

Supplemental Material for “Gulf of St. Lawrence and Estuary Dataset (GOSLED): a 20-year compilation of quality-controlled biogeochemical observations (2003-2023)”

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S1 Regional map

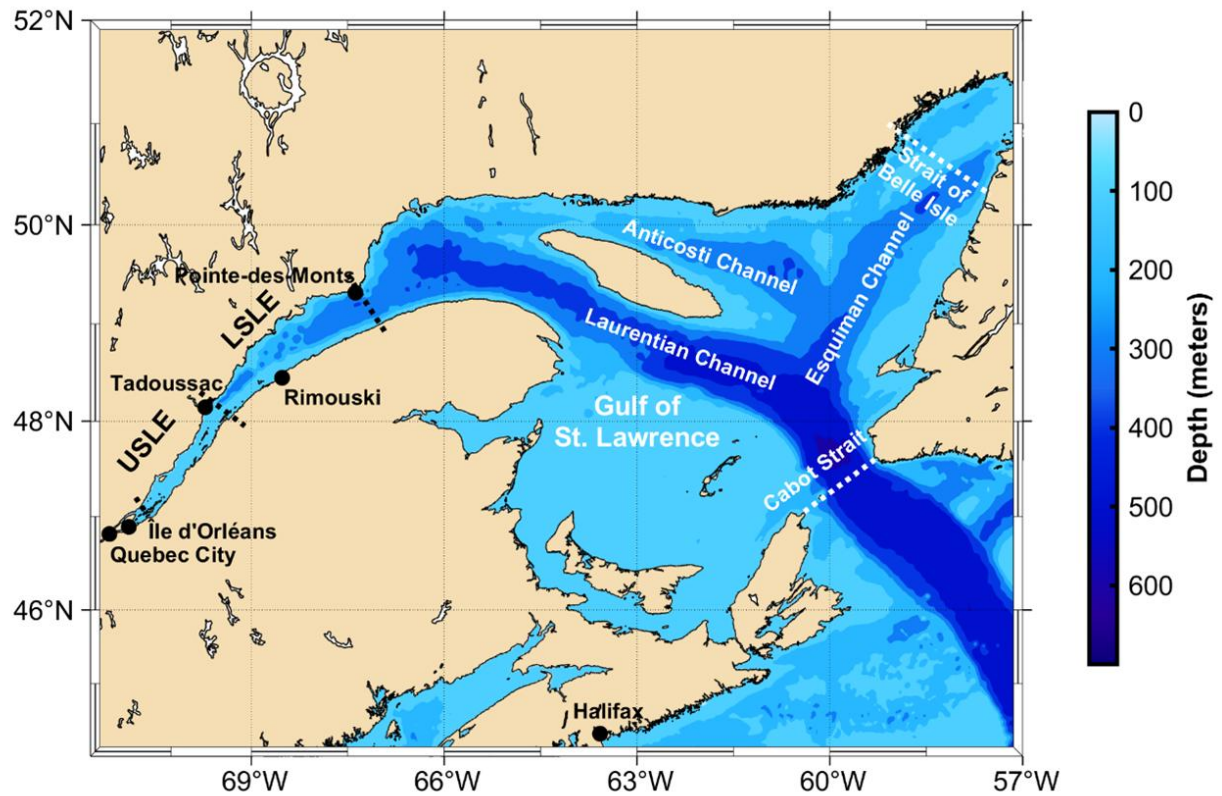
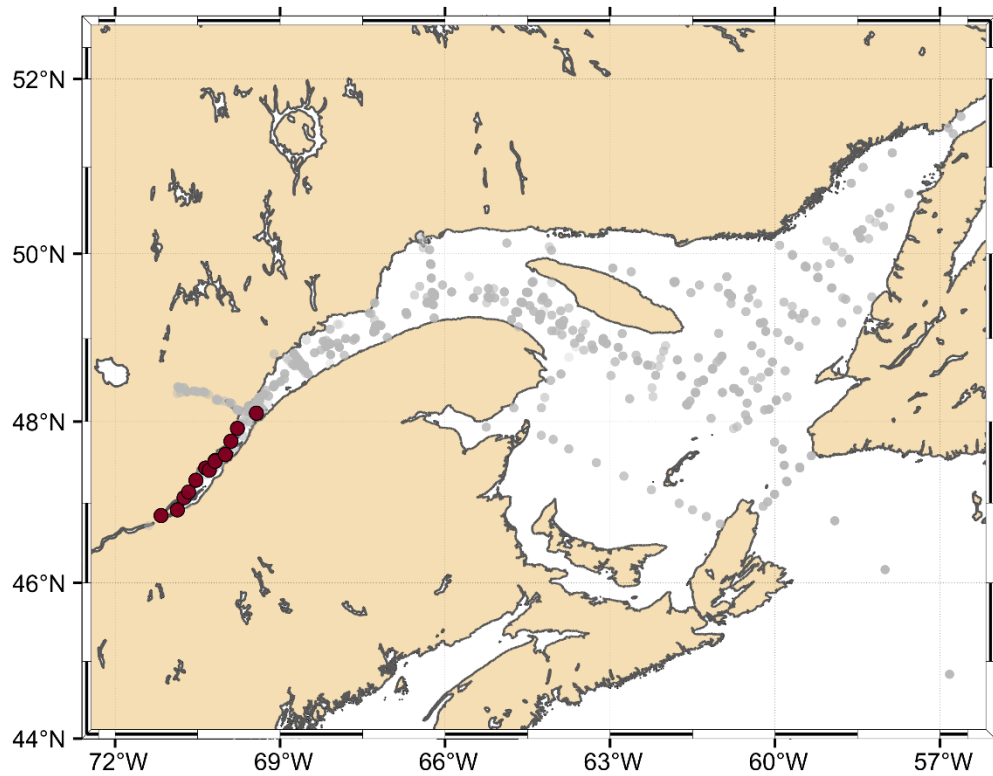


Figure S1. Map of the St. Lawrence Estuary and Gulf (GSL) showing the Upper (USLE) and Lower Estuary (LSLE) and major channel features (Laurentian, Anticosti, and Esquiman Channels). This map was originally published in and reproduced from Nesbitt et al., (2025).

S2 Individual cruise maps



60 Figure S2. Cruise 01 (2003-05-08 to 2003-05-11); 17 stations. Regions: LSLE and USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, dissolved oxygen (DO), total alkalinity (TA), dissolved organic carbon (DOC).

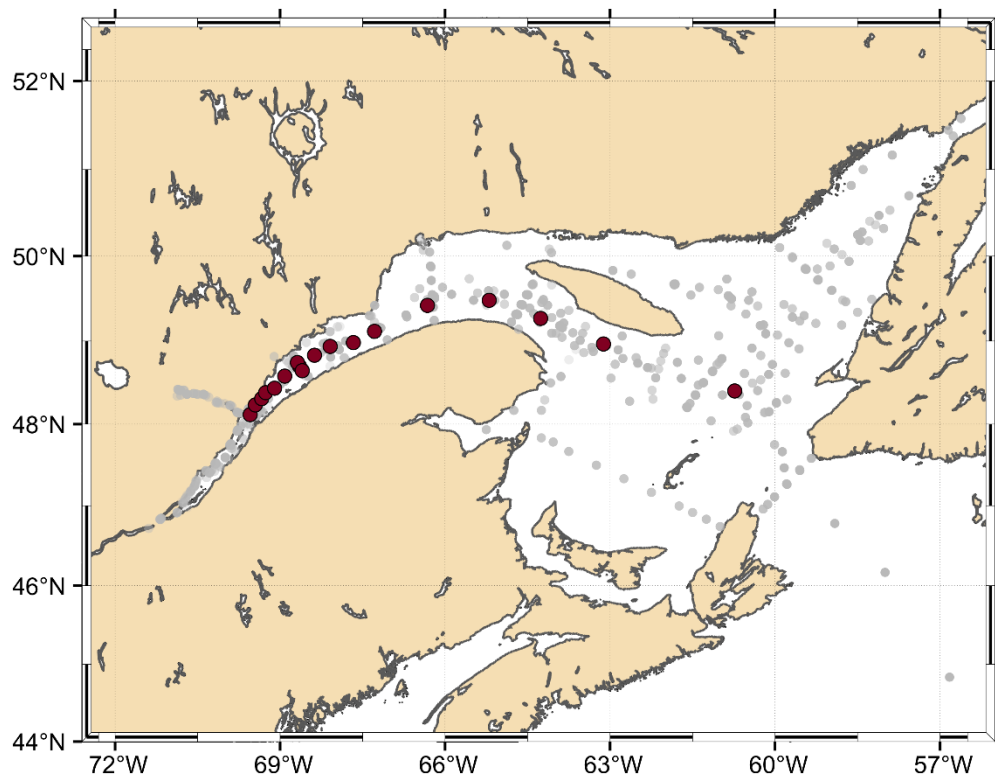


Figure S3. Cruise 02 (2003-07-09 to 2003-07-14); 19 stations. Regions: Gulf of St. Lawrence (GSL; LC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA.

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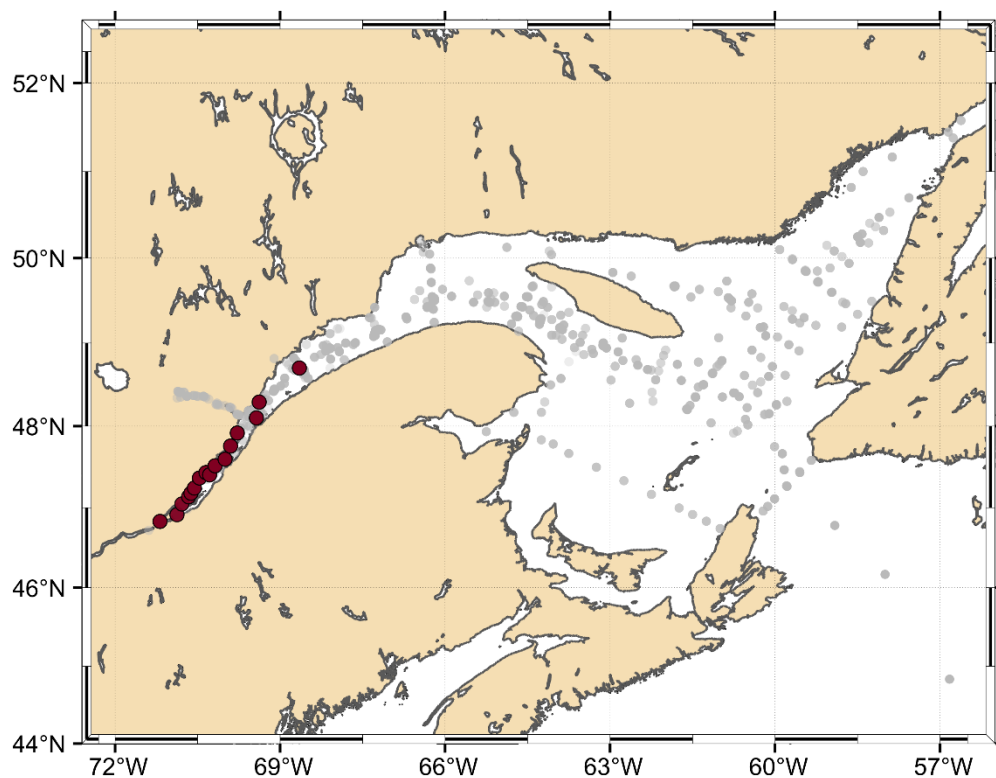


Figure S4. Cruise 03 (2006-06-11 to 2006-06-16); 18 stations. Regions: LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , soluble reactive phosphate (SRP), DOC, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$.

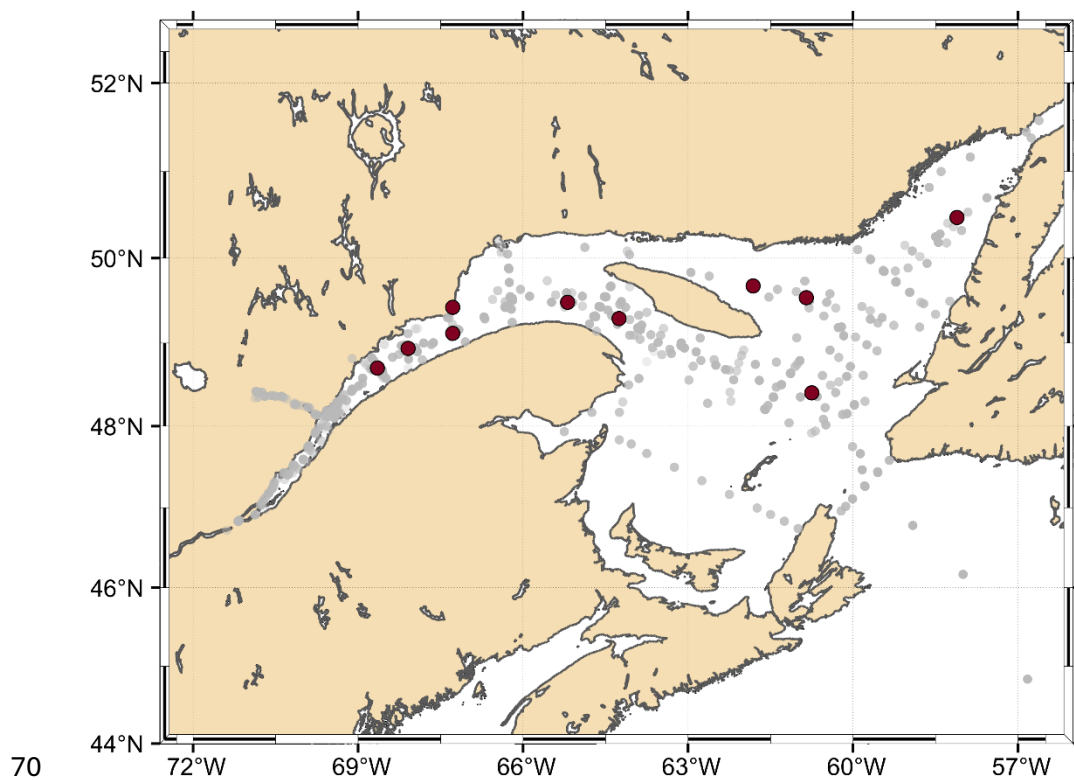
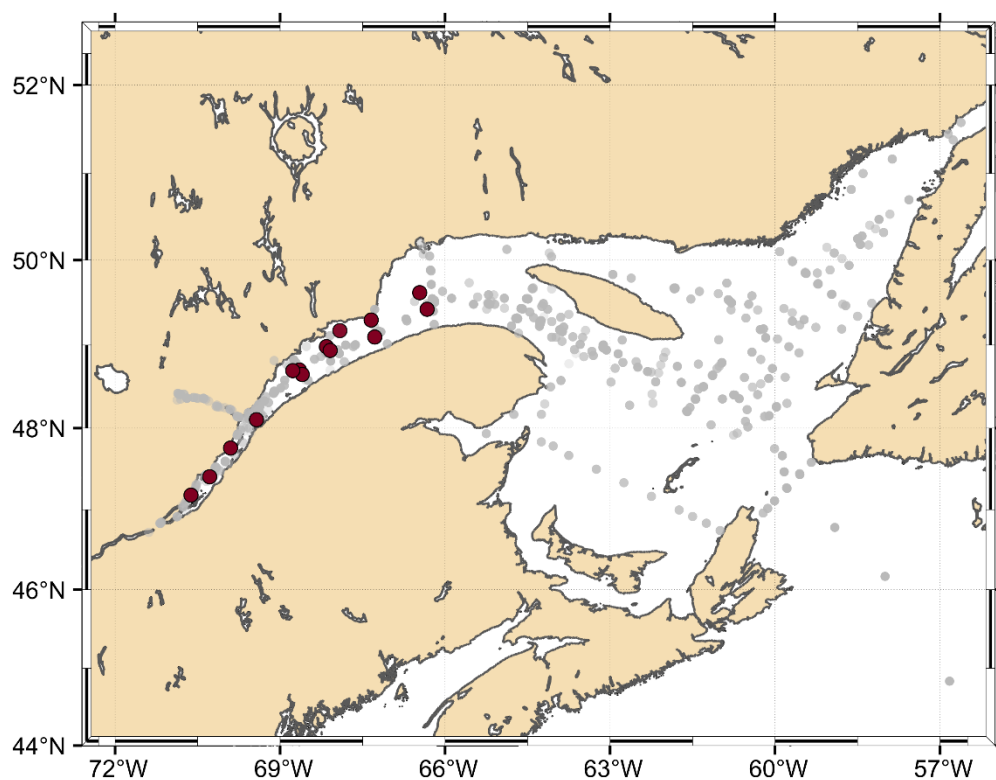


Figure S5. Cruise 04 (2006-08-15 to 2006-08-20); 11 stations. Regions: GSL (AC, LC, EC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , DOC, $\delta^{13}C_{DIC}$, $\delta^{13}C_{DOC}$.



75 **Figure S6. Cruise 05 (2007-05-14 to 2007-05-19); 15 stations. Regions: GSL (LC), LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS}, SRP, DOC, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.**

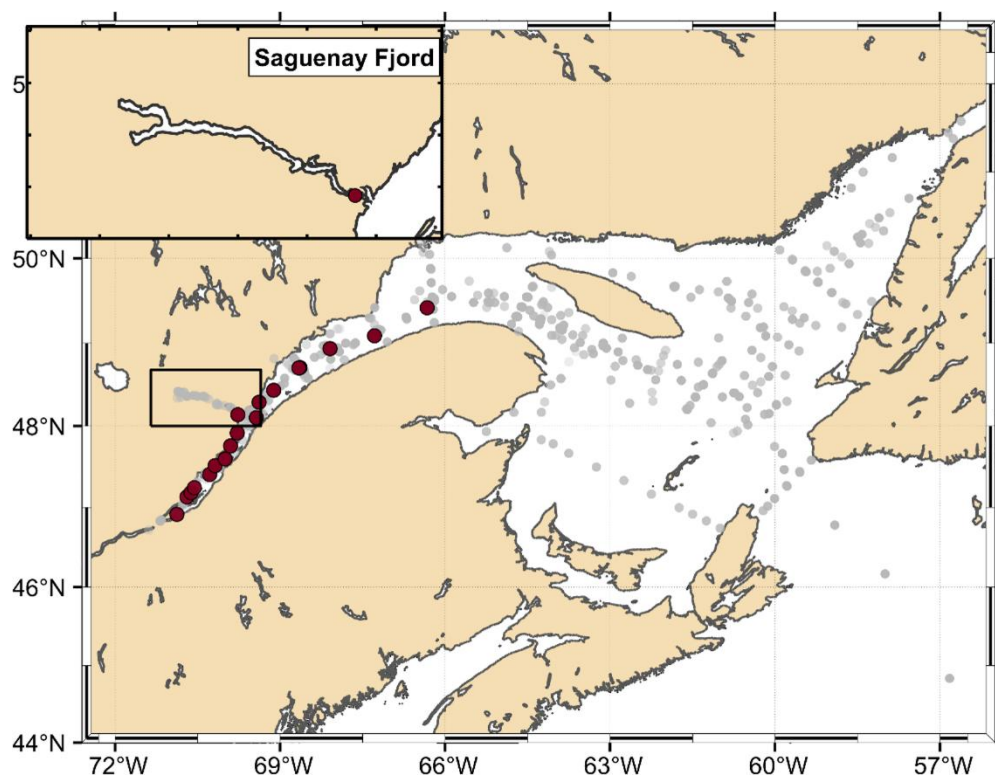


Figure S7. Cruise 06 (2009-06-08 to 2009-06-13); 18 stations. Regions: GSL (LC), LSLE, USLE, Saguenay Fjord (SF). Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS}, Silicate (DSi), DOC, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

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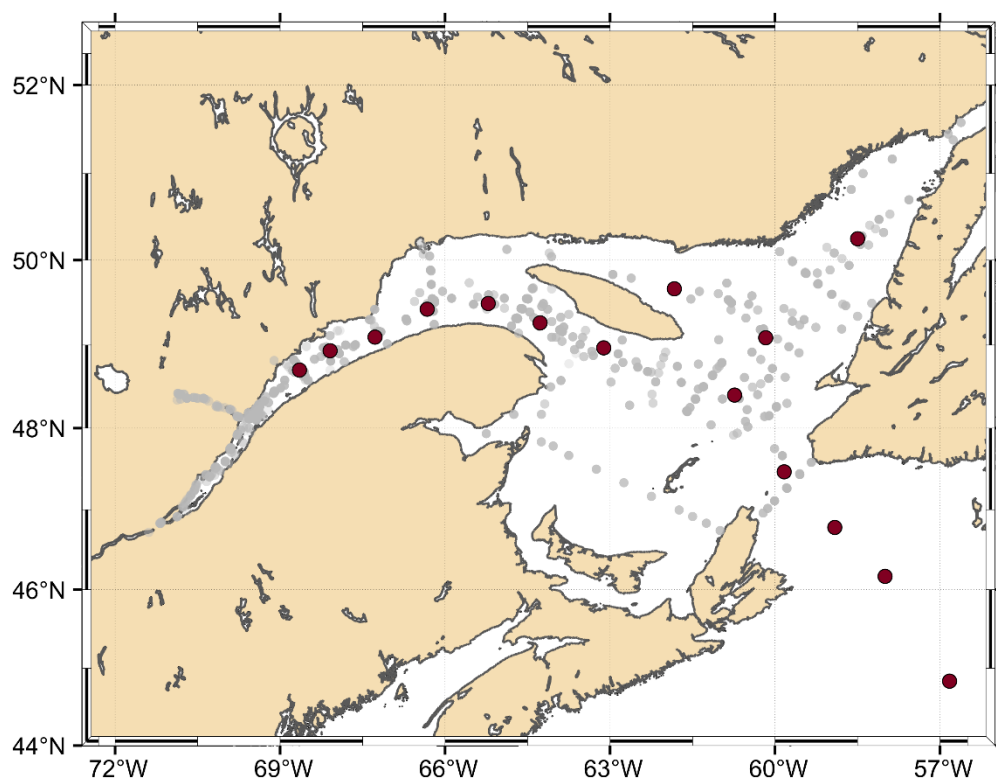


Figure S8. Cruise 07 (2010-07-02 to 2010-07-11); 15 stations. Regions: GSL (LC, AC, EC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , DSi , DOC, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

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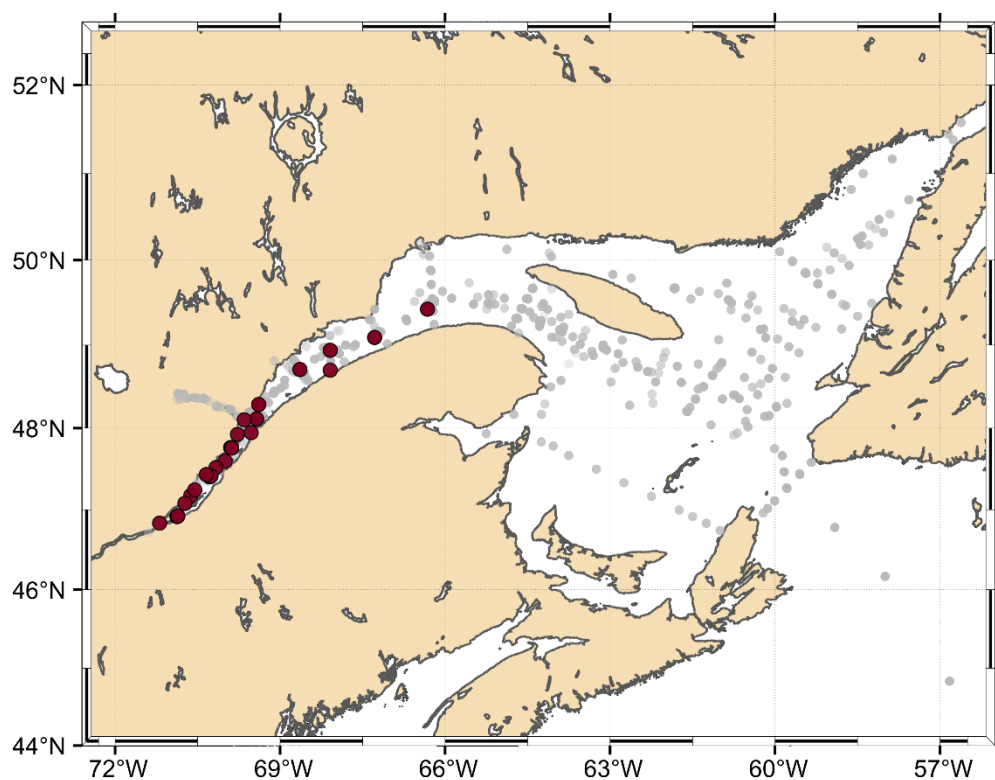


Figure S9. Cruise 08 (2011-05-16 to 2011-06-02); 23 stations. Regions: GSL (LC), LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , fugacity of CO_2 ($f\text{CO}_2$), DSi, SRP, DOC, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

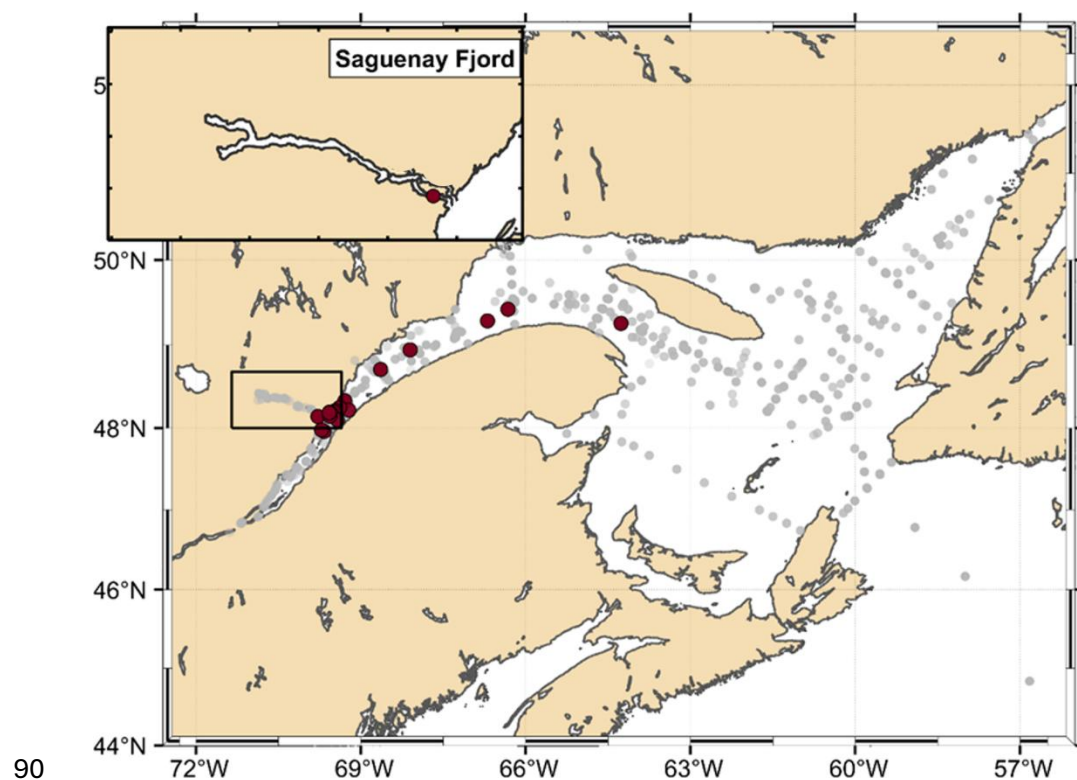


Figure S10. Cruise 09 (2013-06-03 to 2013-06-13); 19 stations. Regions: GSL (LC), LSLE, USLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , DSi, SRP, Nitrate (NO_3^-), Nitrite (NO_2^-), Ammonium (NH_4^+), DOC, $\delta^{13}\text{C}_{\text{DOC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

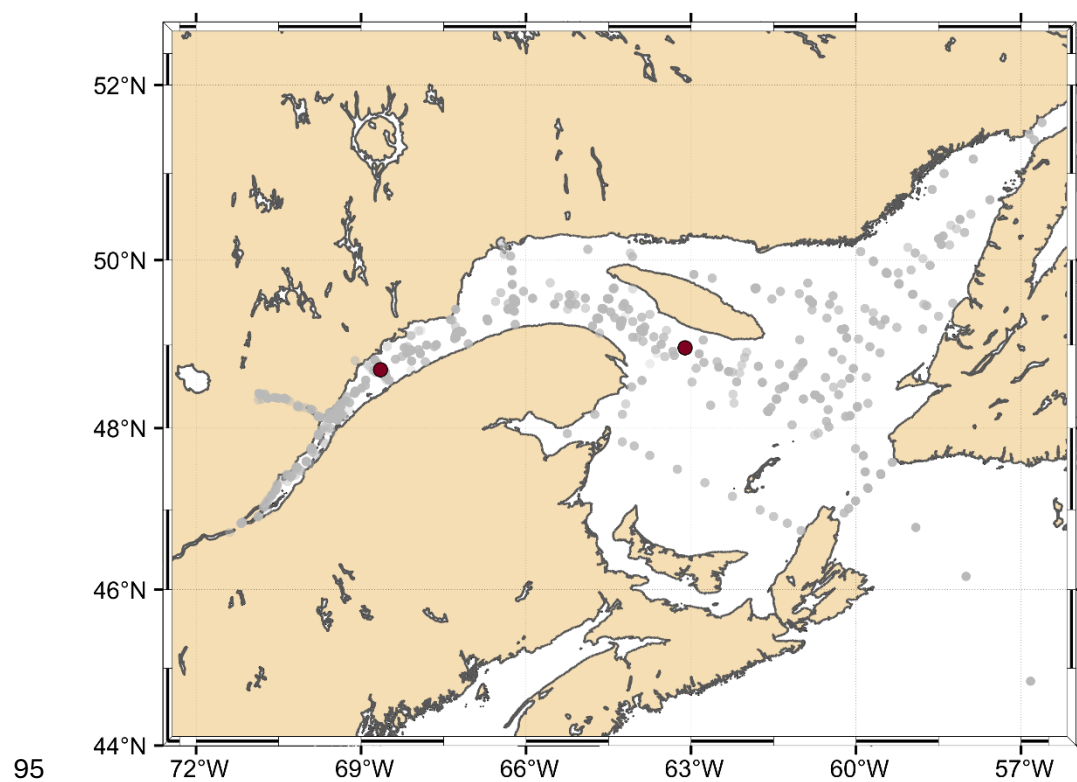
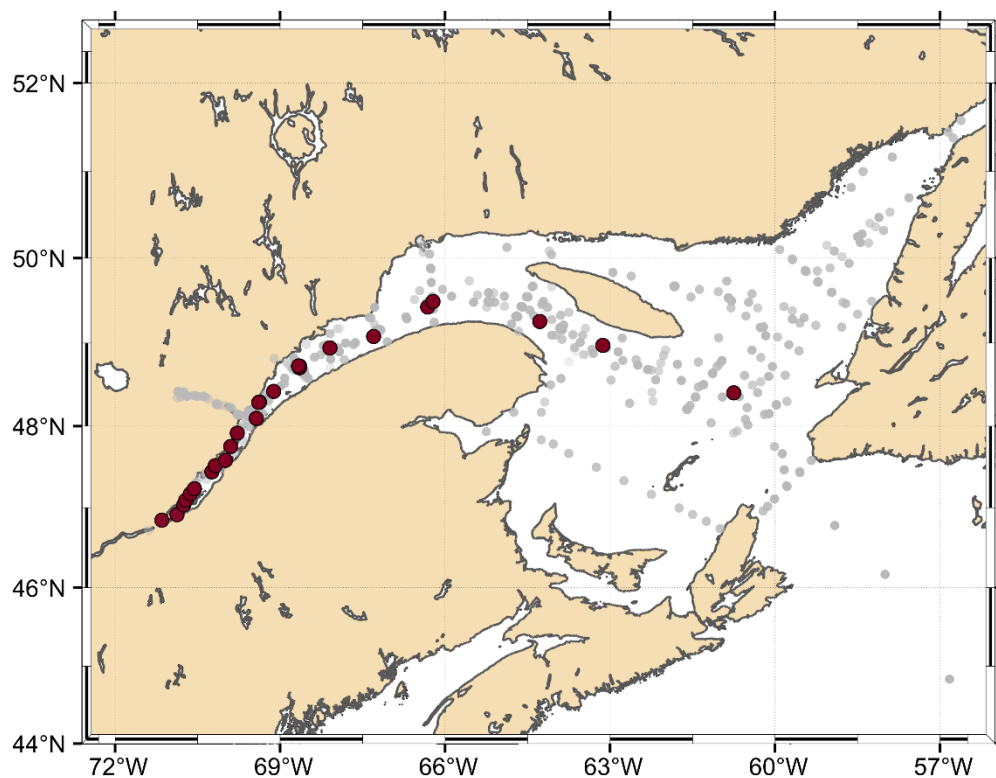


Figure S11. Cruise 10 (2014-09-13 to 2014-09-15); 2 stations. Regions: GSL (LC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , DSi , SRP , $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.



100 **Figure S12.** Cruise 11 (2016-05-18 to 2016-05-26); 27 stations. Regions: GSL (LC), LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS}, DSi, SRP, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

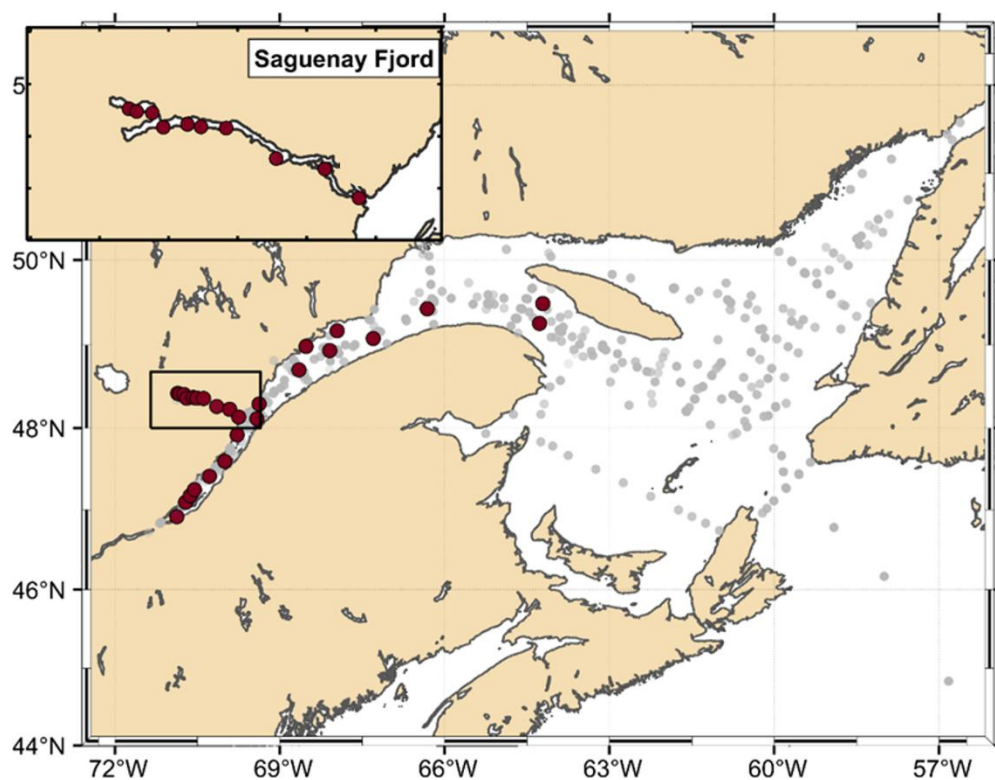


Figure S13. Cruise 12 (2017-06-13 to 2017-06-20); 27 stations. Regions: GSL (LC), LSLE, USLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS}, DSi, SRP, DOC, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

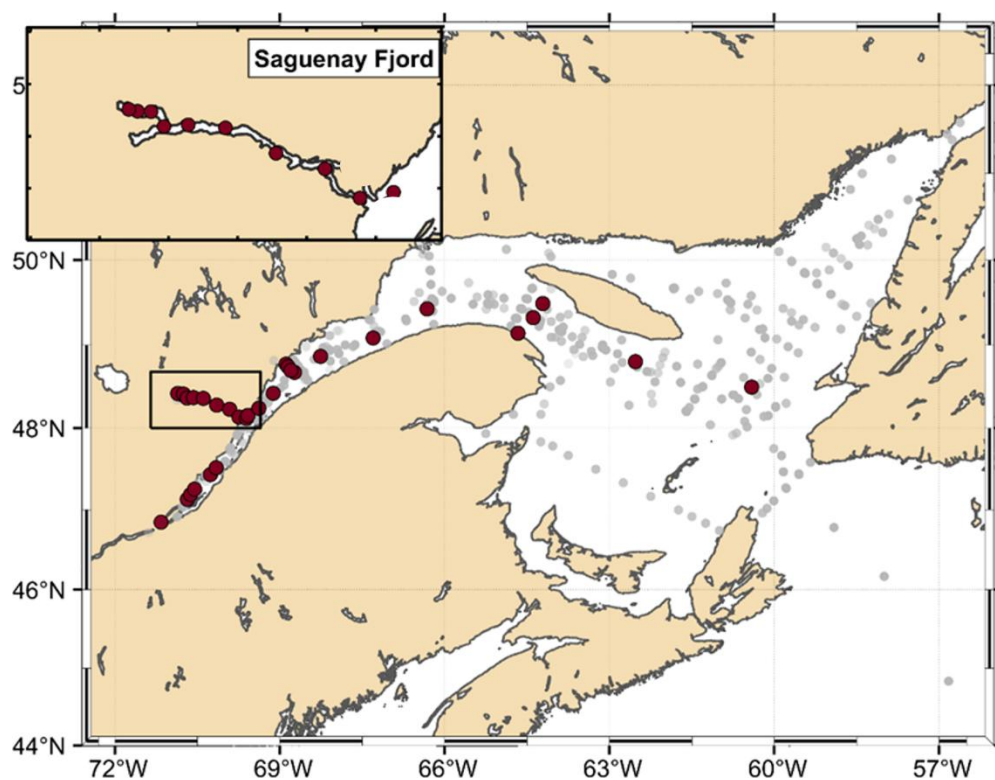


Figure S14. Cruise 13 (2018-05-24 to 2018-06-01); 31 stations. Regions: GSL (LC), LSLE, USLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , fCO_2 , DSi , DOC , $\delta^{18}O_{H_2O}$.

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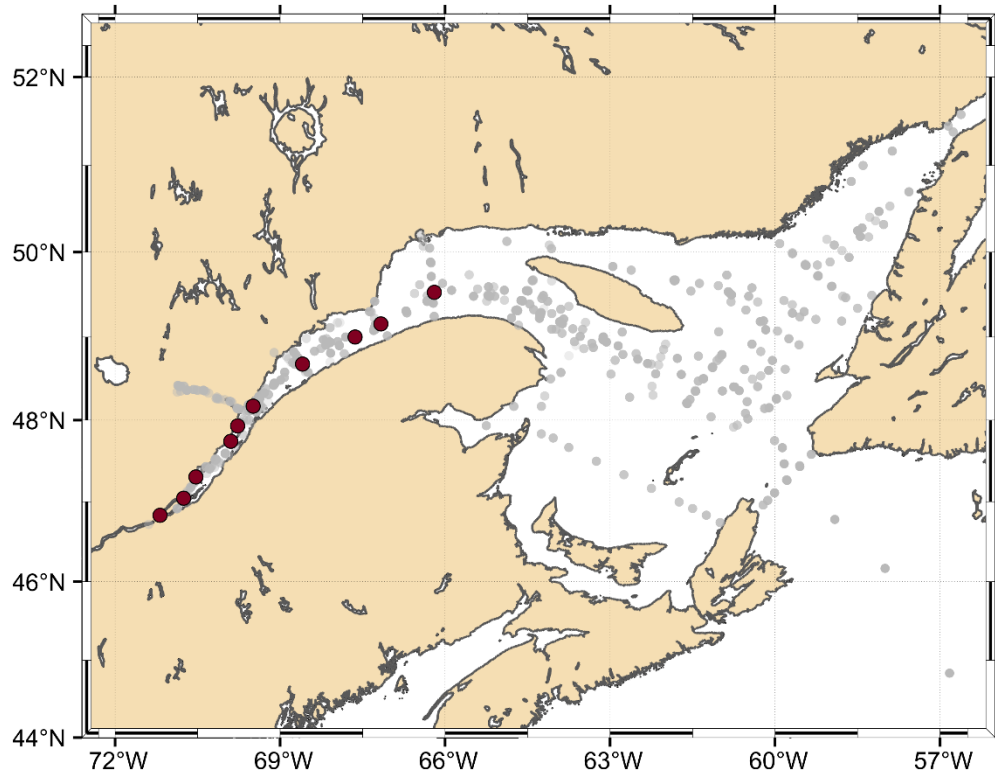


Figure S15. Cruise 14 (2019-02-03 to 2019-02-07); 10 stations. Regions: GSL (LC), LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, TA, pH_{TS} , DSi , SRP , NO_3^- , NO_2^- , $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

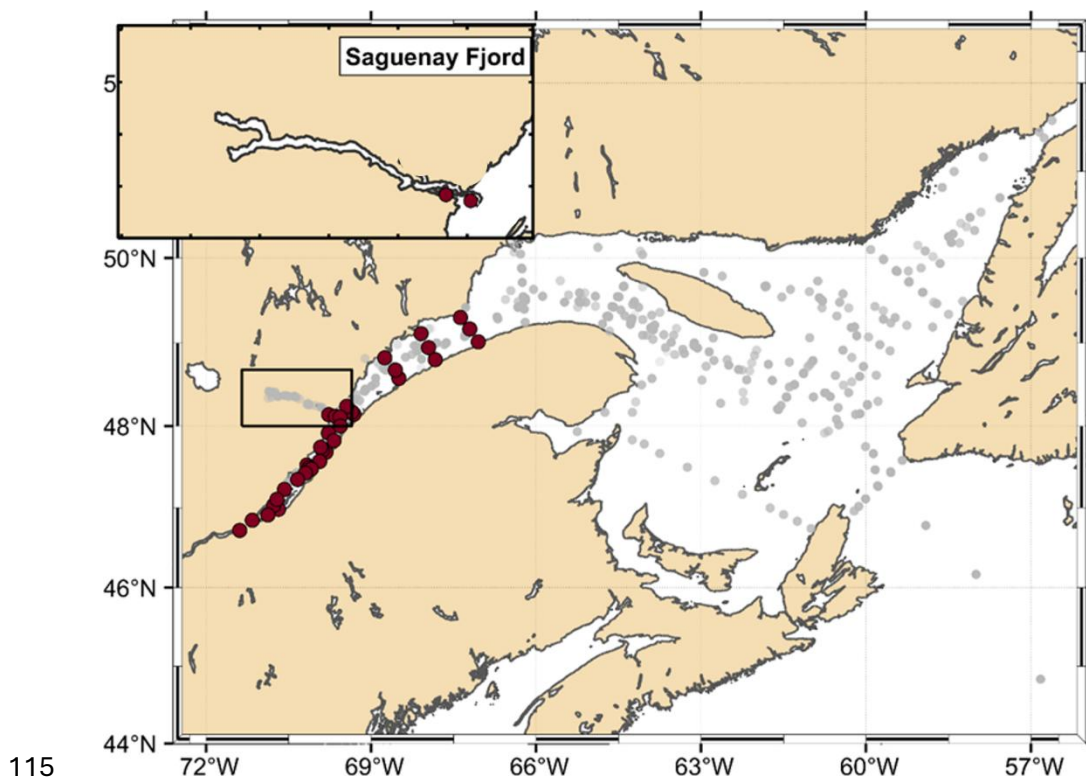
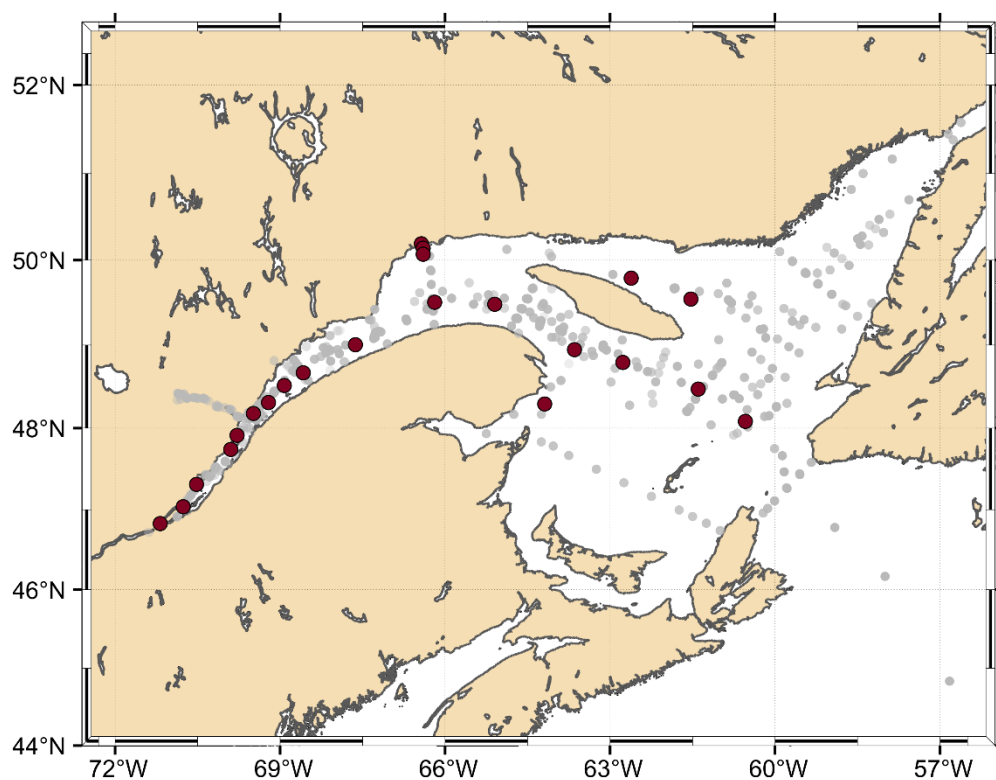


Figure S16. Cruise 15 (2019-06-19 to 2019-06-30); 35 stations. Regions: LSLE, USLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , DSi, SRP, NO_3^- , NO_2^- , $\delta^{18}O_{H_2O}$.



120 **Figure S17.** Cruise 16 (2020-02-28 to 2020-03-13); 22 stations. Regions: GSL (LC, AC), LSLE, USLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , $\delta^{13}C_{DIC}$, $\delta^{18}O_{H_2O}$.

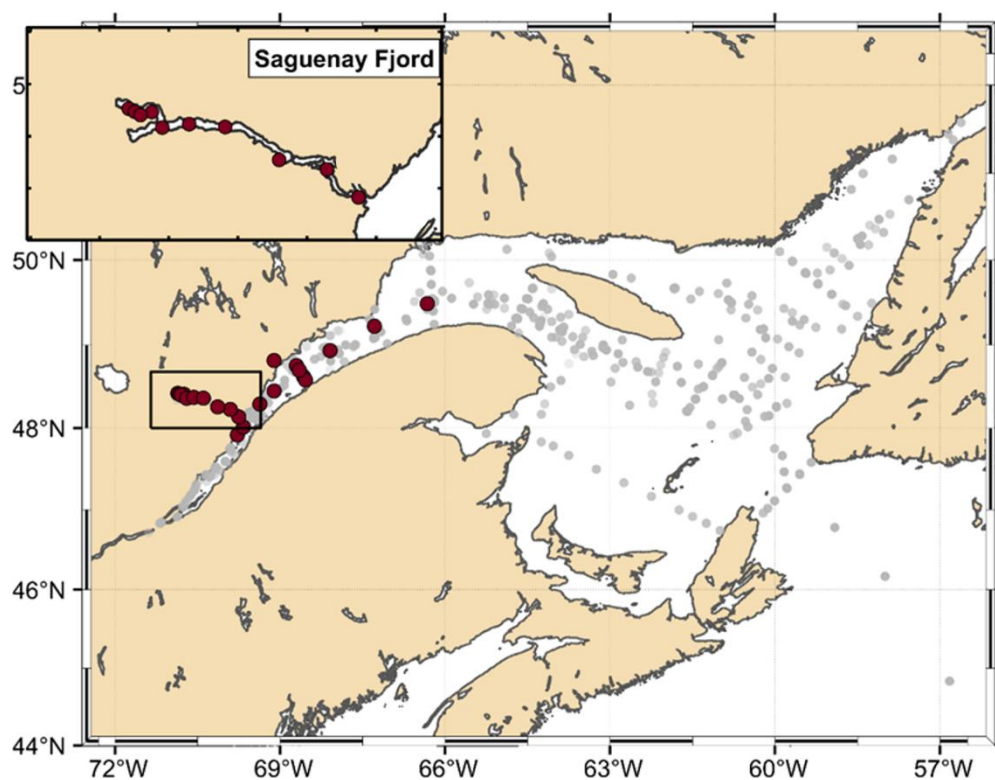


Figure S18. Cruise 17 (2021-08-25 to 2021-08-30); 23 stations. Regions: GSL (LC), LSLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , fCO_2 , DOC, $\delta^{13}C_{DIC}$, $\delta^{18}O_{H_2O}$.

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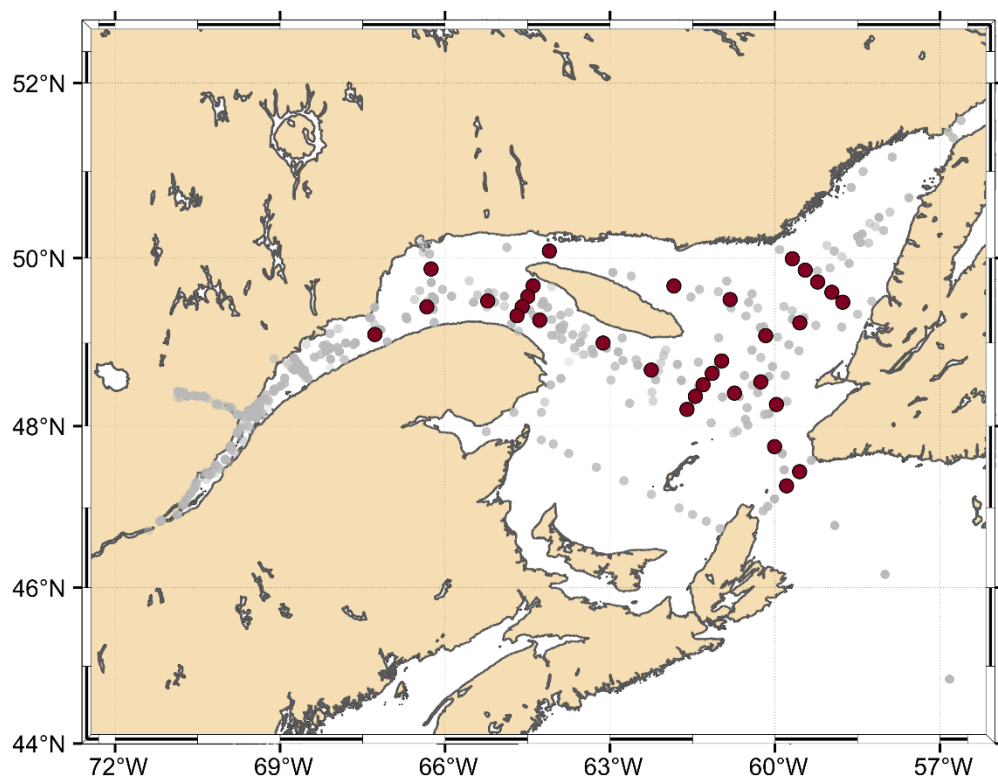


Figure S19. Cruise 18 (2021-10-22 to 2021-10-29); 32 stations. Regions: GSL (LC, AC, EC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{TS} , DSI, SRP, NO_3^- , NO_2^- , NH_4^+ , DOC, total dissolved nitrogen (TN), $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta\text{D}_{\text{H}_2\text{O}}$.

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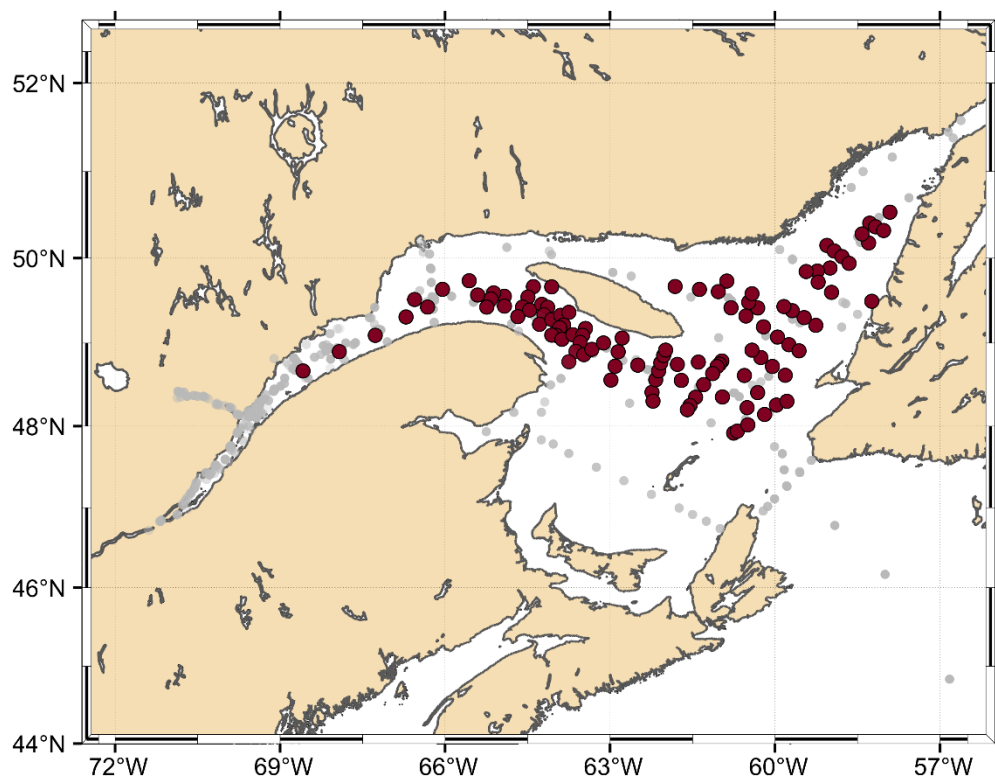


Figure S20. Cruise 19 (2022-06-11 to 2022-06-23); 112 stations. Regions: GSL (LC, AC, EC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{Ts}, DSI, SRP, NO₃⁻, NO₂⁻, NH₄⁺, nitrous oxide (N₂O), $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta\text{D}_{\text{H}_2\text{O}}$, CFC-12, SF₆, CF₃CF₃.

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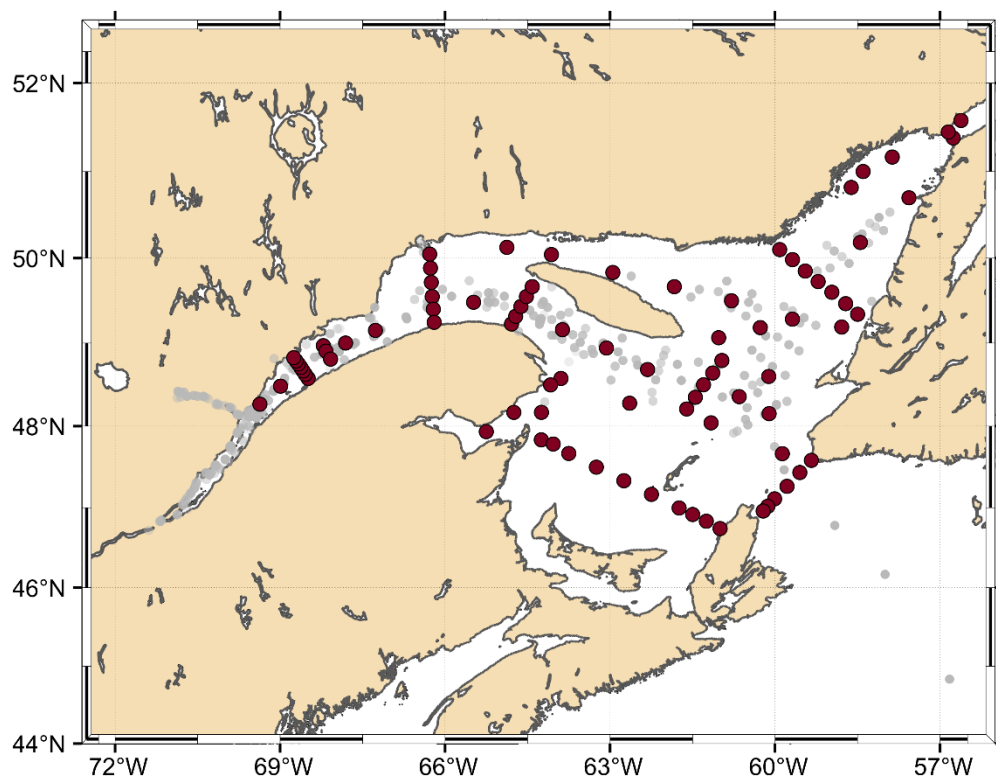


Figure S21. Cruise 20 (2022-10-25 to 2022-11-10); 85 stations. Regions: GSL (LC, AC, EC), LSLE. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, pH_{Ts}, DSi, SRP, NO₃⁻, NO₂⁻, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta\text{D}_{\text{H}_2\text{O}}$, CFC-12, SF₆, CF₃SF₅.

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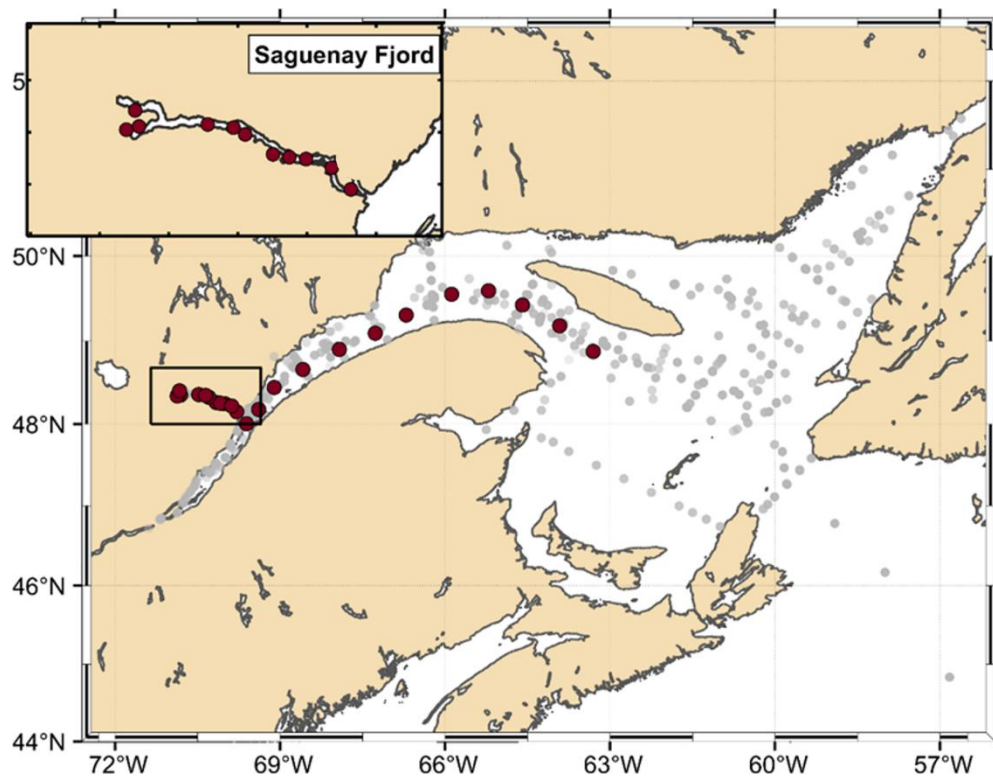


Figure S22. Cruise 21 (2023-07-05 to 2023-07-11); 23 stations. Regions: GSL (LC), LSLE, SF. Red circles indicate stations occupied during this cruise, while grey circles show all stations sampled across the entire dataset. Variables measured: CTD profiles, DO, DIC, TA, $\delta^{13}\text{C}_{\text{DIC}}$.

S3 Description of analytical methods

This section documents the analytical protocols used for the Gulf of St. Lawrence and Estuary Dataset (GOSLED), including instrumentation, calibration, and precision/uncertainty. Each subsection lists a method code that links to the parameter-cruise cross reference (Table S1).

Hydrography

CTD-1: CTD Temperature (CTDTEMP) and Salinity (CTDSAL)

Conducted by: Various research groups (McGill, ISMER, Dalhousie, DFO-MLI)

In-situ temperature and practical salinity were measured with a Sea-Bird SBE 911+ CTD equipped with dual platinum thermistors and conductivity cells. Sensors were factory-calibrated within 12 months prior to deployment. Conductivity calibrations were verified pre- and post-cruise against discrete salinity samples analyzed by potentiometric titration (AgNO_3 standardized using IAPSO reference seawater). In most cases, discrete samples were collected from near-surface waters (~ 3 m), as salinity can vary significantly over the length of the Niskin bottle in the upper water column. On select cruises (i.e. June 2013, November 2017, May 2018, June 2019, etc.), discrete salinity samples spanning the full water column were analyzed in the DFO-MLI laboratory with a Guildline Autosol 8400 salinometer calibrated with IAPSO standard seawater. The instrument has an accuracy of $S_P < 0.002$. Raw data (24 Hz) were processed with SBE Data Processing software: de-spiking, alignment of conductivity to temperature and pressure, thermal-lag correction, and 1 dbar bin averaging. The reproducibility of these measurements was typically ± 0.5 %.

Dissolved Oxygen

O2-1: Winkler Dissolved Oxygen (Oxygen)

165 *Conducted by: Various research groups (McGill, ISMER, Dalhousie, DFO-MLI)*

Discrete Niskin-bottle samples were analyzed onboard by Winkler titration (Grasshoff et al., 2009). Samples were drawn via short, flexible silicone tubing with minimal air contamination into volumetrically calibrated bottles. Immediately upon collection, manganous chloride and alkaline iodide reagents were added, the bottles were capped, stirred and the precipitate allowed to settle before acidification and titration within 1-2 h using amperometric or starch-indicator endpoints. Replicate precision was typically within $\pm 0.5\%$, corresponding to $\pm 1\text{--}2\ \mu\text{mol kg}^{-1}$ for oxygen concentrations of 200-300 $\mu\text{mol kg}^{-1}$. These values served as primary standards for calibrating the CTD oxygen sensors (Method O2-2) and as independent discrete measurements in the dataset.

170

O2-2: CTD Dissolved Oxygen (CTDOXY)

Conducted by: Various research groups (McGill, ISMER, Dalhousie, DFO-MLI)

175 A Sea-Bird SBE-43 Clark-type membrane sensor provided continuous O_2 profiles. Each sensor was factory-calibrated and adjusted to paired Winkler measurements (O2-1). Raw sensor voltages were converted to O_2 concentrations ($\mu\text{mol kg}^{-1}$) following Sea-Bird's calibration equation that applies in-situ pressure and temperature compensation. Precision of the calibrated data was $\pm 1\text{--}2\ \mu\text{mol kg}^{-1}$ with total uncertainty $\leq 2\%$.

pH on the Total Scale (pH_{TS} measured)

180 Sample handling (all pH_{TS} methods): for onboard measurements, seawater sampled directly from Niskin bottles were transferred to 125 mL plastic bottles without headspace. The latter were immersed in water bath maintained at $25(\pm 0.1)\ ^\circ\text{C}$ before spectrophotometric measurements; for delayed measurements, samples were transferred to and stored in 250 mL or 500 mL borosilicate glass bottles, HgCl_2 -poisoned and kept dark/cool; cell pathlength = 10 cm unless otherwise noted; temperature $25.00 \pm 0.05\ ^\circ\text{C}$.

185 *pH-1: Spectrophotometric pH_{TS} (2021 and prior, Salinity > 5)*

Conducted by: A. Mucci group (McGill University)

pH_{TS} was determined spectrophotometrically using m-cresol purple and phenol red indicators on a HP-8453A UV-Vis diode-array spectrophotometer (5 cm quartz cell, $25 \pm 0.1\ ^\circ\text{C}$). The salinity dependence of the dissociation constants and molar absorptivities of the indicators were taken from Robert-Baldo et al. (1985) and Clayton and Byrne (1993). Replicate precision was better than ± 0.005 pH units (see Delaigue et al. (2020) for further details). Dye additions were kept $\leq 2\ \mu\text{L}$ per 10 mL to minimize perturbation.

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pH-2: Potentiometric pH

Conducted by: A. Mucci group (McGill University)

195 For low-salinity waters, pH was measured on the NBS scale using a Radiometer GK2401C combination electrode at $25 \pm 0.1\ ^\circ\text{C}$ linked to a PHM84 pH/mV meter, calibrated with NIST (formerly NBS) traceable buffers (4.00, 7.00, 10.00). For samples whose S_p was greater than 3, pH(NBS) was subsequently converted to the total hydrogen scale, pH_{TS}, according to the electrode response to a TRIS (tris(hydroxymethyl)aminomethane) buffer solution prepared at $S_p = 5, 10, 15, 25, 30$ or 35, whichever was closest to the sample salinity, and for which the pH_{TS} was assigned at $25\ ^\circ\text{C}$ (Millero, 1986). Precision was better than ± 0.005 pH units.

200 *pH-3: Spectrophotometric pH_{TS} (AZMP 2022)*

Conducted by: Fisheries and Oceans Canada (MLI)

205 Samples were HgCl_2 -poisoned and stored in the dark until analysis. pH_{TS} was measured spectrophotometrically using purified m-cresol purple (Robert Byrne, University of South Florida) in 10 cm quartz cells maintained at $25 \pm 0.05\ ^\circ\text{C}$ on Agilent Cary 60 spectrophotometers (Gibb et al., 2023). Absorbances (434, 578, 730 nm) were recorded. Daily TRIS ($S_p = 30$) measurements verified accuracy ± 0.003 pH units. No explicit dye-perturbation correction was applied.

pH-4: Spectrophotometric pH_{TS} (post 2021)

Conducted by: CERC.OCEAN (Dalhousie University)

- 210 pH_{TS} was measured with an Apollo SciTech AS-Spec- pH_2 automated system (Fradette, 2025). An Agilent Cary 60 spectrophotometer and Tecan Cavro XLP syringe pump delivered 11 μL of purified mCP per 10 mL sample to a 10 cm water-jacketed cell (25.00 ± 0.05 °C). Double-dye additions (11 μL , 22 μL) quantified dye perturbation (β); absorbances (434, 487, 578, 705 nm) were baseline and impurity-corrected (Douglas and Byrne, 2017a, b; Liu et al., 2011). Daily Dickson CRM checks yielded accuracy and repeatability of ± 0.004 pH units.

pH-5: Spectrophotometric pH_{TS} (2023)

- 215 *Conducted by: L. Pascal (Université du Québec à Rimouski, ISMER)*

Identical to pH-1.

Total Alkalinity (TALK)

Sample handling (all TA/DIC): borosilicate bottles filled overflowing, no headspace, poisoned with HgCl_2 (100 μL sat. per 250 mL), stored dark at room temperature; measurements corrected to 25 °C.

- 220 *TA-1: Radiometer (pre Sept.2021)*

Conducted by: A. Mucci group (McGill University)

Total Alkalinity was measured using a Radiometer TitraLab 865 with a Red Rod pHC2001 electrode; HCl titrant (0.1 M in 0.45 M NaCl) standardized with Dickson CRMs. Reproducibility was better than ≤ 0.1 %.

TA-2: VINDTA 3C (pre Sept.2021)

- 225 *Conducted by: A. Mucci (McGill University) and H. Thomas (Dalhousie University)*

Total Alkalinity was measured on a VINDTA 3C (Mirianda) following (Dickson et al., 2007). Each sequence included triplicate CRMs and blank corrections. Precision was ± 2 $\mu\text{mol kg}^{-1}$, and accuracy was ≤ 0.05 % vs CRMs.

TA-3: Metrohm Open-Cell (post Sept.2021)

Conducted by: CERC.OCEAN (Dalhousie University)

- 230 Measurements were conducted using a Metrohm LL-ECOTRODE Plus and Dosimat 876 Plus titrator connected to an Agilent 34970A voltmeter. Open-cell titrations followed Dickson et al. (2007); CRMs #186 and #197 were run daily. Precision was ± 3 $\mu\text{mol kg}^{-1}$.

TA-4: VINDTA C Open-Cell

Conducted by: Fisheries and Oceans Canada (MLI)

- 235 TA was determined using a VINDTA 3C system via open-cell potentiometric titration following established protocols (Dickson et al., 2007; Mintrop et al., 2000). Titrations were performed with 0.1 M hydrochloric acid to the Gran equivalence point using a computer-controlled Dosimat dispenser (Metrohm AG) coupled to a combination glass electrode (Aquatrode). Certified Reference Materials were analyzed regularly (approximately every 2 days) and used to adjust titrant concentration, with the resulting correction factor applied to all TA calculations. Analytical
240 precision from replicates was better than ± 0.1 %.

Dissolved Inorganic Carbon (DIC)

DIC-1: Coulometry / VINDTA (pre Sept.2021)

Conducted by: A. Mucci (McGill University), G. Chaillou (ISMER_UQAR), and H. Thomas (Dalhousie University)

245 DIC was quantified by SOMMA coulometry or VINDTA 3C; 2014 samples used a SciTech Apollo NDIR analyzer. Calibrations with gravimetrically-prepared Na₂CO₃ and CRM solutions. Precision was ± 0.2 %.

DIC-2: CRDS (post Sept.2021)

Conducted by: CERC.OCEAN (Dalhousie University)

250 DIC and δ¹³C_{DIC} were measured simultaneously with an Apollo AS-D1 acidification system coupled to a Picarro G2201-i CRDS (Cheng et al., 2019; Su et al., 2019). Two-point CRM calibration (#186, #197); Precision was ± 4 μmol kg⁻¹ and δ¹³C ± 0.15 ‰.

DIC-3: Coulometry / VINDTA 3C

Conducted by: Fisheries and Oceans Canada (MLI)

255 DIC was measured using a VINDTA 3C system following automated acidification and purge-and-trap extraction. Samples were acidified with phosphoric acid (1 M, 8.5 %) and warmed to 25 °C. Released CO₂ was purged with ultrahigh-purity nitrogen gas, dried, and directed into a coulometric cell for titration and photometric quantification (Johnson et al., 1993). Duplicate or triplicate analyses indicate an analytical precision of better than ± 0.1 %.

Fugacity of CO₂ (fCO₂ insitu measured)

fCO₂-1: Pro-Oceanus CO₂-Pro CV

Conducted by: A. Mucci group (McGill University)

260 Continuous measurements were conducted using a CO₂-Pro CV probe (Pro-Oceanus Systems) with NDIR detection with certified gas calibration. Data were logged every 7 s, stable fCO₂ values were achieved after a 15 min equilibration period and averaged over the next 20 min. Relative standard deviations over this period were typically on the order of 0.2 to 6%.

Nutrient (Silicate, Reactive Phosphate, Nitrate, Nitrite, Ammonium)

265 General handling: subsamples filtered through 0.45 μm or 0.8 μm polyethersulfone disposable syringe filters; acid-washed and DI-rinsed labware; for shipboard NH₄⁺ immediate analysis; for others frozen at -20 °C or -80 °C within minutes of collection.

NUT-1: Phosphate and Silicate Spectrophotometry (pre Sept 2021)

Conducted by: A. Mucci group (McGill University)

270 Soluble reactive phosphate (SRP) and dissolved silicate (DSi) were measured spectrophotometrically according to procedures described in Grasshoff et al. (2009). Methods used were a phospho-molybdate-antimony reaction (10 cm cell) for SRP and a molybdate-blue method (1 cm cell) for DSi (Grasshoff et al., 2009). Detection limits were ≈ 0.01 μmol L⁻¹ and precision was typically better than ≤ 5 %.

NUT-2: NO₃⁻, NO₂⁻, SRP, and DSi (pre Sept.2021)

275 *Conducted by: J-É Tremblay's group (Université Laval)*

NO₃⁻, NO₂⁻, SRP, and DSi measured on a Bran + Luebbe AutoAnalyzer III using the Hansen & Koroleff (2007) protocols. DL 0.02–0.10 μmol L⁻¹; replicate precision ± 3 %.

NUT-3: NH₄⁺ Fluorometry (pre Sept 2021)

Conducted by: J-É Tremblay's group (Université Laval)

280 NH₄⁺ was analyzed by the fluorometric OPA method (Holmes et al., 1999). Detection limit was 0.01 μmol L⁻¹ and precision was better than ± 0.02 μmol L⁻¹.

NUT-4: Skalar SAN++ (post Sept.2021)

Conducted by: CERC.OCEAN (Dalhousie University)

285 Nutrients were measured on a Skalar SAN++ continuous-flow analyzer. Calibrations used KANSO CRMs every 20 samples and analytical QA/QC followed McGrath et al. (2019). Precision was better than $\pm 3 \%$ with detection limits ranging $0.02\text{--}0.05 \mu\text{mol L}^{-1}$ depending on the nutrient.

NUT-5: Seal Analytical AutoAnalyzer 3 and Alpkem AutoAnalyzer (AZMP 2022)

Conducted by: Fisheries and Oceans Canada (MLI)

290 Nutrients were analyzed using Seal Analytical AutoAnalyzer 3 (Blais et al., 2023; Gibb et al., 2023). Colorimetric methods employed included cadmium reduction for $\text{NO}_3^- + \text{NO}_2^-$ and ascorbic-acid molybdate for SRP and DSi. Calibrations were conducted with certified standards (SUPELCO, LabChem). Detection limits ranged from $0.007\text{--}0.03 \mu\text{mol L}^{-1}$ and precision was better than $\pm 3 \%$.

NUT-6: Seal Analytical AutoAnalyzer 500 (2023)

Conducted by: Université du Québec à Rimouski (ISMER)

295 Identical to NUT-2.

Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TN)

DOC-1: Aurora OI 1030C HTCO or Shimadzu TOC-VCPH 5000A HTCO (pre Sept.2021)

Conducted by: Y. Gélinas' group (Concordia University)

300 DOC was measured with an Aurora OI 1030C HTCO or a Shimadzu TOC-VCPH 5000A HTCO analyzer at 680°C (Barber et al., 2017; Lalonde et al., 2014). Samples were filtered ($0.7 \mu\text{m}$ pre-combusted GF/F), acidified (pH 2), and stored at 4°C . β -alanine or potassium hydrogen phthalate (KHP) standards were used for calibration and precision was better than $\pm 0.1 \text{ mg C L}^{-1}$.

DOC-2: Shimadzu TOC-L TNM-L (post Sept.2021)

Conducted by: CERC.OCEAN (Dalhousie University)

305 DOC and TN were analyzed on a Shimadzu TOC-L CPH with TNM-L module (ASTM D8-83-16). Samples were filtered through $0.45 \mu\text{m}$ membrane filters prior to analysis. Combustion was carried out at 720°C , oxidized C and N to CO_2 and NO , detected by NDIR and chemiluminescence. Calibrations were conducted with KHP and KNO_3 standards. Precision was better than $\pm 2 \mu\text{mol C kg}^{-1}$ and $\pm 0.2 \mu\text{mol N kg}^{-1}$.

Stable Isotopes (Delta C_{13} DIC, Delta C_{13} DOC, Delta O_{18} H₂O, and Delta D H₂O)

310 ISO-1: $\delta^{13}\text{C}_{\text{DIC}}$ -IRMS (pre Sept.2021)

Conducted by: A. Mucci group (McGill University)

Samples (HgCl_2 -poisoned) were analyzed at on a Micromass Isoprime CF-IRMS + MultiFlow system at the GEOTOP (UQÀM) Stable Light Isotope Laboratory (Dr. J.-F. Hélie). Results were normalized to NBS-19/LSVEC. Precision was better than $\pm 0.1 \text{ ‰}$.

315 ISO-2: $\delta^{13}\text{C}_{\text{DIC}}$ Picarro CRDS (Post-2021)

Conducted by: CERC.OCEAN (Dalhousie University)

$\delta^{13}\text{C}_{\text{DIC}}$ was measured simultaneously with DIC (DIC-2) on the Apollo AS-D1 + Picarro G2201-i system (Cheng et al., 2019; Su et al., 2019). CRMs #186/#197 were used for calibration. Precision was better than $\pm 0.15 \text{ ‰}$.

ISO-3: $\delta^{13}C_{DOC}$ Aurora OI 1030C + IRMS

320 Conducted by: Y. G  linas' group (Concordia University)

DOC-derived CO₂ from an Aurora OI 1030C HTCO was analyzed on a GV/V Isoprime IRMS (Barber et al., 2017; Lalonde et al., 2014). Precision was typically ± 0.2 – 1.0 ‰ (matrix dependent).

ISO-4: $\delta^{18}O$ of H₂O (pre Sept.2021)

Conducted by: A. Mucci group (McGill University)

325 $\delta^{18}O$ was measured by CO₂ equilibration (Epstein and Mayeda, 1953) on a Micromass AquaPrep + Isoprime universal triple collector IRMS in dual inlet mode at the GEOTOP (UQ  M) *Stable Light Isotope Laboratory* (Dr. J.-F. H  lie). Data were normalized against the three internal reference waters, themselves calibrated against Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Standard Light Arctic Precipitation (V-SLAP). The results are reported on the δ scale in ‰ relative to V-SMOW. Precision was better than ± 0.05 ‰.

330 ISO-5: $\delta^{18}O$ and δD of H₂O (post Sept.2021)

Conducted by: CERC.OCEAN (Dalhousie University)

$\delta^{18}O$ and δD were measured by Picarro L2130-i CRDS calibrated to V-SMOW2/SLAP2 (Walker et al., 2016). The results are reported on the δ scale in ‰ relative to V-SMOW. Precision was better than ± 0.05 ‰ and ± 0.8 ‰ respectively.

335 Nitrous Oxide (N₂O), Transient Tracers (CFC-12 and SF₆), and a Deliberate Tracer (CF₃SF₅)

TRC-1: N₂O GC-ECD

Conducted by: CERC.OCEAN (Dalhousie University)

Discrete 20 mL sample vials were analyzed on an Agilent 7890B GC-ECD with a 7697A headspace sampler. Analytical methods are described in detail in Pascal et al. (2025). The detection limit was ≈ 0.2 nM and precision were better than ± 2 %.

340

TRC-2: CFC-12 and SF₆ GC-ECD purge-and-trap

Conducted by: T. Tanhua's group (GEOMAR)

Utilizing a GC-ECD in combination with a purge-and-trap unit (PT5) and following methods described in Bullister et al. (2002) and Tanhua et al. (2004). Detection limits were 0.02 pmol kg⁻¹ (CFC-12), 0.03 fmol kg⁻¹ (SF₆) and precision was better than ≈ 2 %.

345

TRC-3: CF₃SF₅

Conducted by: T. Tanhua's group (GEOMAR)

Analyzed using the same GC-ECD + purge and trap system described in TRC-2 and in further detail in (Gerke et al., 2024, 2026; Stevens et al., 2024). Calibrated was conducted with custom, in house standards and results yielded a precision of ± 3 %.

350

Table S1. Analytical methods applied for each cruise included in the Estuary and Gulf of St. Lawrence dataset (GOSLED, 2003–2023). Each row lists the start and end dates of sampling and the analytical method codes corresponding to Section S1 (Description of Analytical Methods). Method codes identify instrumentation, calibration procedures, and analytical laboratories used for each parameter.

Cruise #	Start date	End date	Methods
1	2003/05/08	2003/05/11	CTD-1, O2-2, TA-1, DOC-1
2	2003/07/09	2003/07/14	CTD-1, O2-1, O2-2, TA-1, pH-1
3	2006/06/11	2006/06/16	CTD-1, O2-2, TA-1, pH-1, pH-2, NUT-1, DOC-1, ISO-1, ISO-3
4	2006/08/15	2006/08/20	CTD-1, O2-1, O2-2, TA-1, pH-1, DOC-1, ISO-1, ISO-3
5	2007/05/14	2007/05/19	CTD-1, O2-2, TA-1, pH-1, pH-2, NUT-1, DOC-1, ISO-1, ISO-3, ISO-4
6	2009/06/08	2009/06/13	CTD-1, O2-1, TA-1, pH-1, pH-2, NUT-1, DOC-1, ISO-1, ISO-4
7	2010/07/02	2010/07/11	CTD-1, O2-1, O2-2, TA-1, pH-1, NUT-1, DOC-1, ISO-4
8	2011/05/16	2011/06/02	CTD-1, O2-1, O2-2, TA-1, pH-1, pH-2, fCO ₂ -1, NUT-1, DOC-1, ISO-1, ISO-4
9	2013/06/03	2013/06/13	CTD-1, O2-1, O2-2, TA-1, pH-1, pH-2, NUT-2, NUT-3, DOC-1, ISO-3, ISO-4
10	2014/09/13	2014/09/15	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, NUT-1, ISO-4
11	2016/05/18	2016/05/26	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, NUT-1, ISO-1, ISO-4
12	2017/06/13	2017/06/20	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, NUT-1, DOC-1, ISO-1, ISO-4
13	2018/05/24	2018/06/01	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, fCO ₂ -1, NUT-1, DOC-1, ISO-4
14	2019/02/03	2019/02/07	CTD-1, O2-1, O2-2, TA-1, pH-1, pH-2, NUT-2, ISO-4
15	2019/06/19	2019/06/30	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, NUT-2, ISO-4
16	2020/02/28	2020/03/13	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, ISO-1, ISO-4
17	2021/08/25	2021/08/30	CTD-1, O2-1, O2-2, TA-1, TA-2, DIC-1, pH-1, pH-2, fCO ₂ -1, DOC-1, ISO-1, ISO-4
18	2021/10/22	2021/10/29	CTD-1, O2-1, O2-2, TA-3, DIC-2, pH-1, NUT-4, DOC-2, ISO-2, ISO-5
19	2022/06/11	2022/06/23	CTD-1, O2-1, O2-2, TA-3, DIC-2, pH-1, NUT-4, TRC-1, TRC-2, TRC-3, ISO-2, ISO-5
20	2022/10/25	2022/11/10	CTD-1, O2-1, O2-2, TA-4, DIC-2, DIC-3, pH-3, NUT-5, ISO-2, ISO-4, TRC-2, TRC-3
21	2023/07/05	2023/07/11	CTD-1, O2-1, O2-2, TA-3, DIC-2, pH-6, ISO-2, NUT-6

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