻¹ threshold. Future work should test how this oxygen threshold affects the benthic community and its impact on sediment chemistry.

Ocean warming and increased stratification of the upper ocean caused by global climate change will likely lead to the expansion in area and severity of hypoxic environment over the next century (Sarmiento et al., 1998; Matear et al., 2000; Plattner et al., 2001; Bopp et al., 2002; Matear and Hirst, 2003; Shaffer et al., 2009; Keeling et al., 2010; Zhang et al., 2010). As a matter of fact, Stramma et al. (2009) documented a vertical expansion of the oxygen minimum zones (OMZs) in the eastern tropical Atlantic and the equatorial Pacific over the past 50 years, concomitant with the global ocean warming (Levitus et al., 2000). If the bottom-water oxygen level in the LSLE continues to decrease to the point of ecosystem collapse, bottom-water oxygen concentrations might control benthic element fluxes. Iron and arsenic accumulated in the pore-water and reactive phase of the sediment could be released to the overlying water column altering bottomwater chemical composition and threatening the health of this ecosystem. Similarly, nutrients such as phosphate would also be released from the sediment to the bottom waters, which would enhance primary production when these are upwelled near Tadoussac and, in turn, increase the oxygen demand and consumption in the bottom water and exacerbate the hypoxic conditions. Ultimately, in an extreme scenario, the oxic-anoxic redox boundary would migrate into the water column and dissolved sulfide would accumulate in the overlying water. The upwelling of dissolved sulfide near Tadoussac would have severe repercussions on the marine mammal population and local tourism. In conclusion, the LSLE seems to be on borrowed time and its health depends on changes to come in the North Atlantic Ocean circulation.

5.2 References

- Belley R., P. Archambault, B. Sundby, F. Gilbert and J. M. Gagnon (2010) Environmental variables influencing macrobenthic diversity and bioturbation in the Estuary and Gulf of St. Lawrence, Canada, Cont. Shelf Res. 30, 1302– 1313.
- Belzile N. and J. Lebel (1986) Capture of arsenic by pyrite in near-shore marine sediments. Chem. Geol. 54, 279–281.
- Bopp L., C. LeQuéré, M. Heimann, A. C. Manning and P. Monfray (2002) Climate-induced oceanic oxygen fluxes: Implications for the contemporary carbon budget, Global Biogeochem. Cyc. 16, 10.10292001GB001445.
- Bourque M. and P. Archambault (submitted) Spatio-temporal patterns of infaunal community structure in the deep estuary and Gulf of St. Lawrence (Quebec, Canada) in relation to environmental conditions, Mar. Ecol.
- Bugden G. L. (1991) Changes in the temperature-salinity characteristics of the deeper waters of the Gulf of St. Lawrence over the past several decades, in The Gulf of St. Lawrence: Small sea or big estuary?, Can. Spec. Publ. Fish. Aquat. Sci. 113, edited by J.-C. Therriault, pp. 139–147.
- Genovesi L., A. de Vernal, B. Thibodeau, C. Hillaire-Marcel, A. Mucci and D. Gilbert (2011) Recent changes in bottom water oxygenation and temperature in the Gulf of St. Lawrence: Micropaleontological and geochemical evidence, Limnol. Oceanogr. 56(4), 1319–1329, doi:10.4319/lo.2011.56.4.1319.
- Gilbert D. (2004) Propagation of temperature signals along the north-west Atlantic continental shelf edge and into the Laurentian Channel, paper presented at the ICES Annual Science Conference, Vigo, Spain.
- Gilbert D., D. Chabot, P. Archambault, B. Rondeau and S. Hébert (2007) Appauvrissement en oxygène dans les eaux profondes du St-Laurent marin: Causes possibles et impacts écologiques, Nat. Can. 131, 67–75.
- Gilbert D., B. Sundby, C. Gobeil, A. Mucci and G. H. Tremblay (2005) A seventy-two-year record of diminishing deep-water oxygen in the St. Lawrence Estuary: The northwest Atlantic connection, Limnol. Oceanogr. 50, 1654– 1666, doi:10.4319/lo.2005.50.5.1654.
- Katsev S., G. Chaillou, B. Sundby and A. Mucci (2007) Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the Lower St. Lawrence Estuary, Limnol. Oceanogr. 52(6), 2555–2568.
- Keeling R. F., A. Körtzinger and N. Gruber (2010) Ocean desoxygenation in a warming world, Annu. Rev. Mar. Sci. 2, 199–229.
- Lehmann M. F., B. Barnett, Y. Gélinas, D. Gilbert, R. J. Maranger, A. Mucci, B. Sundby and B. Thibodeau (2009) Aerobic respiration and hypoxia in the

Lower St. Lawrence Estuary: Stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning, Limnol. Oceanogr. 54(6), 2157–2169.

- Levitus S., J. I. Antonov, T. P. Boyer and C. Stephens (2000) Warming of the world ocean, Science 287, 2225–2229.
- Matear R. J. and A. C. Hirst (2003) Long-term changes in dissolved oxygen concentrations in the ocean caused by protracted global warming, Glob. Biogeochem. Cycles 17(4), 1125, doi:10.1029/2002GB001997.
- Matear R. J., A. C. Hirst and B. I. McNeil (2000) Changes in dissolved oxygen in the Southern Ocean with climate change. Geochem. Geophys. Geosystems 1, 2000GC000086.
- Middelburg J. J., G. Klaver, J. Nieuwenhuize, A.Wielemaker, W. de Haas and J. F. W. A. Van der Nat (1996) Organic matter mineralization in intertidal sediments along an estuarine gradient, Mar. Ecol. Prog. Ser. 132, 157–168.
- Mucci A., M. Starr, D. Gilbert and B. Sundby (2011) Acidification of Lower St. Lawrence Estuary bottom waters. Atmosphere-Ocean 49, 206–213.
- Plattner G.-K., F. Joos, T. F. Stocker and O. Marchal (2001) Feedback mechanisms and sensitivities of ocean carbon uptake under global warming, Tellus 53B, 564–592.
- Sarmiento J. L., T. M. C. Hughes, R. J. Stouffer and S. Manabe (1998) Simulated response of the ocean carbon cycle to anthropogenic climate warming. Nature 393, 245–249.
- Shaffer G., S. M. Olsen and J. O. P. Pedersen (2009) Long-term ocean oxygen depletion in response to carbon dioxide emissions from fossil fuels, Nature Geoscience 420, 1–5.
- Stramma L., G. C. Johnson, J. Sprintall, V. Mohrholz (2008) Expanding Oxygen-Minimum Zones in the Tropical Oceans, Science 320, 655–658.
- Thibodeau B., A. de Vernal and A. Mucci (2006) Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleontological and geochemical evidence, Mar. Geol. 231, 37–50, doi:10.1016/j.margeo.2006.05.010.
- Walker B. H., J. M. Anderies, A. P. Kinzig and P. Ryan (2006) Exploring resilience in social-ecological systems through comparative studies and theory developments: Introduction to the special issue, Ecology and Society 11(1), <u>http://www.ecologyandsociety.org/vol11/iss1/art12/</u>.
- Zhang J., D. Gilbert, A. Gooday, L. Levin, W. Naqvi, J. Middelburg, M. Scranton, W. Ekau, A. Pena, B. Dewitte, T. Oguz, P. M. S. Monteiro, E. Urban, N. Rabalais, V. Ittekkot, W. M. Kemp, O. Ulloa, R. Elmgren, E. Escobar-Briones, and A. Van der Plas (2010) Natural and human-induced hypoxia and consequences for coastal areas: synthesis and future development, Biogeosciences 7, 1443–1467.