

Supplemental Material for “The coupled oxygen and carbon dynamics in the subsurface waters of the Gulf and Lower St. Lawrence Estuary and Implications for Artificial Oxygenation”

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S1 Extended Review of Previous Modeling Efforts

Savenkoff et al. (1996) assumed a homogenous, 150 m thick, deep layer with no significant vertical diffusion within the layer or across its upper boundary and applied the along-channel advection velocity of Bugden (1991; $u = 5.0 \times 10^{-3} \text{ m s}^{-1}$). They derived an oxygen utilization rate (OUR) estimate of $7 \times 10^{-2} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ (or $5.4 \times 10^{-2} \mu\text{mol C m}^{-2} \text{ s}^{-1}$) from the DO gradient ($\Delta\text{O}/\Delta\text{C}$ of 138/106) between two stations separated by ~570 km (Cabot Strait and Western GSL), attributing ~60% of the deep-layer dissolved oxygen (DO) depletion to the sediment oxygen demand (SOD) and the remainder to pelagic respiration in the bottom 150 m of the water column.

Benoit et al. (2006) employed a 2D coupled advection-diffusion-diagenetic model to constrain the oxygen budget in the deep layer of the Laurentian Channel (LC) along a 700 km horizontal transect. They applied the along-channel advection velocity proposed by Gilbert (2004; $u = 1.0 \times 10^{-2} \text{ m s}^{-1}$) along with the diffusion coefficients of Bugden (1991; $K_H = 8.2 \times 10^2 \text{ m}^2 \text{ s}^{-1}$, $K_Z = 8.2 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$) and assumed that pelagic respiration was negligible. They reported OUR estimates for the bottom 100 m of the water column for two scenarios with differing organic matter fluxes: $2.7 \times 10^{-2} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the Gulf of St. Lawrence (GSL) and Lower St. Lawrence Estuary (LSLE) (low-flux scenario), and $2.7 \times 10^{-2} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the GSL increasing to $>1.3 \times 10^{-1} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the LSLE (high-flux scenario).

Lehmann et al. (2009) measured the concentration and the stable oxygen isotope composition of DO in the water column of the LSLE and GSL and used a 1D diffusion-reaction model with an along-channel advection velocity of $1.0 \times 10^{-2} \text{ m s}^{-1}$ (Gilbert, 2004) to estimate the relative contribution of benthic and pelagic respiration on the OUR of the bottom 100 m of the LC. They estimated an average net community respiration rate of $1.74 \times 10^{-1} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ of which they attributed ~64% to SOD and ~36% to pelagic respiration.

Finally, Bourgault et al. (2012) revisited previous estimates (Benoit et al., 2006; Lehmann et al., 2009) using idealized, reverse 1D numerical simulations, historical DO observations and their mixing estimates based on flow turbulence measurements. Based on their model results, they concluded that pelagic, not benthic, respiration was the dominant oxygen sink in the bottom waters of the LSLE and GSL and this sink would have to be ~5x larger than the SOD, assuming a transit time between Cabot Strait and the head of the LSLE (~750 km) of 2.2 years (Gilbert, 2004; $u = 1.0 \times 10^{-2} \text{ m s}^{-1}$), or ~2x larger than the SOD for a transit time of 4.4 years (Bugden, 1991; $u = 5.0 \times 10^{-3} \text{ m s}^{-1}$). Bourgault et al. (2012) concluded that to maintain the observed conditions, K_Z would need to be $\ll 1.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ for $u = 1.0 \times 10^{-2} \text{ m s}^{-1}$ and $\ll 5.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ for $u = 5.0 \times 10^{-3} \text{ m s}^{-1}$. They estimated an average OUR of $1.59 \times 10^{-1} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$ for the bottom 100 m of the LC along a 750 km transect for an along-channel horizontal velocity of $1.0 \times 10^{-2} \text{ m s}^{-1}$. The authors noted that using the advection velocity of Bugden (1991; $5.0 \times 10^{-3} \text{ m s}^{-1}$), this rate would be $7.9 \times 10^{-2} \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$. These OUR estimates were later reproduced by Jutras et al. (2020). Hence, previous OUR estimates (converted to $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$) vary widely due to inconsistencies in the dispersion parameters employed and are summarized in Table 1 in the main manuscript.

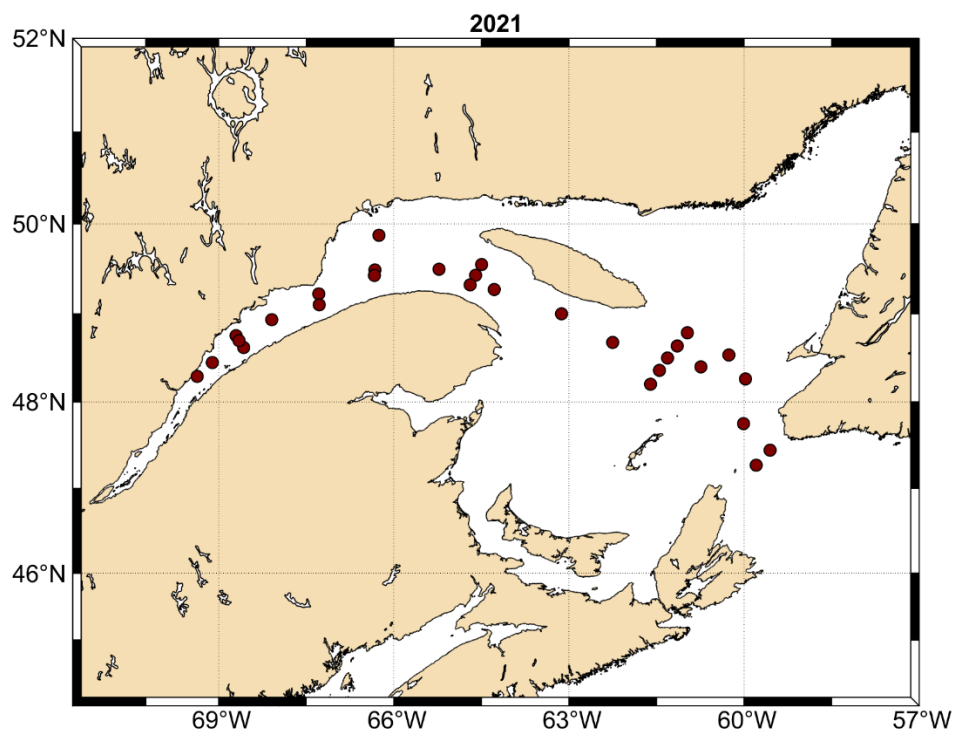
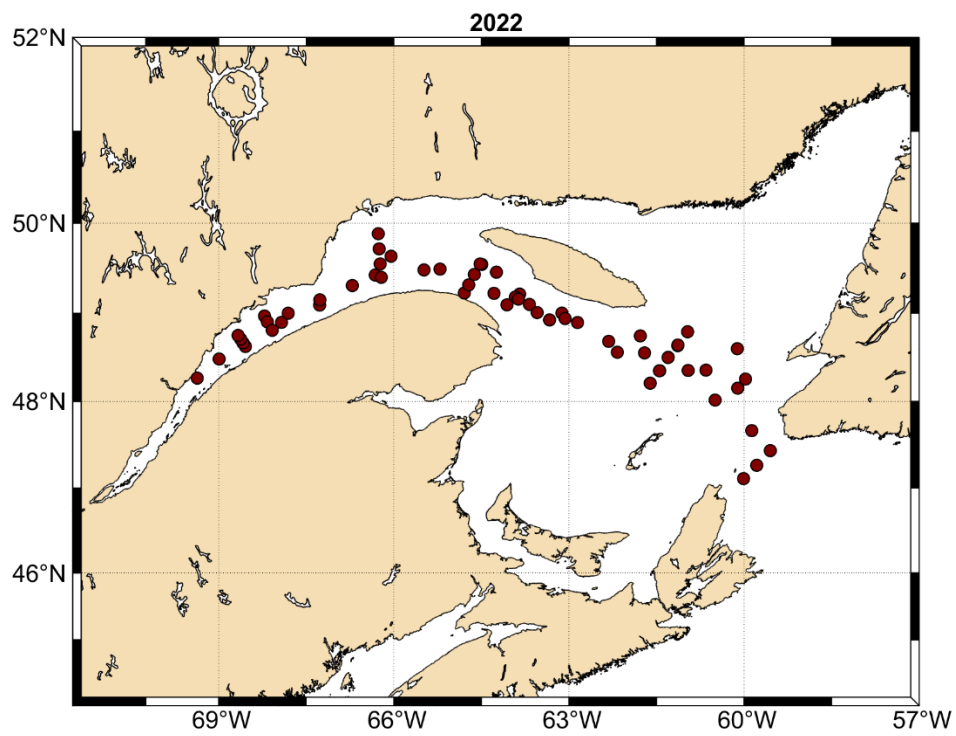


Figure S2.1: TReX program sampling stations along the Laurentian Channel for the year 2021 for which data were used in this study.



75 Figure S2.2: TReX program sampling stations along the Laurentian Channel for the year 2022 for which data were used in this study.

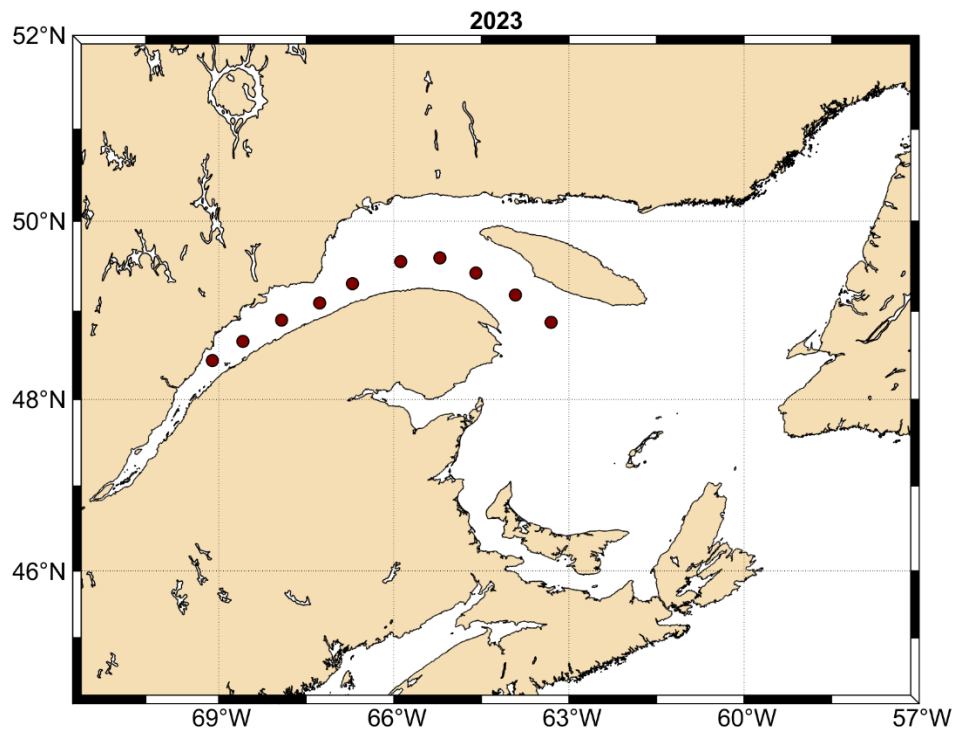


Figure S2.3: TReX program sampling stations along the Laurentian Channel for the year 2023 for which data were used in this study.

80 S3 Historical Data Set (2003-2020) Analytical Methods and Station Coverage

T and S_p were determined in situ using the rosette CTD probe. The conductivity probe was calibrated by the manufacturer over the winter prior to the cruises. In addition, the S_p of surface waters was determined by potentiometric argentometric titration at McGill University and calibration of the $AgNO_3$ titrant with IAPSO standard seawater. The reproducibility of these measurements is typically better than $\pm 0.5 \%$.

85 Water samples destined for A_T measurements were transferred to 250 mL glass bottles. They were poisoned with a few crystals of mercuric chloride ($HgCl_2$), and bottles sealed using a ground-glass stopper and Apiezon® Type-M high-vacuum grease. A_T was measured using an automated Radiometer (TitraLab865®) potentiometric titrator and a Red Rod® combination pH electrode (pHC2001) at McGill University. The diluted HCl titrant was calibrated prior, during and after each titration session using certified reference materials (CRMs) provided by Andrew Dickson
 90 (Scripps Institution of Oceanography). Raw titration data were processed with a proprietary algorithm designed for shallow endpoint detection. Based on replicate analyses of the same samples and CRMs, the reproducibility of the measurements was better than 0.1 %.

DO concentrations were determined on board by Winkler titration on distinct water samples recovered directly from the Niskin bottles, following the method described by (Grasshoff et al., 2009). The relative standard deviation, based

95 on replicate analyses of samples recovered from the same Niskin bottle, was 0.5 %. These measurements served to calibrate the SBE-43 oxygen probe mounted on the rosette sampler.

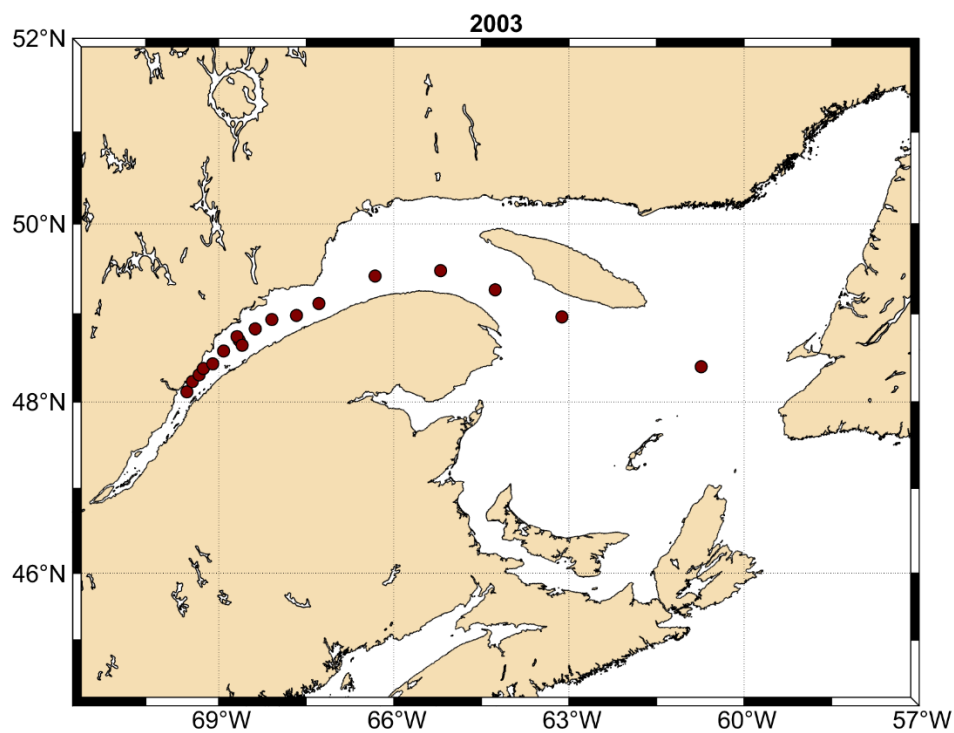
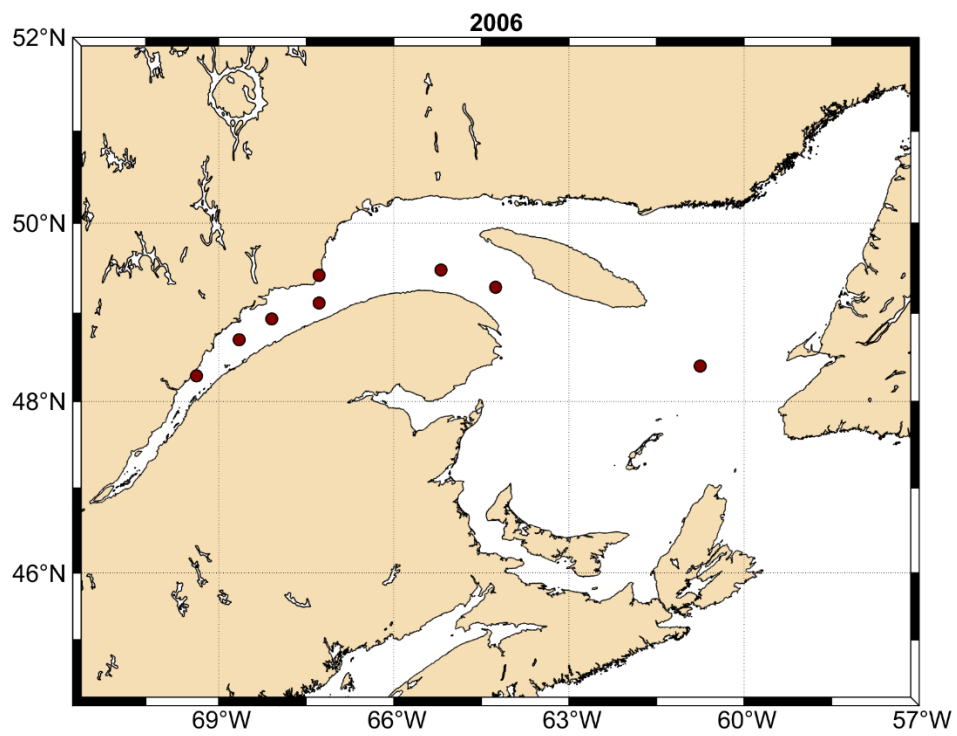


Figure S3.1: Sampling stations along the Laurentian Channel for the year 2003 for which data were used in this study.



100 **Figure S3.2: Sampling stations along the Laurentian Channel for the year 2006 for which data were used in this study.**

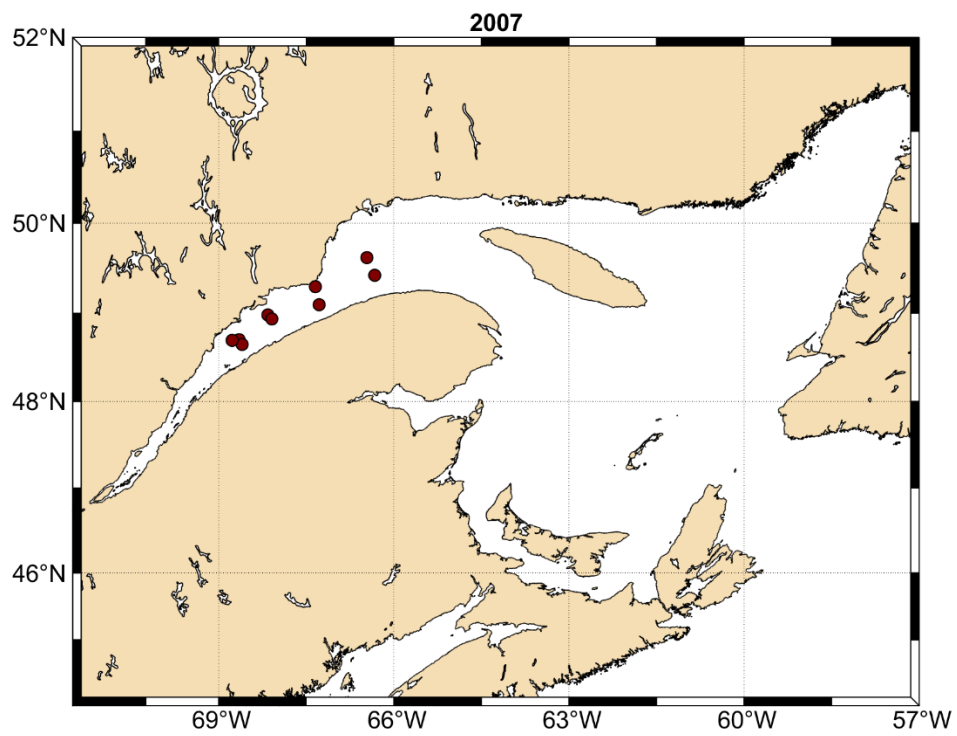


Figure S3.3: Sampling stations along the Laurentian Channel for the year 2007 for which data were used in this study.

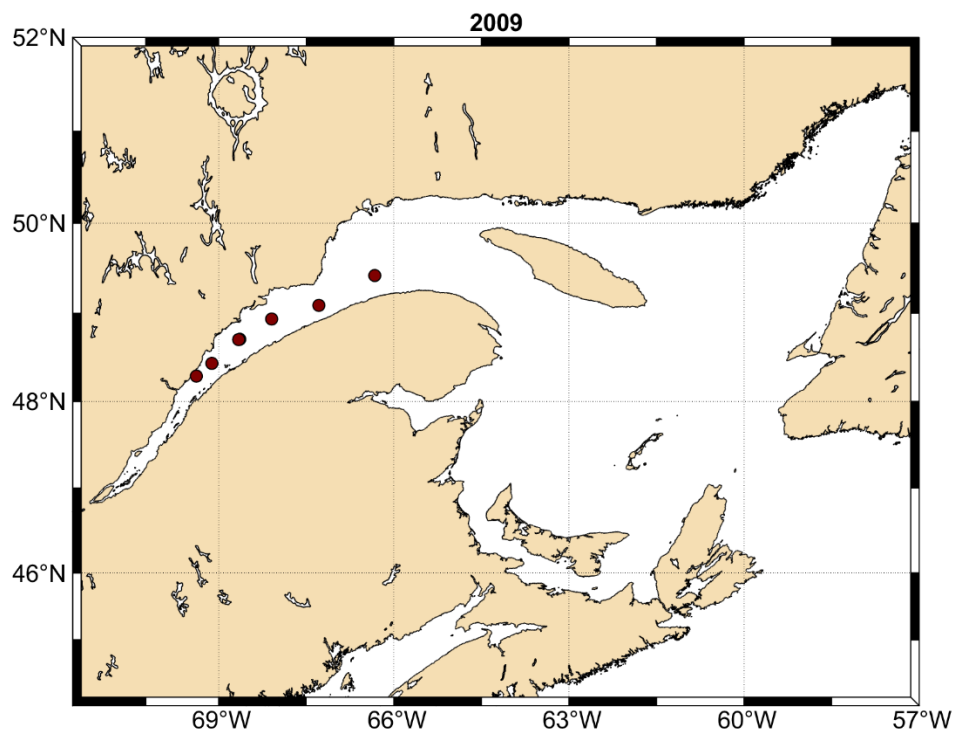
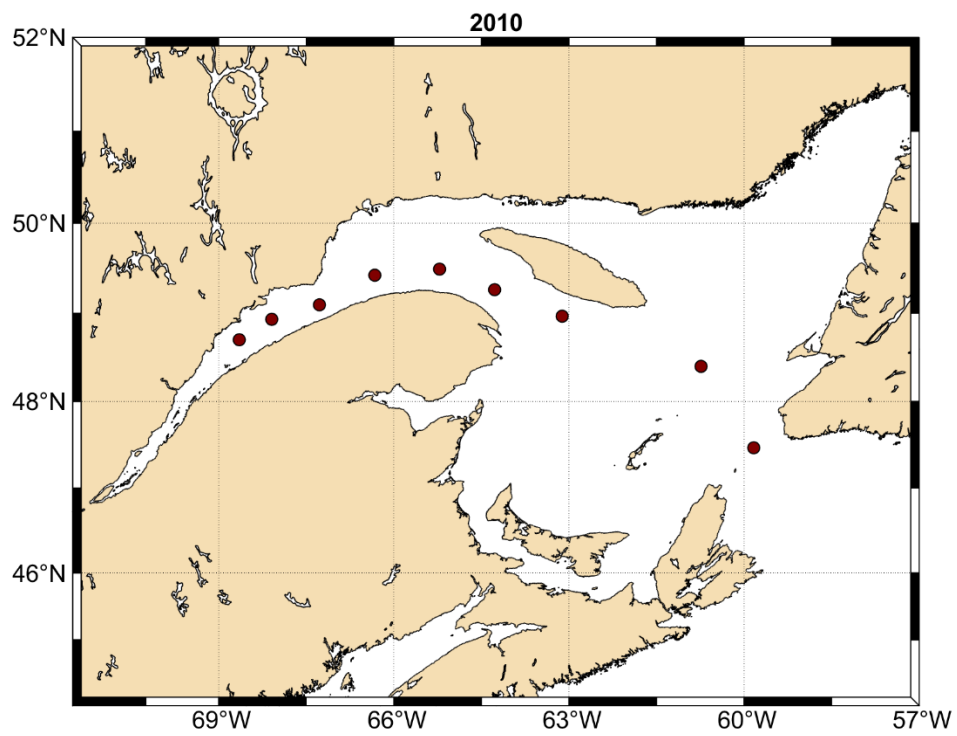


Figure S3.4: Sampling stations along the Laurentian Channel for the year 2009 for which data were used in this study.



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Figure S3.5: Sampling stations along the Laurentian Channel for the year 2010 for which data were used in this study.

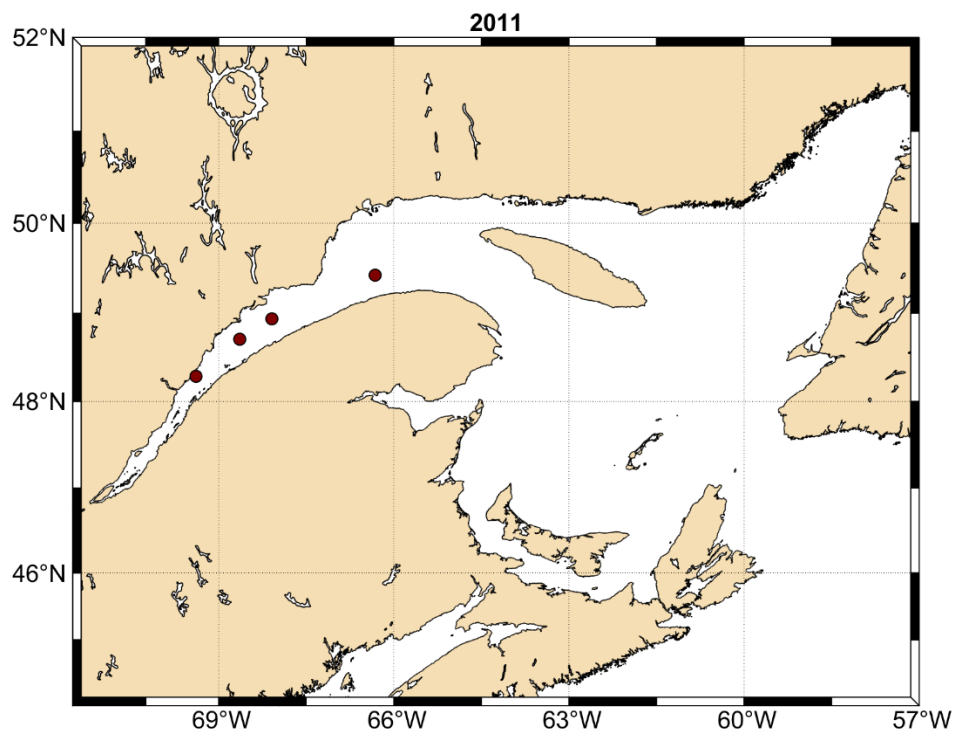
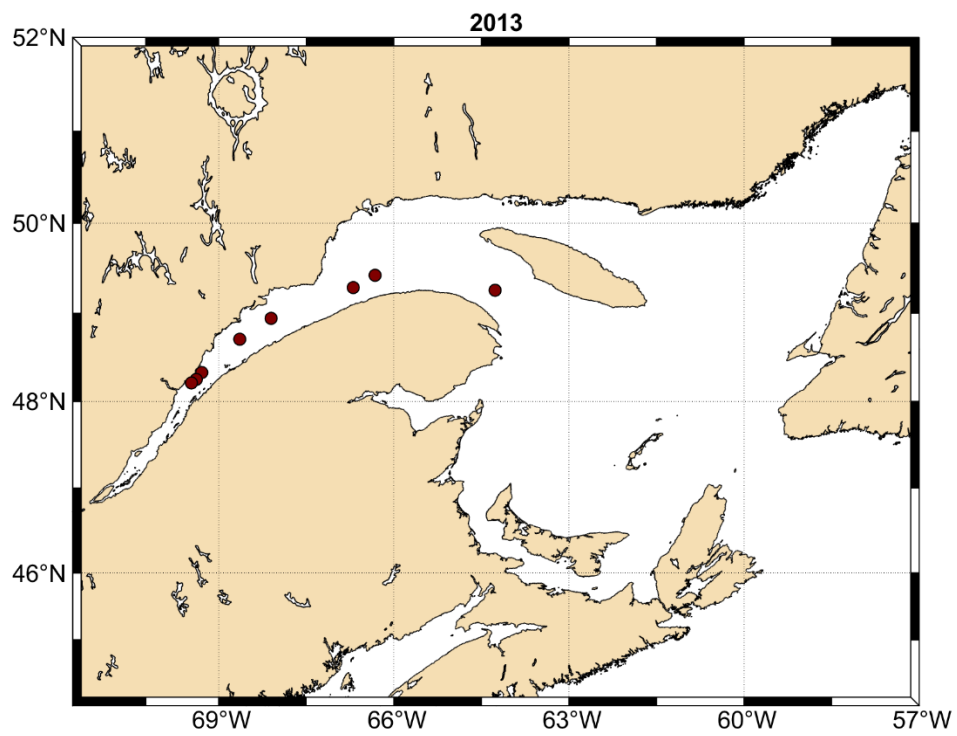


Figure S3.6: Sampling stations along the Laurentian Channel for the year 2011 for which data were used in this study.



110 Figure S3.7: Sampling stations along the Laurentian Channel for the year 2013 and which data were used in this study.

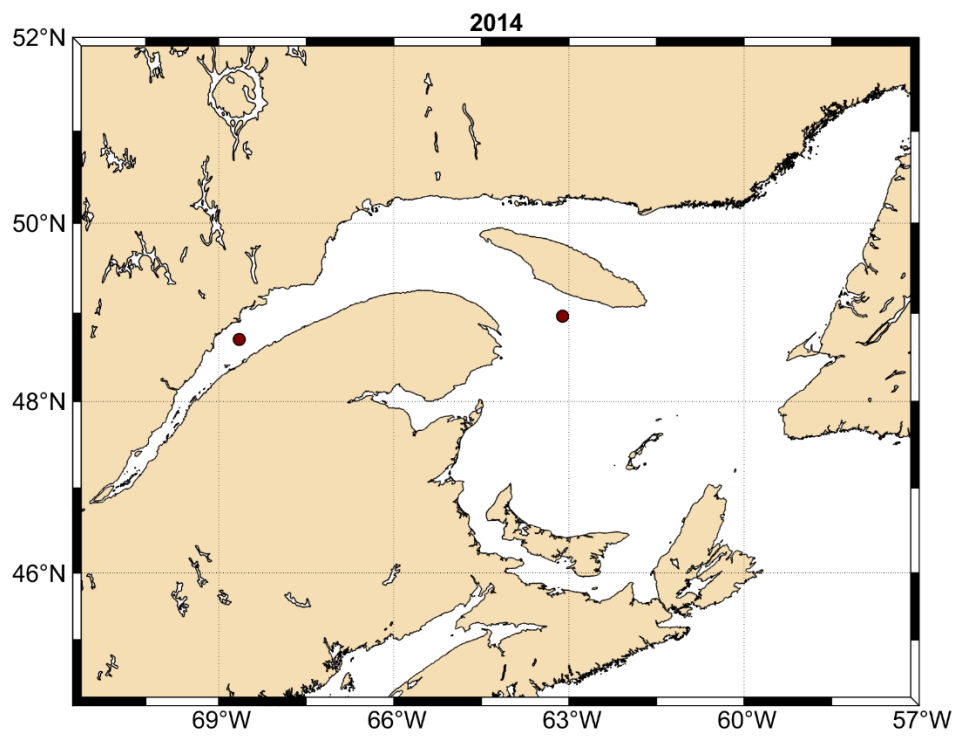


Figure S3.8: Sampling stations along the Laurentian Channel for the year 2014 for which data were used in this study.

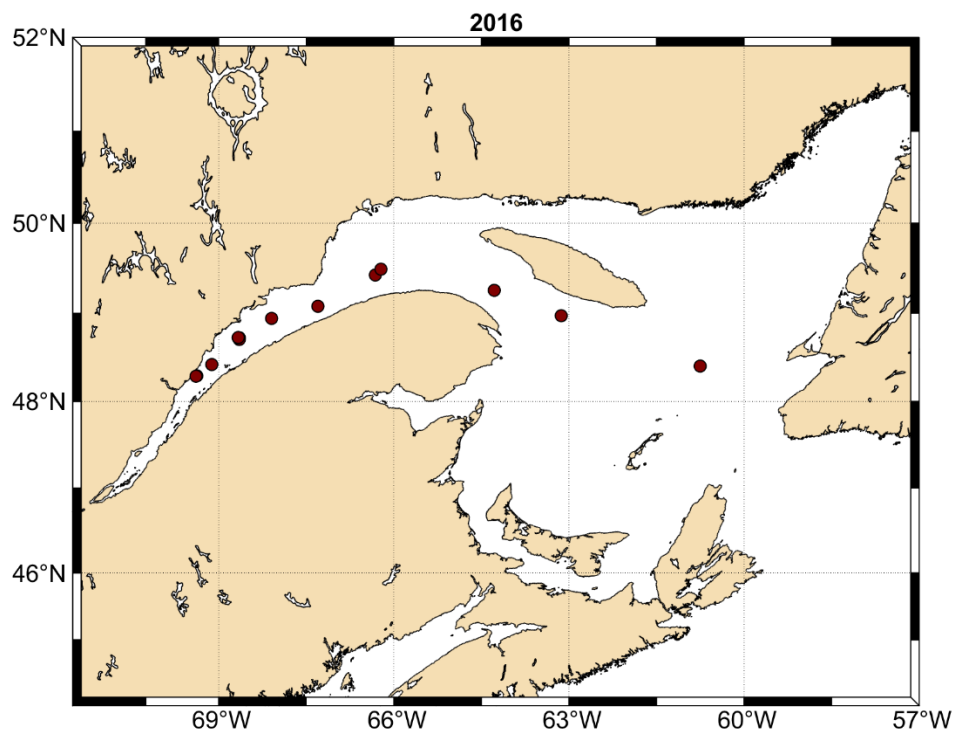
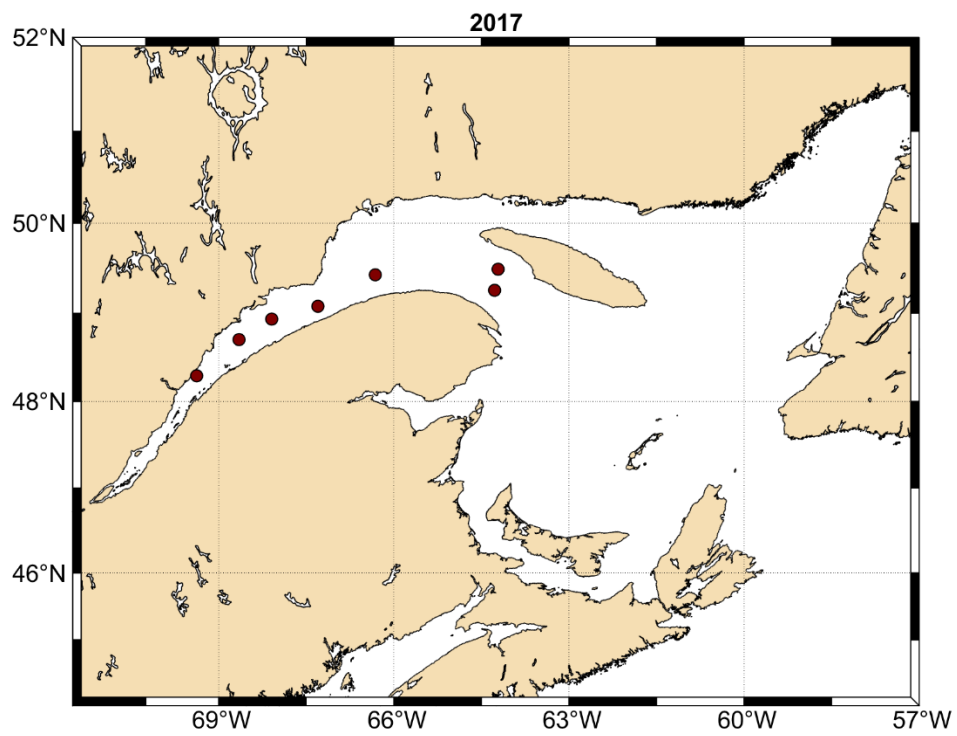


Figure S3.9: Sampling stations along the Laurentian Channel for the year 2016 for which data were used in this study.



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Figure S3.10: Sampling stations along the Laurentian Channel for the year 2017 for which data were used in this study.

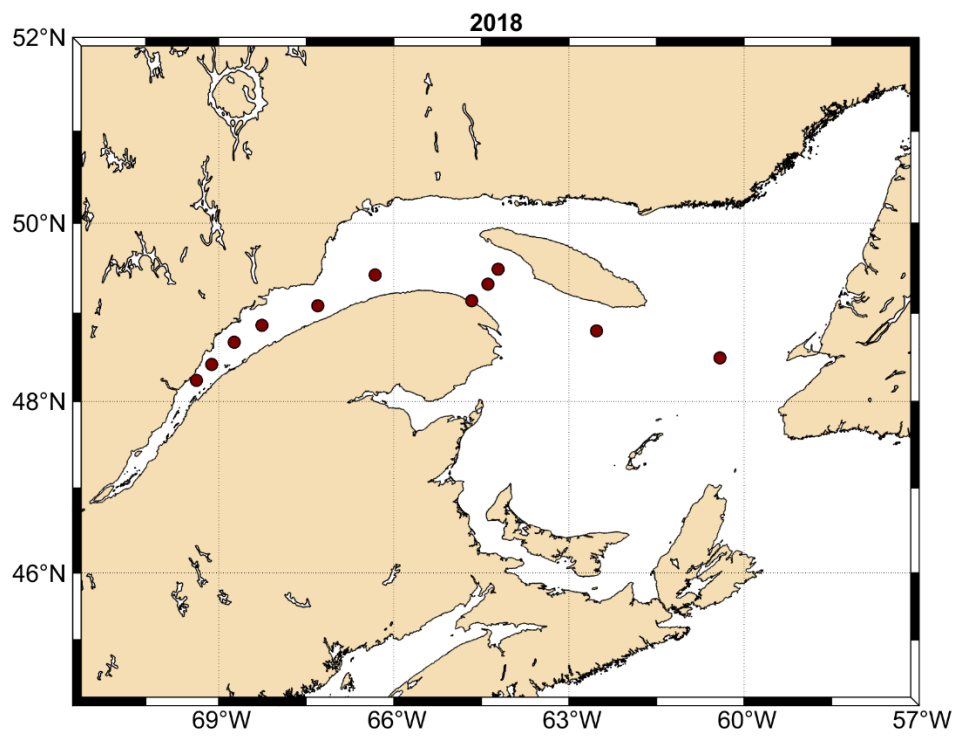
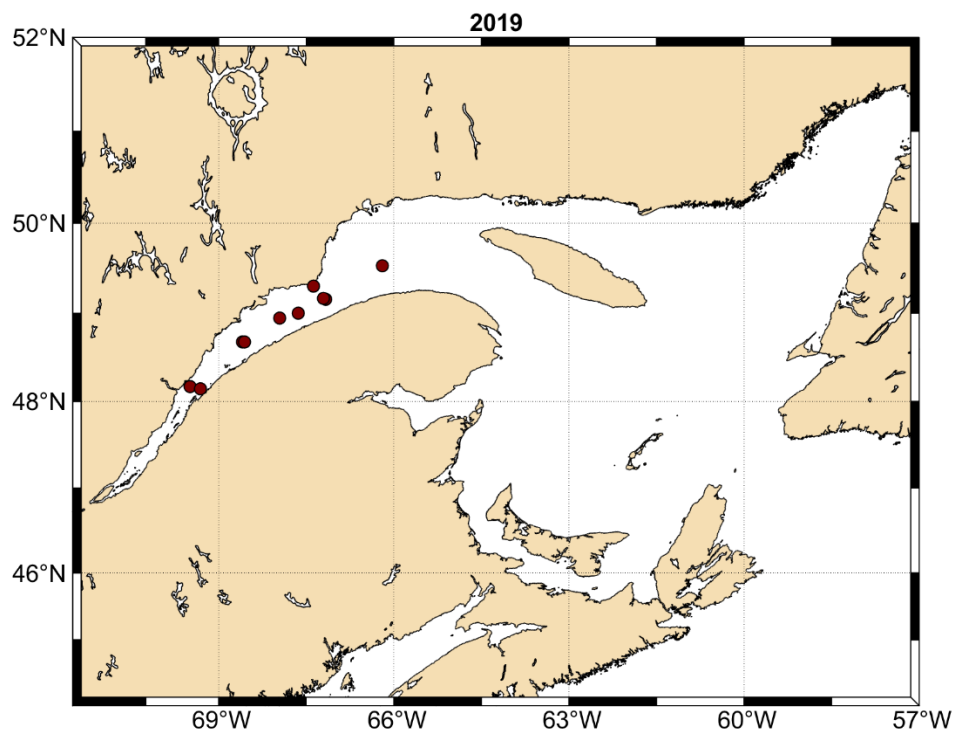


Figure S3.11: Sampling stations along the Laurentian Channel for the year 2018 for which data were used in this study.



120 Figure S3.12: Sampling stations along the Laurentian Channel for the year 2019 for which data were used in this study.

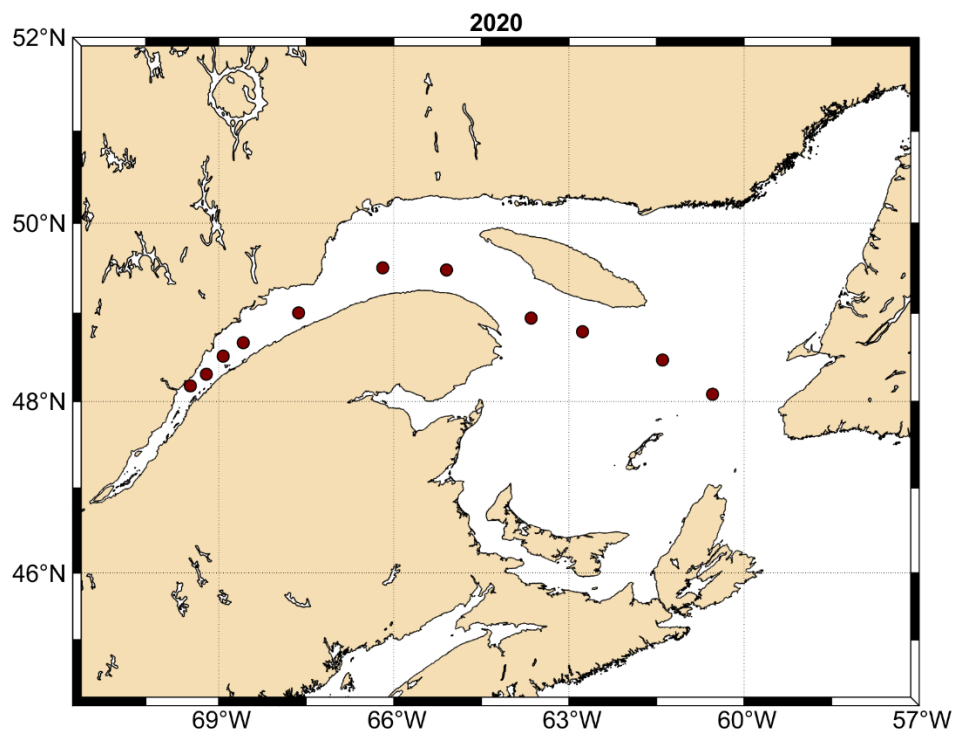
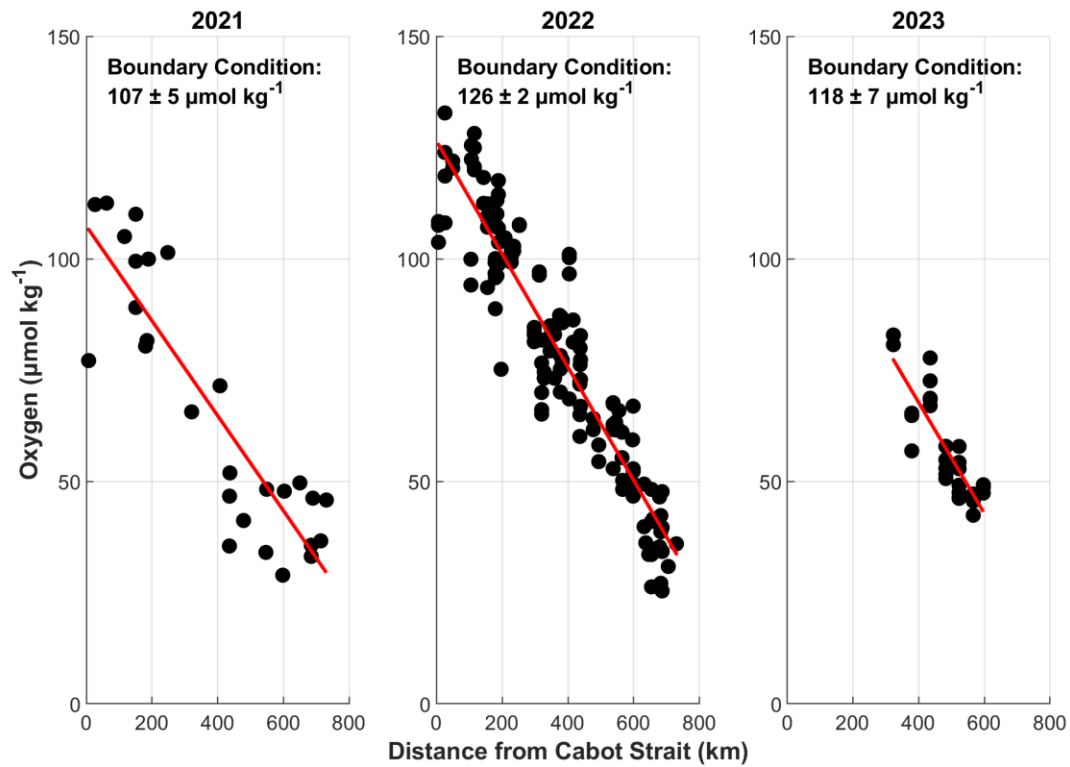


Figure S3.13: Sampling stations along the Laurentian Channel for the year 2020 for which data were used in this study.

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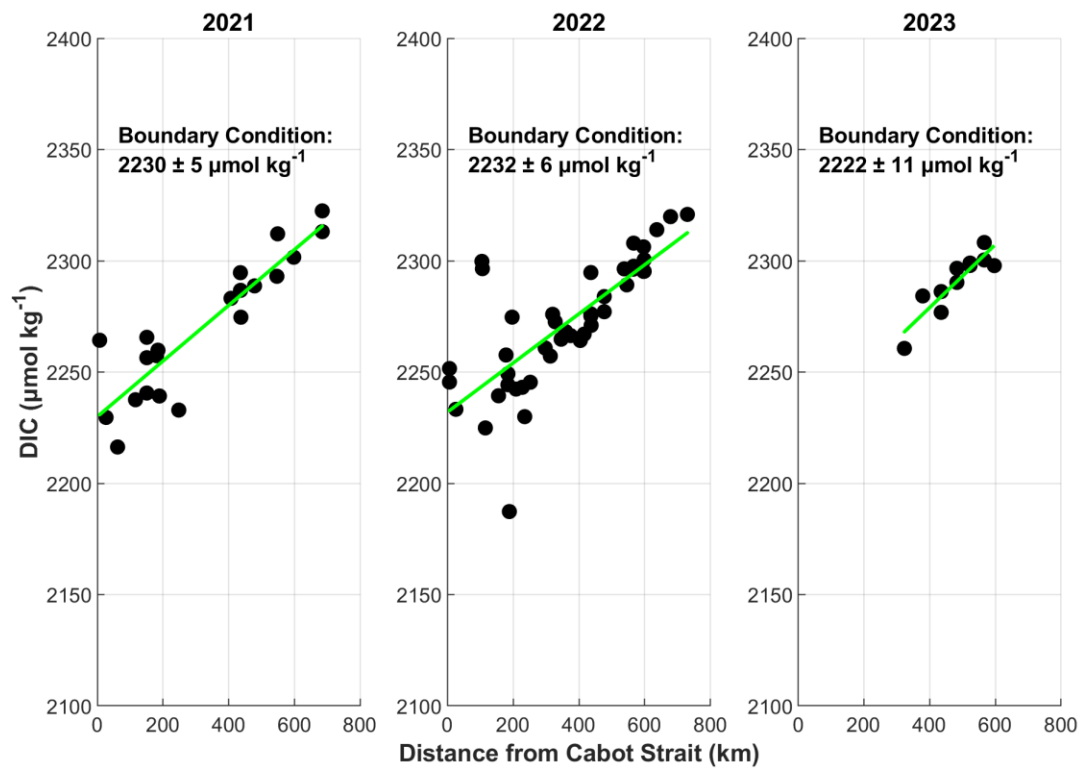
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S4 Inflow Boundary Condition Estimations (along-channel regressions)



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Figure S4.1: Along-channel regressions of dissolved oxygen concentrations between the 27.15 and 27.30 kg m^{-3} isopycnals over the distance from Cabot Strait. Boundary conditions for each year (2021-2023) are derived from the intercepts at Cabot Strait (0 km).



140 Figure S4.2: Along-channel regressions of DIC concentrations between the 27.15 and 27.30 kg m^{-3} isopycnals over the distance from Cabot Strait. Boundary conditions for each year (2021–2023) are derived from the intercepts at Cabot Strait (0 km).

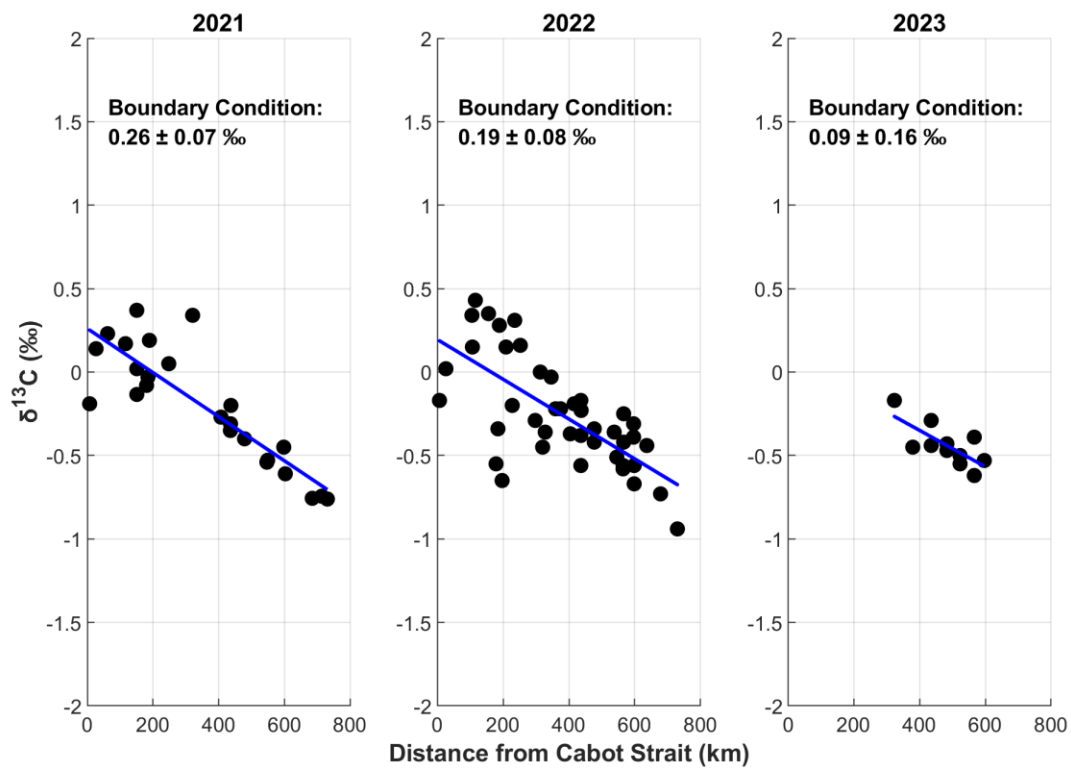


Figure S4.3: Along-channel regressions of $\delta^{13}\text{C}_{\text{DIC}}$ composition between the 27.15 and 27.30 kg m^{-3} isopycnals over the distance from Cabot Strait. Boundary conditions for each year (2021–2023) are derived from the intercepts at Cabot Strait (0 km).

S5 1D Model Boundary Conditions and LS Fit S Terms

Table S5.1: Boundary condition oxygen concentrations (\pm standard deviation, $\mu\text{mol kg}^{-1}$), fitted source terms (S, $\mu\text{mol kg}^{-1} \text{s}^{-1}$), and corresponding Oxygen Utilization Rates (OUR, $\mu\text{mol kg}^{-1} \text{yr}^{-1}$) derived from the advection-diffusion model least-squares fit to observed dissolved oxygen concentrations along the Laurentian Channel for the period 2003–2023. Blank entries indicate years where data were unavailable.

| Year | Boundary Condition | Source Term (S) | OUR |
|-------------|--------------------|------------------------|------------------------------------|
| 1999 | 162 \pm 19 | | |
| 2000 | 177 \pm 15 | | |
| 2001 | 145 \pm 17 | | |
| 2002 | 155 \pm 10 | | |
| 2003 | 150 \pm 10 | -7.71 $\times 10^{-7}$ | 24.32 |
| 2004 | 141 \pm 7 | | |
| 2005 | 127 \pm 44 | | |
| 2006 | 166 \pm 19 | -6.35 $\times 10^{-7}$ | 20.03 |
| 2007 | 146 \pm 16 | -5.23 $\times 10^{-7}$ | 16.48 |
| 2008 | 165 \pm 11 | | |
| 2009 | 156 \pm 9 | -7.18 $\times 10^{-7}$ | 22.64 |
| 2010 | 156 \pm 13 | -6.73 $\times 10^{-7}$ | 21.22 |
| 2011 | 156 \pm 6 | -7.22 $\times 10^{-7}$ | 22.76 |
| 2012 | 174 | | |
| 2013 | 151 \pm 9 | -7.03 $\times 10^{-7}$ | 22.16 |
| 2014 | 154 \pm 15 | -7.40 $\times 10^{-7}$ | 23.33 |
| 2015 | 142 \pm 1 | | |
| 2016 | 147 | -6.61 $\times 10^{-7}$ | 20.85 |
| 2017 | 143 \pm 9 | -7.87 $\times 10^{-7}$ | 24.83 |
| 2018 | 126 \pm 5 | -7.16 $\times 10^{-7}$ | 22.59 |
| 2019 | 125 \pm 6 | -6.74 $\times 10^{-7}$ | 21.25 |
| 2020 | 110 | -6.33 $\times 10^{-7}$ | 19.97 |
| 2021 | 107 \pm 5 | -6.83 $\times 10^{-7}$ | 21.54 |
| 2022 | 127 \pm 2 | -5.21 $\times 10^{-7}$ | 16.42 |
| 2023 | 118 \pm 7 | -5.66 $\times 10^{-7}$ | 17.84 |
| Mean | | | 21.14 \pm 2.43 |

Table S5.2: Boundary condition dissolved inorganic carbon (DIC) concentrations ($\mu\text{mol kg}^{-1}$), derived source terms (S, $\mu\text{mol kg}^{-1} \text{ s}^{-1}$), and corresponding annual DIC accumulation rates ($\mu\text{mol kg}^{-1} \text{ yr}^{-1}$) from advection-diffusion model least-squares fit for the years 2021–2023.

| Year | Boundary Condition | Source Term (S) | DIC Accumulation Rate |
|-------------|--------------------|-----------------------|------------------------------------|
| 2021 | 2230 ± 5 | 6.32×10^{-7} | 19.92 |
| 2022 | 2232 ± 6 | 4.68×10^{-7} | 14.75 |
| 2023 | 2222 ± 11 | 6.37×10^{-7} | 20.09 |
| Mean | | | 18.25 ± 2.48 |

Table S5.3. Boundary condition stable carbon isotope ($\delta^{13}\text{C}_{\text{DIC}}$) values (‰), derived source terms (S, $\text{‰ kg}^{-1} \text{ s}^{-1}$), and corresponding annual $\delta^{13}\text{C}_{\text{DIC}}$ dilution rates (‰ yr^{-1}) from advection-diffusion model least-squares fit for the years 2021–2023.

| Year | Boundary Condition | Source Term (S) | $\delta^{13}\text{C}_{\text{DIC}}$ Dilution Rate |
|-------------|--------------------|------------------------|--|
| 2021 | 0.26 ± 0.07 | -6.67×10^{-9} | 0.21 |
| 2022 | 0.19 ± 0.08 | -5.47×10^{-9} | 0.17 |
| 2023 | 0.09 ± 0.16 | -5.54×10^{-9} | 0.17 |
| Mean | | | 0.19 ± 0.02 |

S6 – Temperature Analysis: Q₁₀ and Linear Regression

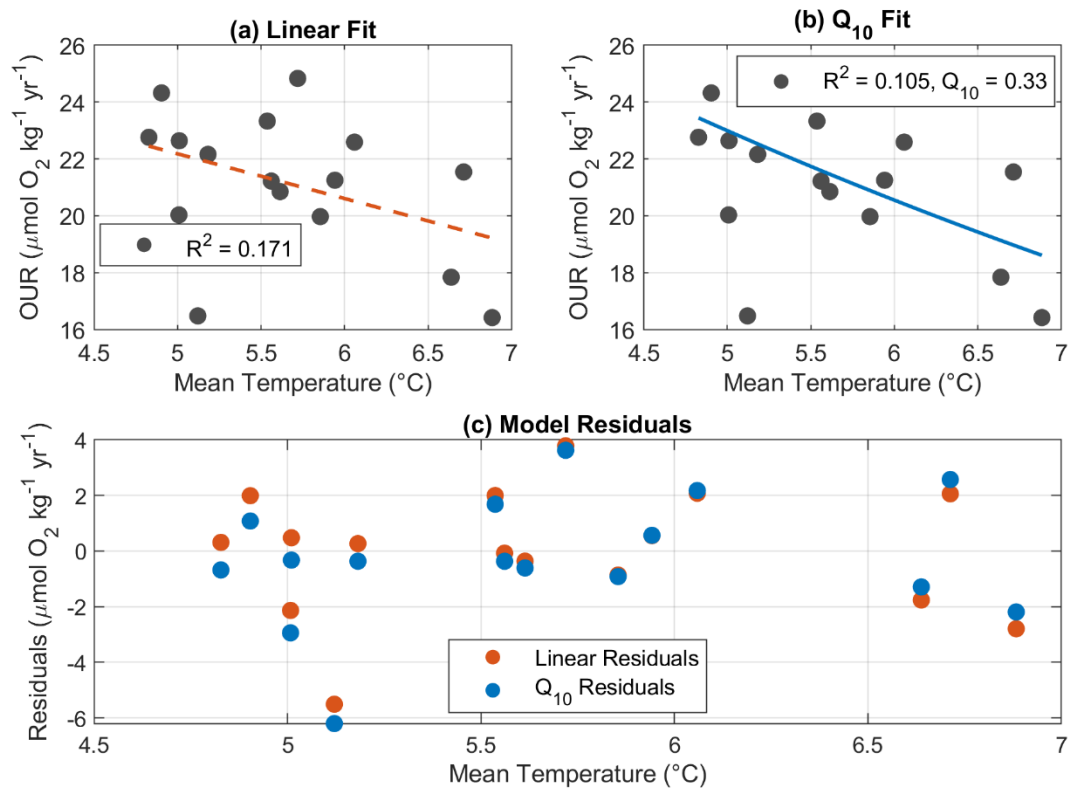


Figure S6.1: Comparison of modeled Oxygen Utilization Rate (OUR) as a function of mean temperature. (a) Linear least-squares regression fit with an R^2 value of 0.171, indicating a weak negative correlation between OUR and mean temperature. (b) Q_{10} model fit with an R^2 value of 0.105 and a Q_{10} value of 0.33, suggesting a similarly weak temperature dependence. (c) Model residuals for both the linear (orange) and Q_{10} (blue) fits, highlighting the deviations between the observed and predicted OUR values. The low R^2 values suggest limited influence of temperature on interannual OUR variability.

S7 A_T/S_P Linear Regression for 2021-2023 TReX Data

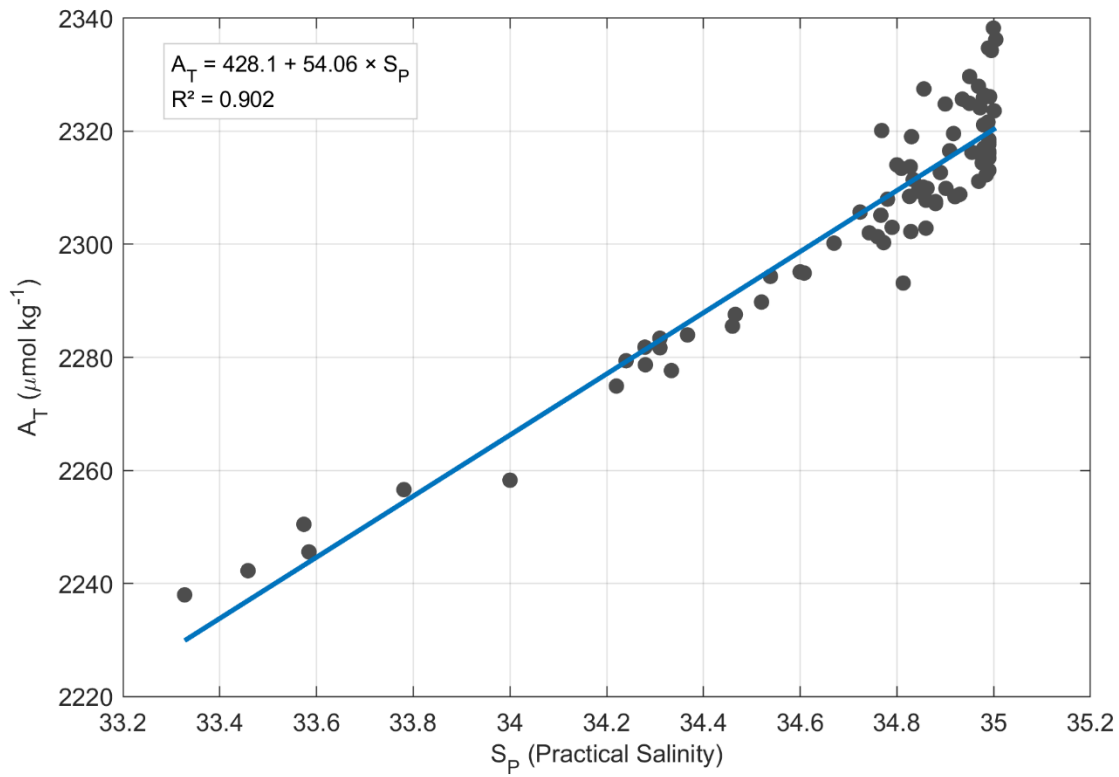


Figure S7.1. Linear relationship between total alkalinity (A_T) and practical salinity (S_P) for the Laurentian Channel (data from the 2021-2023 TReX Program). The fitted linear regression is described by $A_T = 428.1 + 54.06 \times S_P$ with an R^2 value of 0.902. This relationship suggests that S_P is the dominant driver of A_T variability in the deep layer. At high salinity (>34.7), a distinct “hockey stick shape” emerges, which could be attributed to a change in the dominant water mass entering through the Cabot Strait in ~2020, possibly influenced by a shift in the end-member composition (Jutras et al., 2020, 2023a, b).

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