Methane and nitrous oxide concentrations and sea–air fluxes in western Long Island Sound, a eutrophic urban estuary: Hourly to seasonal variability

Cara C. M. Manning[1], Anagha Payyambally[1], Josie L. Mottram[1], and Kelsey Ward[1]

[1]University of Connecticut, Department of Marine Sciences, Groton, CT, 06340, USA

Correspondence to: Cara C. M. Manning (cara.manning@uconn.edu)

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Methane and nitrous oxide concentrations and sea–air fluxes in western Long Island Sound, a eutrophic urban estuary: Hourly to seasonal variability

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[1]University of Connecticut, Department of Marine Sciences, Groton, CT, 06340, USA

Correspondence to: Cara C. M. Manning (cara.manning@uconn.edu)

Abstract. Western Long Island Sound is a seasonally hypoxic urban estuary undergoing anthropogenic change, which may influence concentrations and emissions of the potent greenhouse gases methane (CH_4) and nitrous oxide (N_2O). To provide a benchmark of current gas distributions in this system, enabling detection of future changes and comparison with data from other estuaries worldwide, we obtained the first water column profiles of dissolved CH_4 and N_2O concentrations in western Long Island Sound. We collected samples at seven stations along an 18 km transect in August 2023, October 2023, and May 2024. CH_4 concentrations and sea–air fluxes were highest in August (mean concentration of 101 nmol kg^{-1} and mean sea–air flux of 154 μmol m^{-2} d^{-1}) and lowest in May (mean concentration of 32 nmol kg^{-1} and mean sea–air flux of 62 μmol m^{-2} d^{-1}). Conversely, N_2O concentrations and sea–air fluxes were highest in May (mean concentration of 12.0 nmol kg^{-1} and mean sea–air flux of 4.8 μmol m^{-2} d^{-1}) and lowest in August (mean concentration of 10.1 nmol kg^{-1} and mean sea–air flux of 2.5 μmol m^{-2} d^{-1}). Surface concentrations and sea–air fluxes of CH_4 and N_2O were highest at the westernmost station (closest to New York City) in all three seasons, suggesting that there is a persistent source of surface water to western Long Island Sound with high concentrations of CH_4 and N_2O. To investigate short-term variability in CH_4, N_2O, and oxygen (O_2), we collected samples every 4 h over 28 h at the middle station of the transect, in all three months. We concluded that there is measurable short-term variability in all three gases, and that the drivers of variability in these dissolved gases are complex and not dominated by tidal advection or light levels alone.

Keywords: methane; nitrous oxide; oxygen; hypoxia; estuary; diel cycle

1. Introduction

Long Island Sound (LIS) is an urban estuary that receives wastewater discharge from the most populous city in the USA, New York City, and undergoes seasonal hypoxia. Hypoxic conditions, often defined as dissolved oxygen (O_2) concentrations lower than 64 μmol L^{-1} (2 mg L^{-1}), can be harmful or fatal to a range of marine life (Diaz and Rosenberg, 2008; Vaquer-Sunyer and Duarte, 2008). Eutrophication (excess nitrogen inputs from human activities, including point source wastewater discharge and runoff) contributes to hypoxia in LIS by driving the overproduction of photosynthetic organisms at the surface and consumption of O_2 at depth from decomposition (Parker and O'Reilly, 1991; Varekamp et al., 2014).

Regionally, hypoxia is most severe in western LIS due to the restricted circulation and proximity to wastewater inputs from New York City (Lee and Lwiza, 2008; Whitney and Vlahos, 2021). The East River is a tidal estuary between Manhattan and Brooklyn/Queens which discharges Hudson River water and New York City wastewater into western LIS (Figure 1). There are currently six wastewater treatment plants in the East River which collectively discharge wastewater from 4 million of the 8 million residents of New York City (NYCDEP, 2025). These wastewater treatment plants contributed a nitrogen (N) loading of 2 x 10^6 kg N y^{-1} in 2016, accounting for >95% of the total N load from the East River, 18% of the total N loading to LIS in 2016 (Vaudrey, 2017) and 11% of the N load to LIS from 1995−2016 (Vlahos et al., 2020). The East River is the largest source of freshwater to western LIS, with a mean surface advective flux of 260 m^3 s^{-1} (Gay et al., 2004; Vlahos et al., 2020). The majority of the N load from larger rivers in the eastern and central LIS, such as the Connecticut River (mean discharge 500 m^3 s^{-1}), does not enter western LIS (Gay et al., 2004; Vlahos et al., 2020). For western LIS, Vlahos et al. (2020) determined that the East River is likely the largest source of N, contributing (3.2 ± 2.2) × 10^6 kg N y^{-1}, as compared to other rivers which contributed (2.6 ± 0.8) × 10^6 kg N y^{-1}, atmospheric deposition which contributed (1.2 ± 0.2) × 10^6 kg N y^{-1}, and lateral transport from central LIS which contributed (0.3 ± 1.7) × 10^6 kg N y^{-1} for the period 1995−2016. The study of Vlahos et al. (2020) defined western LIS to include all areas west of the Housatonic River; because our study focuses on only the westernmost half of this region, the influence of the East River will be even more prominent (Figure 1). Prior observations in the East River have demonstrated elevated nutrient levels associated with wastewater input to this system (Bowman, 1977; Li et al., 2018; Wallace, 2020). Wastewater treatment plant upgrades over recent decades have reduced the amount of N pollution entering LIS by 60% from the year 2000 baseline and reduced the 5-year average overall hypoxic area in LIS. However, hypoxia continues to occur annually in western LIS, and the hypoxic area in the far western sound actually increased from 2017 to 2023 (Whitney and Vlahos, 2021; Duvall et al., 2024). Ongoing and future climate change contributes to the persistence of hypoxia in western LIS: warming temperatures reduce the solubility of O_2 in water and may also increase respiration rates and stratification (Parker and O'Reilly, 1991; Wilson et al., 2008; Irby et al., 2018; Whitney and Vlahos, 2021). Other temperate urban estuaries also experience interacting stressors from nutrient pollution and climate change (Howarth et al., 2011; Irby et al., 2018).

Methane (CH_4) and nitrous oxide (N_2O) are potent greenhouse gases that have a lower atmospheric concentration than carbon dioxide (CO_2), but much higher global warming potentials (heat-trapping ability per unit mass; Forster et al., 2021). Reported emissions of CH_4 and N_2O are widely variable across different coastal and estuarine systems (Robinson et al., 1998; Seitzinger et al., 2000; de Wilde and de Bie, 2000; Naqvi et al., 2010; Harley et al., 2015; Capelle and Tortell, 2016; Kock et al., 2016; Rosentreter et al., 2021; Zheng et al., 2022). For example, a recent global meta-analysis reported that published estuarine sea–air gas fluxes range from 0 to 50,000 μmol m^{-2} d^{-1} for CH_4 and −60 to 500 μmol m^{-2} d^{-1} for N_2O (Zheng et al., 2022). Previous publications with data from LIS reported measurements of benthic N_2O and CH_4 production, groundwater-associated N_2O fluxes, and sedimentary CH_4 concentrations (Martens and Berner, 1974; Martens and Berner, 1977; Young et al., 2016; Mazur et al., 2021). To our knowledge there are no published water column measurements of N_2O or CH_4 concentrations or sea–air fluxes in LIS.

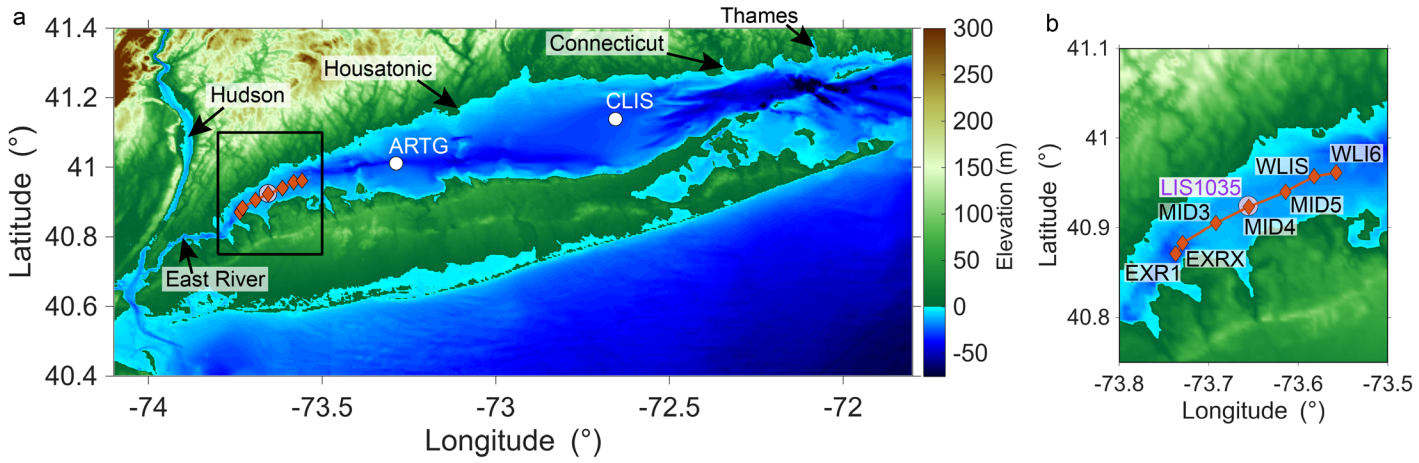

Figure 1. Maps of Long Island Sound and the transect sampled

a) The locations of stations sampled on each cruise are shown as orange diamonds and the stations sampled only in May 2024 (ARTG and CLIS) are shown with white circles. Large rivers influencing LIS are shown with black arrows (the Hudson, Housatonic, Connecticut, Thames, and East River). Elevation data were retrieved from The GEBCO Grid (GEBCO Compilation Group, 2024). b) Enlargement of the black-lined area in panel a), showing the station used for current speed predictions (LIS1035), near MID4, with a purple circle.

Alt Text: Map of the study area showing elevation above and below sea level and the locations of the stations at which data were collected. One panel shows all of LIS and the other shows an enlargement of the region near 40.9° N, 73.65° W where the water sampling transect was centered.

Biochemical reactions are associated with the production and consumption of CH_4 and N_2O (Reeburgh, 2007; Bange et al., 2010). CH_4 is produced and consumed through anaerobic and aerobic processes associated with organic matter diagenesis, chemotrophic reactions, the metabolism of methylated phosphorus and sulfur species, and photochemical reactions occurring in the water column, sediments, and sinking particles (Ward et al., 1987; Reeburgh, 2007; Mau et al., 2013; Damm et al., 2015; Repeta et al., 2016; Bianchi et al., 2018; Li et al., 2020; Fazi et al., 2021; Perez-Coronel and Beman, 2022; Hall et al., 2025). Anaerobic methanogenesis has previously been reported in LIS sediments in some of the earliest work on marine sedimentary organic matter diagenesis (Martens and Berner, 1974; Martens and Berner, 1977). The balance between these CH_4 sources and sinks influences estuarine emissions of CH_4 (Mao et al., 2022).

N_2O is generated as a byproduct during ammonium oxidation, the first step of nitrification, a chemoautotrophic process that yields energy from the conversion of ammonium to nitrite (NH_4^+ to NO_2^-; Ward, 2008). Additionally, N_2O is an intermediate in heterotrophic denitrification, an anaerobic organic matter degradation process (Bange et al., 2010). Depending on environmental conditions, denitrification can either be a net source or sink of N_2O, with suboxic conditions tending to favor net N_2O production (incomplete denitrification) and anoxic conditions favoring N_2O consumption (complete denitrification; Bange et al., 2010; Kock et al., 2016). Additionally, nitrification and denitrification can be coupled through the process of nitrifier denitrification, where the oxidation of NH_4^+ to NO_2^- is followed by reduction of NO_2^- to nitrogen gas (N_2) through intermediates, including N_2O (Wrage et al., 2001).

This study focused on CH_4 and N_2O dynamics in LIS. Our objectives were to obtain the first water column measurements of these gases, characterize hourly to seasonal variability, and calculate their sea–air fluxes. In coastal systems, biogeochemical parameters can vary on sub-daily timescales due to both physical and biological forcing (e.g., due to daily changes in tidal phase and light levels), but this variability has rarely been explored for CH_4 and N_2O. We evaluated how sampling time influences their concentrations and calculated fluxes. We determined the contribution of CH_4 and N_2O to the C and N budgets for LIS and compared their fluxes, after conversion to CO_2-equivalents, with previously published CO_2 data for western LIS. We place the results of this study in the context of other estuarine studies and discuss potential drivers of

the observed trends. This study contributes new data to support broader scientific understanding of greenhouse gas dynamics in urban estuaries.

2. Methods

2.1 Sampling locations, timing, and procedures

We collected samples during cruises on the R/V *Connecticut* (August 2–3, 2023, October 19–20, 2023, and May 22–23, 2024). On each cruise, we collected water column profiles at the same seven stations spanning an 18 km transect (Figure 1). These stations were sampled on day 2 over a 6-h period, beginning at approximately 07:00 local time at the westernmost station (EXR1) and proceeding sequentially toward the easternmost station (WLI6). Two of the stations were sampled repeatedly: station MID4 was sampled every 4 h over a 28-h period (eight times in total, beginning near 08:00 on day 1 and continuing until approximately 12:00 on day 2), and station EXRX was sampled at approximately 09:00 on days 1 and 2. For both EXRX and MID4, the final profile was collected as part of the seven-station transect on day 2. Station depths ranged from 13 m to 32 m.

During the May 2024 cruise only, we sampled at stations CLIS and ARTG (closer to the mouth of the estuary) following the sample collection at WLI6 on day 2. To identify seasonal variability using a consistent dataset, the observations at stations CLIS and ARTG have not been included in the discussion and visualizations of this manuscript but are included in the datasets archived to PANGAEA (Manning et al., 2026a; 2026b).

Water samples were collected from Niskin bottles attached to a rosette equipped with conductivity-temperature-depth (CTD) and O_2 sensors (Sea-Bird Electronics SBE 9 with SBE 43). Additionally, to get near-bottom water at each station, a Niskin bottle was lowered by hand to approximately 1 m above the seafloor and manually closed. Seven depths were sampled at every station. The shallowest sample on each cast was collected at approximately 2 m depth and is hereafter referred to as the “surface” sample.

The water sample temperature, salinity, and O_2 concentrations reported in this paper and the accompanying datasets were taken from the sensor data corresponding to the time the bottle was closed (after at least 30 s of stabilization at a fixed depth). Due to the strong stratification of the system (median mixed layer depth 5 m), along with the slow response time (hysteresis) of the SBE43 O_2 sensor (Martini et al., 2007; Bittig et al., 2018) and the delayed response of the salinity sensor due to the internal pump, there were often offsets between the upcast and downcast that could not be eliminated even after accounting for these delays. On the downcast, the profiler was moving at roughly 1 m s^{-1} and the measured O_2 values lagged significantly behind the in situ values.

The temperature, salinity, and O_2 data for each near-bottom sample were taken from the CTD data matching with the deepest bottle closed on the corresponding rosette cast. Although a CTD and O_2 sensor attached to a frame without a rosette was deployed by hand to obtain a reading nearer to the bottom, the CTD frame stirred up sediment as it approached the seafloor, leading to erroneous salinity readings and making this method unreliable. O_2 was calibrated as described in Section 2.3 and the other CTD sensors used the manufacturer’s calibration. Salinity is reported on the unitless practical salinity scale (PSS-78).

2.2 CH_4 and N_2O sample collection and analysis

Water samples for CH_4 and N_2O analysis (duplicates for each depth) were collected into 120 mL glass serum bottles using flexible PVC tubing, with at least three times the sample volume flowing through the bottle before the sample was sealed. Samples were preserved following published procedures: 0.5 mL of 8 M potassium hydroxide (KOH) was used in August (Magen et al., 2014) and 100 µL of 3.8 g L^{-1} mercuric chloride solution (50% saturation) was used in October and May (Dickson et al., 2007). Experiments in our laboratory have demonstrated that these two preservation methods yield statistically equivalent and stable concentrations for CH_4 and N_2O over storage periods from 0–6 months (Payyambally, 2026). Samples were sealed with bromobutyl rubber stoppers and aluminum crimp seals. Analysis was completed within 5 months of each cruise.

Samples were prepared for analysis using headspace equilibration (Magen et al., 2014; de la Paz et al., 2021). Approximately 22 mL of water sample was removed while the same volume of ultrahigh purity N_2 (5.0 grade) at ambient atmospheric pressure was added. The samples were shaken for 3 h at room temperature. Then, approximately 20 mL of the headspace was transferred to a 12 mL pre-evacuated vial (Labco Exetainer) by injecting 20 mL of brine solution (105 mg L^{-1} NaCl) into the bottom of the sample bottle and inserting a needle into the headspace to transfer the headspace gas into the vial. The Exetainer was filled to >1 atm pressure to prevent air from entering the vial when the needle was removed. The Exetainers contained dried KOH to remove CO_2, which can interfere with the quantification of N_2O (Zheng et al., 2008).

Samples were analyzed using an SRI 8610C gas chromatograph with flame ionization detector (FID) for CH_4 and electron capture detector (ECD) for N_2O. An xyzTek Bandolero autosampler was used to transfer the sample into two loops in sequence, with a 2 mL loop going to the FID and 0.25 mL loop going to the ECD. The sample loop and autosampler tubing were evacuated to below 6 torr, and then a needle was injected into the Exetainer vial, allowing the sample gas to fill the evacuated loops. The injected gas in the sample loop equilibrated to atmospheric pressure before it was transferred to the column. The FID flow path included a HayeSep D pre-column followed by a Shincarbon column to optimize separation of O_2 and CH_4. For the ECD, there was a HayeSep D pre-column followed by two HayeSep D columns with a vent in between to prevent O_2 from reaching the detector. Backflushing the pre-columns prevented water vapor from entering the main separatory columns. For the FID we used N_2 as carrier gas, with hydrogen added to generate the flame, and for the ECD we used N_2 as carrier gas, with P5 (95% CH_4, 5% argon) added as makeup gas at the detector to increase sensitivity.

Samples were calibrated using an Airgas certified standard containing 9.82 ppm CH_4 and 7.97 ppm N_2O in N_2. The Airgas standard was calibrated internally using an air standard from the NOAA Carbon Cycle Greenhouse Gases Group (Boulder, Colorado, USA) to reference all data to the WMO scale (Dlugokencky et al., 2020a; 2020b) with an accuracy of 1% for both CH_4 and N_2O. For each set of water samples run, a set of seven standards ranging from 0 to 9.82 ppm CH_4 and 0 to 7.97 ppm N_2O was prepared by mixing the Airgas standard with pure N_2 using Alicat mass flow controllers and injecting each standard mixture into Exetainers. A linear calibration curve was used for CH_4 and a quadratic calibration curve was used for N_2O (Wilson et al., 2018).

Samples of deionized water equilibrated at room temperature were included in every analytical batch. Community reference materials for CH_4 and N_2O in water are not commercially available, and therefore, preparation of air-equilibrated water samples in house is currently recommended as a quality assurance measure (Wilson et al., 2018). Compared to expected results based on atmospheric gas concentrations in Mashpee, Massachusetts, USA (see Section 2.4), the average error for these samples was 0.32 nmol kg^{-1} for CH_4 and 0.07 nmol kg^{-1} for N_2O. The median precision of duplicate field samples was 4 nmol kg^{-1} (7% relative standard deviation) for CH_4 and 0.3 nmol kg^{-1} (3% relative standard deviation) for N_2O.

2.3 O_2 sample collection and analysis and correction of in situ O_2 data

Discrete samples for measuring O_2 concentration were collected on several casts on each cruise. Duplicate or triplicate samples were collected into 140 mL glass biological oxygen demand (BOD) flasks with flared necks using flexible PVC tubing, with at least three times the sample volume flowing through the bottle before the sample was sealed. O_2 samples were preserved by adding 1 mL of $MnCl_2$ solution and 1 mL of NaI-NaOH solution before inserting a ground glass stopper (Langdon, 2010). The flared neck was filled with water, and the neck and stopper were covered with a latex rubber seal to keep the stopper in place and reduce evaporation. Samples were stored in the dark prior to analysis, which occurred within a few days of each cruise. Analysis was performed via amperometric Winkler titration with a precision of 0.3% based on the standard deviation of replicate samples (Langdon, 2010). The discrete O_2 sample data were used to apply a linear correction factor to the SBE 43 O_2 sensor data for each cruise.

2.4 Equilibrium concentrations and sea–air flux calculations

In this manuscript, we report the saturation anomaly, Δ, as the concentration or percentage over or undersaturation (depending on context). For O_2:

$$\Delta O_2, \mu\text{mol kg}^{-1} = [O_2]_{meas} - [O_2]_{eq} \quad (1)$$

$$\Delta O_2, \% = \frac{[O_2]_{meas} - [O_2]_{eq}}{[O_2]_{eq}} \times 100\% \quad (2)$$

Here $[O_2]_{meas}$ and $[O_2]_{eq}$ are the measured and equilibrium concentrations of O_2, respectively. Equilibrium concentrations were calculated from the measured temperature and salinity following Wiesenburg and Guinasso (1979) for CH_4 and Weiss and Price (1980) for N_2O using MATLAB functions by Manning and Nicholson (2026). All gas concentrations are reported in molal units (mol kg^{-1}) to allow the gases to be used as conservative tracers, following the conventions of the Global Ocean Ship-Based Hydrographic Investigations Program (GO-SHIP) and Biogeochemical Argo (Bittig et al., 2018; Thierry et al., 2025).

Sea–air gas flux was calculated for CH_4 as follows, and an analogous approach was used for N_2O:

$$F = k\left([CH_4]_{meas} - [CH_4]_{eq}\right). \quad (3)$$

Here positive values indicate a net sea-to-air flux (i.e., outgassing), and *k* is the gas transfer velocity calculated with the equation of Wanninkhof et al. (2014), which is a function of the wind speed at 10 m height and the Schmidt number (ratio of the seawater kinematic viscosity to the gas diffusivity). The Schmidt number is calculated for CH_4 following Jähne et al. (1987) and for N_2O following Wanninkhof (2014), which uses coefficients based on prior publications by Hayduk and Laudie (1974) and Wilke and Chang (1955).

For calculating equilibrium concentrations, the dry atmospheric concentrations of CH_4 and N_2O were set to 2020 ppbv and 338 ppbv, respectively. These concentrations are taken from preliminary surface flask measurements from Mashpee, Massachusetts, USA (station MSH) from the NOAA Carbon Cycle Greenhouse Gases group website (Andrews et al., 2023; Miller et al., 2026) and represent the average over the three cruises (Dlugokencky et al., 1994; 2020a; 2020b; Hall et al., 2007; Lan et al., 2021). Final surface flask results were not available at the time of dataset submission to PANGAEA, but small changes in the atmospheric concentration of both gases would have a negligible impact on the calculated equilibrium concentrations and sea–air fluxes, relative to other sources of error in the measurements and calculations. Final CH_4 data from station MSH were made available after dataset publication and indicate that the atmospheric concentration

was 0.2% higher (2024 ppbv). This difference is much smaller than the measurement uncertainty (e.g., 7%, the mean relative standard deviation for duplicate samples). The dry atmospheric concentrations were adjusted to wet concentrations by assuming 100% relative humidity at the air-sea interface and adjusted to local sea level pressure using the mean sea level pressure from the 15 days prior to each measurement, obtained from a mooring at station EXRX, NOAA buoy 44022 (US Department of Commerce, 2025). Wind speed was measured on the same mooring and extrapolated from the measurement elevation of 3.5 m to 10 m following Hsu et al. (1994).

Because gas transfer velocity is a non-linear function of wind speed, higher wind speeds have a disproportionate effect on the total flux, and therefore gas fluxes calculated based on average wind speeds will underestimate the true flux and fluxes based on instantaneous wind speeds can be biased high or low (Wanninkhof et al., 2009). In the archived dataset, we have reported fluxes calculated by two different methods: using instantaneous winds (15 min average), and using a time-weighted approach incorporating winds up to 15 days prior to sampling (Manning et al., 2026b). The weighted approach follows the equation of Teeter et al. (2018), which is modified from Reuer et al. (2007):

$$k = \frac{\sum_{t=1}^{n} k_t\, \omega_t}{\sum_{t=1}^{n} \omega_t} \tag{4}$$

$$\omega_n = 1,\ \omega_i = \omega_{i+1}(1 - f_{i+1}) \tag{5}$$

$$f_i = \frac{k_i \Delta t}{\mathrm{MLD}} \tag{6}$$

In Equation 4, t is the time index, with $t = n$ representing the time of sampling, and $t = 1$ occurring 15 days prior. The term k_t refers to the gas transfer velocity (m s^{-1}) at time step t, and ω_t is the weighting at index t (ranging from 0 to 1). The variable f_i is the fraction of the mixed layer ventilated at index i, ω_i is the weighting coefficient at index i, MLD is the mixed layer depth, and Δt is the time interval between each wind speed measurement (15 min in this study). We use a time interval of 15 min so that $f_i \leq 1$ at every time point, despite the shallow mixed layer depths. The weighting coefficient decreases going back in time, because it is the product of the current weighting coefficient and the previous weighting coefficient (always ≤ 1), and also decreases when the gas transfer velocity decreases.

The MLD was defined using CTD profiles that were averaged into 1 m depth bins, based on a density difference criterion of 0.125 kg m^{-3} relative to the shallowest bin (centered at 2 m or 3 m). The mixed layer depth was assumed to be constant in time for the flux calculation. Mixed layer depths ranged from 3 m to 14 m (median of 5 m, mean of 5.8 m).

A weighting period of 15 days was selected due to the shallow MLD. The mean residence time of both CH_4 and N_2O was 4 days (calculated from the ratio of the MLD to the gas transfer velocity). Additionally, the meteorological sensors on the buoy at EXRX malfunctioned beginning in September 2023 and were replaced 16 days prior to the October cruise. For this reason, a longer weighting period in October was not possible. For May and August, where 30 days of wind speed data was available prior to the cruise, we compared the gas transfer velocities calculated using a weighting period of 15 days and 30 days and found that they agreed within 3%.

In this manuscript, we focus on the time-weighted flux results, consistent with many other publications reporting CH_4 and N_2O fluxes, because this method better reflects the typical gas flux occurring over multiple days in each season and allows for more robust seasonal comparisons (Townsend-Small et al., 2014; Capelle et al., 2019; Zhan et al., 2021; Manning et al., 2022; Schuler and Tortell, 2023). In August, the instantaneous fluxes were on average four times lower than the weighted fluxes, whereas in May the instantaneous fluxes were on average three times higher than the weighted fluxes, due to short-term variability in wind speeds.

Typical uncertainty in sea–air gas fluxes was estimated to be 24% for CH_4 and 26% for N_2O using a Monte Carlo error analysis that incorporated the largest known sources of uncertainty (quantified here as relative standard deviation): the parameterization of *k* as a function of wind speed, at 20% per Wanninkhof et al. (2014); the measured wind speed, at 3% per the sensor manufacturer's specifications; and the gas concentration, at 12% for CH_4 and 4% for N_2O. The uncertainty in the gas concentrations was estimated based on the relative standard deviation of repeated measurements at station MID4 collected during each cruise; this reflects uncertainty in the fluxes driven by short-term variability in gas concentrations that was not captured by the instantaneous sampling. The uncertainty due to instantaneous sampling is greater than the analytical uncertainty (reproducibility of duplicates). One potential systematic error that is not captured in our error estimates is lateral variability in wind speed along the transect, which could not be quantified as wind speed data were only available at station EXRX. Additionally, we decided to use the parameterization of Wanninkhof et al. (2014), which was developed using open ocean data, rather than a parameterization developed for riverine or estuarine systems. Ho et al. (2011) conducted a tracer release study in the Hudson River (a tidally influenced river that partially flows into the East River) and found that a wind speed-based parameterization developed for the open ocean was accurate in this system; the effect of bottom turbulence was negligible. Given the deeper depths in our study region (13–32 m) as compared to the average depth of 6 m in the Hudson River study, we expect bottom turbulence to play a smaller role in western LIS. Currently, scientists lack a broad consensus on the appropriate gas exchange parameterization for estuarine systems due to the variable impacts of factors including wind speed, fetch, currents, bottom-driven turbulence, turbidity, and surfactants (Raymond and Cole, 2001; Borges et al., 2004; Upstill-Goddard, 2006; Abril et al., 2009). Our estimated uncertainties in the gas fluxes represent a lower limit.

3. Results and discussion

3.1 Seasonal and spatial trends in hydrography

The sampling months were chosen to reflect the annual variability in hydrographic properties in western LIS. We sampled in August 2023 (near the annual maximum extent of hypoxia), October 2023 (following seasonal ventilation of the subsurface), and May 2024 (near peak river inflow and prior to the onset of hypoxia). Progressive cooling and freshening occurred from August through May. Specifically, in August, temperature ranged from 20.1°C to 24.1°C and salinity from 26.0 to 27.0; in October, temperature ranged from 17.0°C to 18.1°C and salinity from 24.7 to 26.5; and in May, temperature ranged from 11.4°C to 17.9°C and salinity ranged from 22.4 to 24.2 (Figure 2). Our hydrographic data are consistent with prior observations, which showed the annual minimum salinity in LIS typically occurs in May and is associated with peak river discharge (Lee and Lwiza, 2005; O'Donnell et al., 2008; 2014).

Using transect data at the depths sampled for gases, the in situ temperature was 21.6 ± 0.9°C in August, 17.4 ± 0.4°C in October, and 13.6 ± 1.8°C in May (mean ± standard deviation, n = 106 in each month). Salinity was 26.63 ± 0.27 in August, 25.71 ± 0.52 in October, and 23.39 ± 0.49 in May. October displayed the least stratification, and May displayed the strongest stratification and shallowest MLDs (Figure 3j–l). In October, the thermal gradient reached a minimum, with surface waters typically displaying a lower temperature than the subsurface (mean surface temperature of 17.1°C; mean temperature below 10 m of 17.7°C). Seasonal cooling due to changes in surface heat flux causes a decline in temperature and stratification over fall and winter (Lee and Lwiza, 2008; O'Donnell et al., 2014).

Generally, density and salinity increased from west to east throughout the water column (Figure 3j-o), consistent with prior observations and reflecting the influence of the low salinity waters discharged from the

East River (Lee and Lwiza, 2005; O'Donnell et al., 2008). Within the East River, there is two-layer estuarine flow with net surface transport toward LIS and subsurface transport toward New York Harbor, though the flow direction can reverse temporarily (Blumberg and Pritchard, 1997; Gay et al., 2004). For example, in October, salinity increased from 24.68 at EXR1 to 25.86 at WLIS and 25.74 at WLI6. One notable outlier from these trends was found at station EXRX in May. In May on day 2, when the transect was sampled, EXRX displayed the highest surface density anomaly of all the stations (16.8 kg m^{-3}), in comparison to 16.0 kg m^{-3} at EXR1 to the west and 16.0 to 16.3 kg m^{-3} at the remaining stations to the east. The surface temperature was significantly lower at EXRX (14.5°C), as compared to 16.2–17.3°C at all other stations. The surface salinity at EXRX was 22.88, which fell between the values at the easternmost stations WLIS (22.86) and WLI6 (23.03) and was significantly higher than EXR1 (22.38). The MLD at EXRX was 7 m, as compared to 3 m to 5 m at the remaining stations. Notably, when sampled in May on day 1 of the cruise, EXRX displayed a surface salinity of 22.35, temperature of 16.0°C, density anomaly of 16.1 kg m^{-3}, and MLD of 4 m (Manning et al., 2026a). Overall, these results suggest the temporary presence of a distinct mixed layer water mass at EXRX in May on day 2 of the cruise.

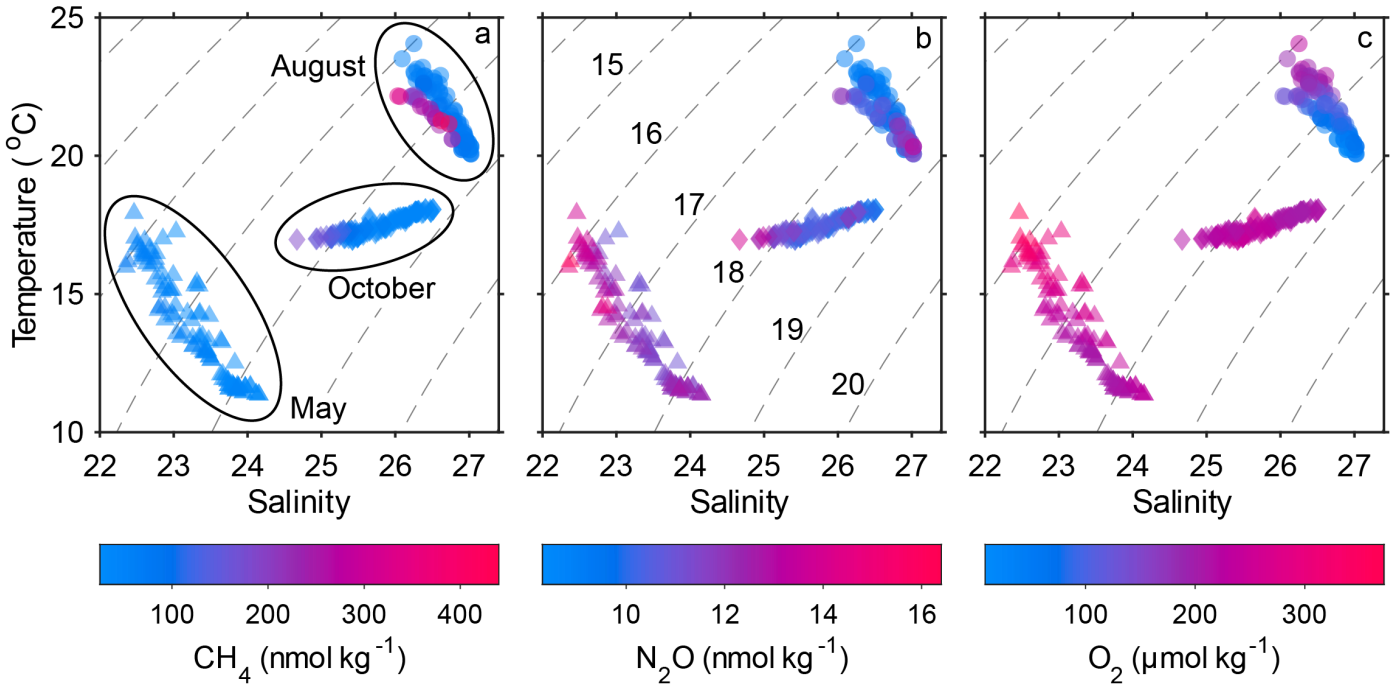

Figure 2. Temperature-salinity plots showing water mass distributions of CH_4, N_2O, and O_2 concentrations.
a) CH_4 concentration, b) N_2O concentration, and c) O_2 concentration during August (circles), October (diamonds) and May (triangles). In panel a, ellipses indicate the cluster of data points from each month. Dashed lines represent the density anomaly (kg m^{-3}), labelled in panel b. All data from all stations are plotted, including repeated profiles at MID4 and EXRX. Salinity is reported on the unitless practical salinity scale (PSS-78).
Alt Text: Scatter plot of dissolved gas concentrations (CH_4, N_2O, and O_2) visualized as a function of temperature and salinity. The data show that distinct water masses were present in each sampling month; all August samples had a higher temperature than measurements in May and October. Conversely, all May samples had a lower salinity than measurements in August and October.

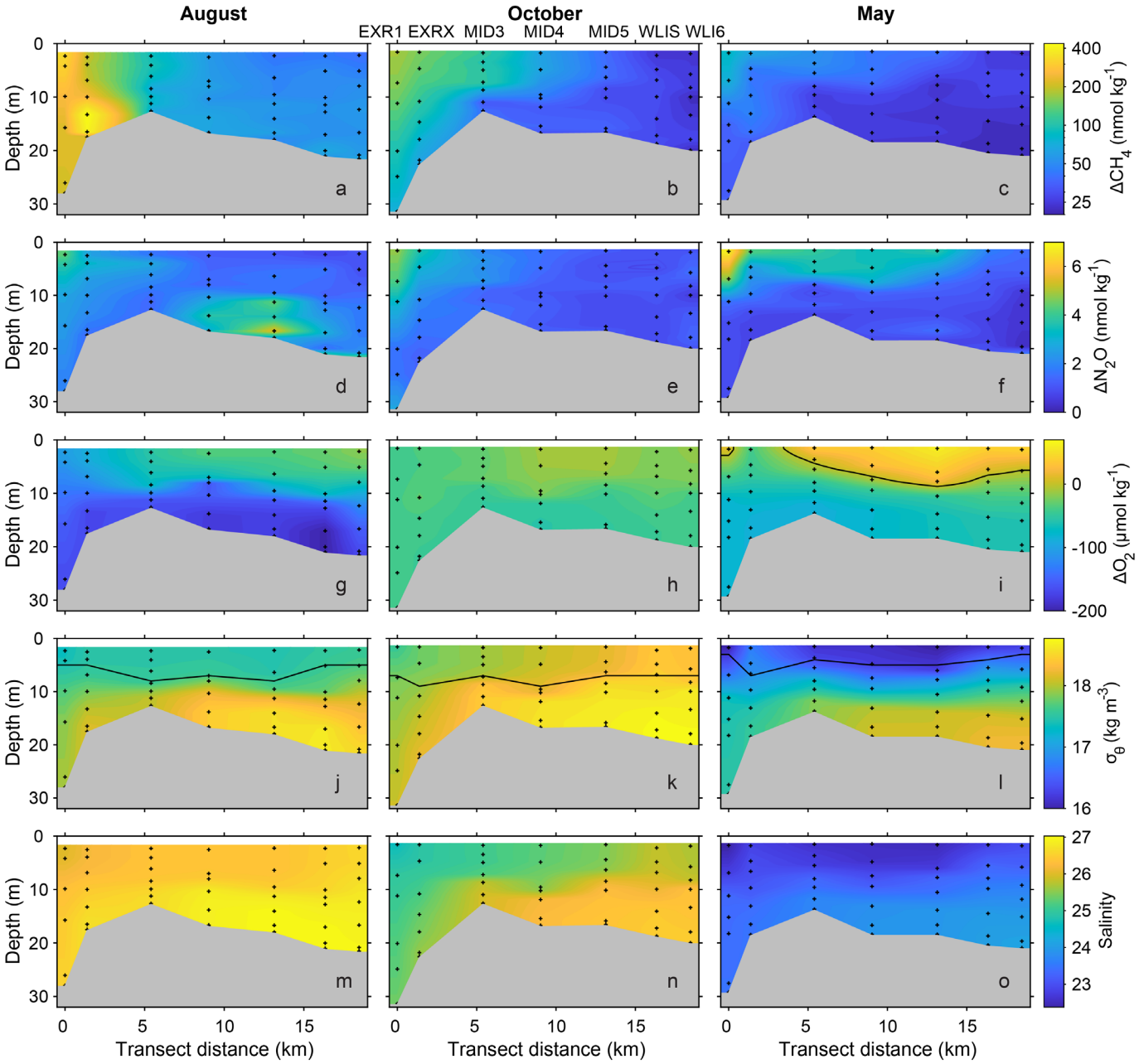

Figure 3. Measurements of dissolved gases and other parameters along the transect in western LIS.
The first three rows show gas saturation anomalies: a–c) ΔCH_4 in nmol kg^{-1}, d–f) ΔN_2O in nmol kg^{-1}, and g–i) ΔO_2 in μmol kg^{-1}. The fourth row (j–l) is the potential density anomaly in kg m^{-3} and the bottom row (m–o) is the salinity, reported on the unitless practical salinity scale (PSS-78). Note that ΔCH_4 is plotted using a logarithmic scale bar to better display the lateral gradients in each season. The black line on panel i represents equilibrium (ΔO_2 = 0 μmol kg^{-1}); O_2 was undersaturated at all stations along the transect in August and October. In the density plots (j–l), the solid line represents the mixed layer depth. The sampling depths are indicated with black circles, and the station names are labelled above panel b. See Figure 1 for the position of the transect.
Alt Text: Depth section contour plots of dissolved gas saturation anomalies (CH_4, N_2O, and O_2), potential density anomaly, and salinity measured in August, October, and May along the seven-station transect shown in Figure 1.

3.2 Seasonal and spatial trends in CH_4, N_2O, and O_2 along the transect in western LIS

Over the three cruises, along the entire transect and at all depths, the range in CH_4 concentration was 25–438 nmol kg^{-1} (saturation anomaly 740–18000%), in N_2O concentration was 8.4–16.3 nmol kg^{-1} (saturation anomaly 2–73%), and in O_2 concentration was 8–372 µmol kg^{-1} (saturation anomaly −96% to 46%) as reported in Table 1 and visualized in Figure 3a–i. On average across the transect, CH_4 concentrations and saturation anomalies were highest in August (mean of 119 nmol kg^{-1}, 4900%) and lowest in May (mean of 38 nmol kg^{-1}, 1200%). Mean N_2O concentrations were highest in May (12.0 nmol kg^{-1}) and lowest in August (10.1 nmol kg^{-1}), whilst the mean N_2O saturation anomaly was highest in August (31%) and similar in October and May (19% in October and 18% in May). Mean O_2 concentrations and saturation anomalies were lowest in August (110 µmol kg^{-1} and −52%) and increased to similar levels in October (220 µmol kg^{-1} and −13%) and May (240 µmol kg^{-1} and −13%). However, O_2 was more homogeneous in October (the saturation anomaly had a standard deviation of 5%, and O_2 was undersaturated at all depths), compared to May (the saturation anomaly had a standard deviation of 15% and reached a maximum of 24%), consistent with a less stratified water column in October (Section 3.1).

Table 1. Temperature, salinity, and gas distributions incorporating measurements along the transect in western LIS from station EXR1 to station WLI6.

Parameter	August		October		May	
	Median[a]	**Mean[b]**	**Median[a]**	**Mean[b]**	**Median[a]**	**Mean[b]**
Temperature (°C)	21.4 (20.9, 22.3)	21.6 ± 0.9	17.3 (17.1, 17.9)	17.4 ± 0.4	13.3 (11.8, 15.2)	13.6 ± 1.8
Salinity[c]	26.6 (26.4, 26.9)	26.6 ± 0.3	25.6 (25.3, 26.2)	25.7 ± 0.5	23.4 (23.0, 23.8)	23.4 ± 0.5
CH_4 concentration (nmol kg^{-1})	68 (58, 194)	119 ± 101	43 (32, 98)	67 ± 44	32 (29, 45)	38 ± 13
CH_4 saturation anomaly (%)	2700 (2300, 8100)	4900 ± 4200	1500 (1200, 3600)	2400 ± 1600	1000 (900, 1500)	1200 ± 500
N_2O concentration (nmol kg^{-1})	9.8 (9.3 10.8)	10.1 ± 1.1	10.2 (9.9, 11.0)	10.5 ± 1.0	11.6 (11.4, 12.5)	12.0 ± 1.1
N_2O saturation anomaly (%)	27 (21, 37)	31 ± 13	16 (13, 22)	19 ± 10	11 (8, 23)	18 ± 15
O_2 concentration (µmol kg^{-1})	89 (69, 159)	110 ± 52	217 (210, 231)	220 ± 14	231 (211, 260)	240 ± 34
O_2 saturation anomaly (%)	−62 (−71, −31)	−52 ± 23	−14 (−16, −8)	−13 ± 5	−19 (−26, −3)	−13 ± 15

[a] Values in parentheses represent the first and third quartile.

[b] Uncertainty is the standard deviation; n = 106 in each month.

[c] Salinity is reported on the unitless practical salinity scale (PSS-78).

The clearest and most seasonally consistent spatial trend in gas concentrations along the transect was that the concentrations of CH_4 and N_2O from the surface to approximately 10 m were highest at the westernmost station, EXR1, and generally decreased eastward, with O_2 showing the opposite trend (Figure 3). Lateral gradients in O_2 in LIS and more severe O_2 depletion in the far western reaches of LIS are both annual features of the O_2 dynamics in LIS (O'Donnell et al., 2014; Whitney and Vlahos, 2021). One exception to this trend was in May 2024 when the westernmost station EXR1 had a higher surface O_2 concentration (276 µmol kg^{-1}) compared to the adjacent station EXRX (233 µmol kg^{-1}). The remaining stations in this transect, to the east of EXRX, had higher and similar O_2 concentrations (290–323 µmol kg^{-1}). However, the CH_4 and N_2O

concentrations at EXR1 and EXRX followed the expected west–east gradient in May (i.e., EXR1 displayed the highest surface concentrations of CH_4 and N_2O). As discussed in Section 3.1, there appeared to be a distinct surface water mass at EXRX in May.

Although O_2 decreased with depth at each station in the transect in all three months, the vertical gradients in CH_4 and N_2O were more variable (Figure 3). In October and May, five to seven of the seven stations had higher CH_4 and N_2O concentrations at the surface than the bottom. In August some stations had both surface and subsurface CH_4 and N_2O peaks; notably, the positions of CH_4 and N_2O maxima did not coincide. The easternmost stations WLIS and WLI6 consistently displayed the lowest surface CH_4 and N_2O concentrations and the smallest vertical ranges in CH_4 concentration. In comparison with N_2O, CH_4 displayed a larger range in concentration and saturation anomaly across the entire transect, as well as a larger range in concentration and saturation anomaly at individual stations on each cruise.

The transect measurements shown in Figure 3 were collected over a 6 h period on each cruise beginning near 08:00 local time. We are unable to evaluate the contribution of temporal differences to the observed spatial trends, given that we only collected one profile at five of the seven stations on each cruise. However, in all three months we observed an enrichment in near-surface CH_4 and N_2O concentrations at the westernmost station (with concentrations decreasing eastward) and depletion in near-surface O_2 concentrations at the westernmost station (with concentrations increasing eastward), giving us confidence that these features were persistent.

3.3 Diel variability in CH_4, N_2O, and O_2 observed in repeat measurements at MID4

To characterize temporal evolution in CH_4, N_2O, and O_2 on sub-daily timescales, we sampled at station MID4 eight times on each cruise (every 4 hours beginning near 08:00 on day 1). We used tidal current speed predictions generated by NOAA for depths of 3 m, 9 m, and 14 m at station LIS1035 (200 m from MID4; Figure 1) to determine the direction of water flow resulting from the semidiurnal tides at MID4 (Bennett et al., 2010; McCardell et al., 2016; Duvall et al., 2024). These predictions have a mean error of 8 minutes or less in the timing of flood, slack and ebb, and current speed root mean square error of 0.04 m s^{-1} (NOAA, 2025). The current predictions indicate that at MID4 during flood tide (positive current speeds), the water flows toward the East River, with a mean flood current direction of 233° at 3 m, 244° at 9 m, and 251° at 14 m. The timing of flood and ebb tides varied with depth. During our three cruises, the peak flood tide (maximum positive current speed on each tidal cycle) occurred first at 14 m, and an average of 18 min later at 9 m, and 38 min later at 3 m (Figure 4a–c). We applied a linear interpolation to the discrete sample data from each profile to estimate the gas concentrations at 3, 9, and 14 m, matching the depths of the tidal current predictions. We then investigated the relationship between tidal stage and interpolated gas concentrations at these three depths.

The concentration of O_2 at MID4 varied with season, depth, and time of day (Figure 4j–l). O_2 concentrations were highest in May (mean of 317 µmol kg^{-1} at 3 m and 212 µmol kg^{-1} at 14 m) and lowest in August (mean of 196 µmol kg^{-1} at 3 m and 49 µmol kg^{-1} at 14 m), matching the seasonal trends across all stations. The variability observed in O_2 at 3 m depth at MID4 over the 28 h repeated sampling was largest in May (range of 87 µmol kg^{-1}, from 276 to 363 µmol kg^{-1}), intermediate in August (range of 37 µmol kg^{-1}, from 179–216 µmol kg^{-1}), and smallest in October (range of 27 µmol kg^{-1}, from 231–258 µmol kg^{-1}). These trends are consistent with the east–west range in O_2 observed along the transect at 3 m depth (Figure 3g–i), which was also largest in May (84 µmol kg^{-1}) and smallest in October (30 µmol kg^{-1}). The range in O_2 at MID4 observed in each month consistently decreased with depth. For example, the range in O_2 in May was 87 µmol kg^{-1} at 3 m depth, 54 µmol kg^{-1} at 9 m depth, and 13 µmol kg^{-1} at 14 m depth.

At MID4, mean CH_4 concentrations were highest in August (55, 64, and 68 nmol kg^{-1} at 3, 9, and 14 m depth, respectively) and lowest in May (46, 30, and 29 nmol kg^{-1} at 3, 9, and 14 m depth, respectively), as shown in Figure 4d–f. Conversely, mean N_2O concentrations were highest in May (12.9, 11.6, and 11.7 nmol kg^{-1} at 3, 9, and 14 m depth, respectively) and lowest in August (8.9, 9.9, and 10.2 nmol kg^{-1} at 3, 9, and 14 m depth, respectively), as shown in Figure 4g–i. For both gases, the seasonal trends at MID4 were consistent with the seasonal trends across the entire transect (Table 1). For each of the three depths evaluated in each of the three months, the CH_4 concentration at MID4 varied by 6 to 25 nmol kg^{-1} over 28 h, and the N_2O concentration varied by 0.4 to 2.2 nmol kg^{-1} over 28 h. Unlike for O_2, we did not observe a consistent decrease in the variability of CH_4 and N_2O with depth in each month. For example, for N_2O, the variability at MID4 was largest at 14 m depth in August and October (2.0–2.2 nmol kg^{-1}) and largest at 3 m depth in May (2.0 nmol kg^{-1}), whereas the lateral variability along the entire transect was largest at 3 m in all three months (3.3–5.3 nmol kg^{-1}) as compared to 9 m and 14 m.

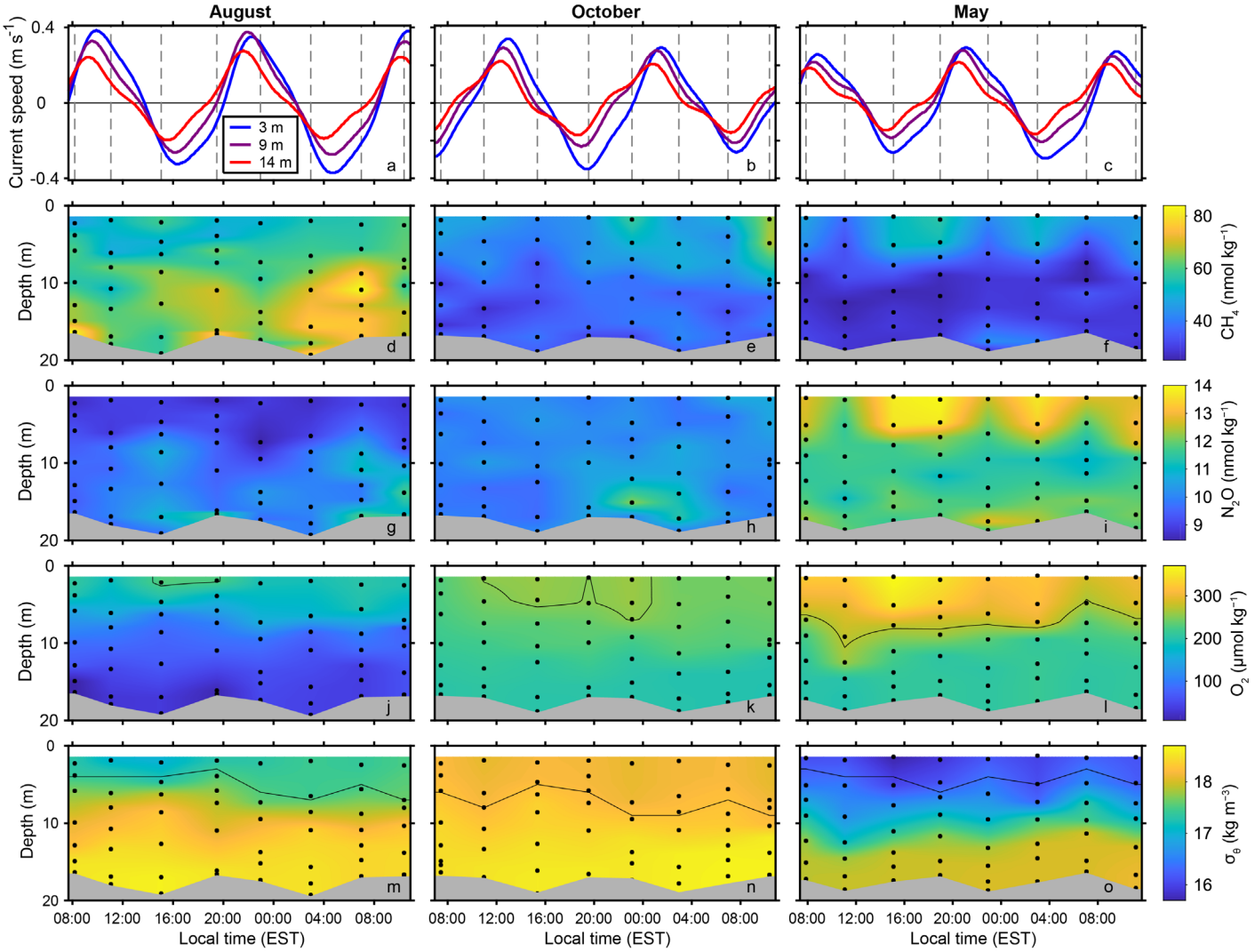

Figure 4. Time-series of repeated measurements at MID4 collected over 28 h in each month.
a–c) Predicted current speed in m s^{-1} at 3 m, 9 m, and 14 m depth (blue, purple, and red lines, respectively) at station LIS1035, near MID4 on a) August 2–3, 2023, b) October 19–20, 2023, and c) May 22–23, 2024. Vertical dashed lines indicate sampling times. Positive current speeds indicate flow toward the southwest (flood tide, increasing water depth). Dissolved gas concentrations in samples collected at station MID4 every 4 h for 28 h: d–f) CH_4 in nmol kg^{-1}, g–i) N_2O in nmol kg^{-1}, j–l) O_2 in µmol kg^{-1}, and m–o) potential density anomaly in kg m^{-3}. Black circles indicate sampling times and depths. Measured bottom depth is variable due to the 2 m tidal range at this site. In the O_2 plots (j–l), the solid black line represents equilibrium (depths above the line are supersaturated), and in the density plots (m–o) the solid line represents the mixed layer depth.

Alt Text: Top panel displays predicted current speeds in August, October, and May at station LIS1035, with a range of −0.4 to 0.4 m s^{-1}. Lower panels display time series of CH_4, N_2O, and O_2 concentrations and potential density anomaly at station MID4.

To further evaluate the influence of diel changes in light and tidal stage on the dissolved gas data, we visualized the MID4 profiles relative to the time of local solar noon (approximately 13:00, varying by month) and relative to tidal phase (peak flood tide) in Figures 5 and 6, respectively. For the evaluation of light effects, we focus our discussion on results at 3 m depth because the daily range in light is largest at this depth. From biological processes alone, we would expect near-surface O_2 to be highest near sunset due to the accumulation of photosynthetic O_2 during the day, and lowest near sunrise, due to the lack of photosynthesis and the continued respiratory consumption overnight (Nicholson et al., 2015; Izett et al., 2024). At 3 m depth, the minimum O_2 concentration in October (231 μmol kg^{-1}) and May (276 μmol kg^{-1}) occurred in the sample collected closest to sunrise, as would be expected for a biologically dominated diel signal (Figure 5). However, in August, the minimum O_2 concentration (179 μmol kg^{-1}) occurred at 2 h before solar noon, with three profiles collected earlier in the morning but after sunrise showing a higher O_2 concentration (193–204 μmol kg^{-1}). In all three months, the maximum O_2 concentration at 3 m depth occurred 2–3 hours after local solar noon, but in all cases, there was a profile collected closer to sunset with a lower O_2 concentration at 3 m. Thus, our sampling at 4 h resolution suggests that near-surface O_2 is likely varying in response to diel changes in photosynthesis rates, but that other factors must also be important drivers. At 9 m and 14 m, there was also a lack of consistent relationship with time of day.

The diel light-driven cycle in CH_4 and N_2O concentrations in western LIS was not known a priori, given that the relative importance of different light-dependent sources and sinks was unknown. For example, nitrification rates are inhibited by light and enhanced by increases in NH_4^+ availability, which can vary daily due to changes in phytoplankton demand (Smith et al., 2014; Proctor et al., 2023). Other studies indicate that both CH_4 and N_2O can be produced in surface waters through photochemical reactions (Tang et al., 2014; Li et al., 2020; Leon-Palmero et al., 2025). At 3 m depth, the minimum CH_4 concentration over 28 h of sampling occurred at 6.5 h, 2.7 h, and −1.8 h relative to solar noon in August, October, and May, respectively, while the maximum CH_4 concentration occurred at −2.6 h, −2.3 h, and 6.1 h relative to local solar noon in August, October, and May, respectively (Figure 5). At 3 m depth, the minimum N_2O concentration occurred at −10.1 h, −9.7 h, and −1.8 h relative to local solar noon in August, October and May, respectively, while the maximum N_2O concentration occurred at −6.0 h, −2.3 h, and 6.1 h relative to local solar noon in August, October, and May, respectively. We conclude that light variability is not the primary driver of daily variability in near-surface CH_4 and N_2O at MID4. For O_2, CH_4, and N_2O, we did not observe any consistent relationships between dissolved gas concentrations and time of day at 9 m and 14 m.

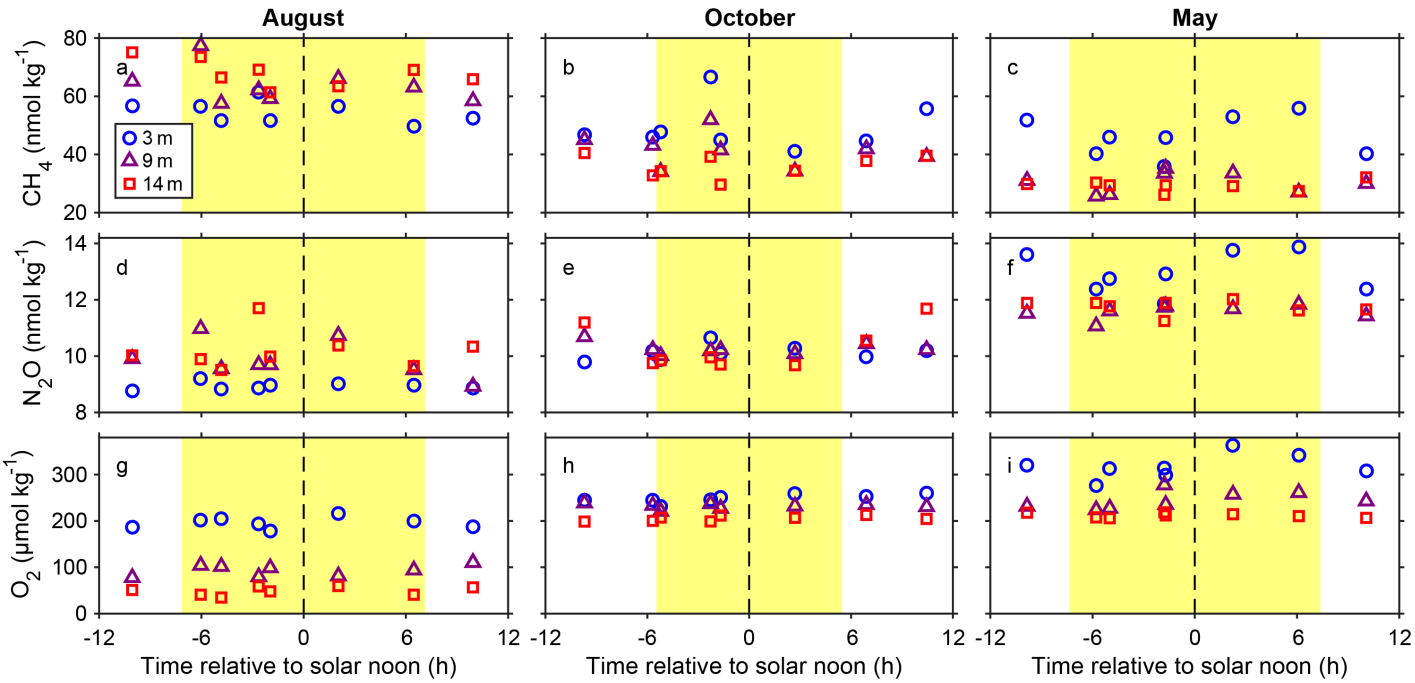

Figure 5. Dissolved gas concentrations at MID4 relative to the timing of solar noon.
Concentrations of: a–c) CH_4 in nmol kg^{-1}, d–f) N_2O in nmol kg^{-1}, and g–i) O_2 in µmol kg^{-1} in August (left), October (center) and May (right column) at depths of 3 m (blue circles), 9 m (purple triangles), and 14 m (red squares). The yellow shaded area is the period from sunrise to sunset.
Alt Text: Timeseries of dissolved gas concentrations (CH_4, N_2O, and O_2) at station MID4 for each cruise, visualized as a function of time relative to solar noon.

To investigate the gas variability relative to tidal phase, we defined the peak flood tide (maximum positive current speed in each tidal cycle) as 0 h and then calculated the time of each profile relative to the closest peak flood (Figure 6). Given the semidiurnal tides at this site, peak ebb will occur at approximately −6.2 h and 6.2 h relative to peak flood. Low and high tide occur at −3.1 h and 3.1 h relative to peak flood, respectively (slack water, current speed of 0 m s^{-1}).

Surface concentrations of CH_4 and N_2O were highest (and O_2 lowest) at the southwestern stations. Therefore, if the observed variability in near-surface gas concentrations was predominantly driven by lateral advection associated with the tides, we would expect CH_4 and N_2O concentrations at 3 m to be lower (and O_2 higher) during periods when water at MID4 had originated from the northeastern sound, i.e., near high tide, the end of the flood current (approximately 3.1 h). Similarly, we would expect CH_4 and N_2O concentrations to be higher (and O_2 lower) near low tide, the end of the ebb current (approximately −3.1 h).

At 3 m depth, the minimum O_2 concentration occurred at 1.2 h, −5.5 h, and −2.4 h relative to peak flood, and the maximum concentration occurred at 5.2 h, −2.4 h, and −6.0 h relative to peak flood in August, October and May, respectively. Thus, only the timing of the minimum O_2 concentration in May (−2.4 h) followed the expected trend for a lateral advection-dominated signal.

Relative to peak flood tide, the maximum concentrations of both CH_4 and N_2O at 3 m depth occurred at −3.4 h in October and −2.1 h in May, while in August, the CH_4 maximum occurred at −0.4 h and the N_2O maximum at −3.8 h. Thus, the timings of all but the maximum CH_4 concentration in August were consistent with variability driven by tidal advection. This result is notable because the CH_4 concentration gradient along the transect in surface waters was largest in August (438 nmol kg^{-1} at westernmost station EXR1, compared to 44 nmol kg^{-1} at WLI6) and therefore we might have expected August to display the greatest sensitivity to tidal advection. The minimum concentrations of CH_4 and N_2O relative to peak flood tide occurred between 1.4 h and 2.4 h in October and May, while in August, the CH_4 minimum occurred at −2.8 h and the N_2O minimum at 4.7

h. Therefore, the timings of the near-surface CH_4 and N_2O minima in October and May were generally consistent with a horizontal advection-dominated signal, but the timings in August were not.

Vertical mixing associated with tides may also influence dissolved gas concentrations. For example, studies using continuous mooring data in western LIS reported that tides contribute to both vertical mixing and lateral O_2 transport. In summer, flood tides can result in vertical transport of well-oxygenated water deeper in the water column, increasing near-bottom O_2 and reducing vertical gradients in O_2 (McCardell et al., 2016; Duvall et al., 2024). However, in this study, at 14 m depth, we again did not see a consistent relationship between tidal phase and O_2 concentrations; the maximum O_2 concentration occurred at 5.8 h, −5.3 h, and 2.9 h relative to peak flood tide in August, May, and October, respectively. For CH_4 and N_2O, the vertical gradient in concentration varied between profiles in a single cruise. For example, in August, CH_4 and N_2O concentrations were always lowest at 3 m, but sometimes there was a subsurface peak at 9 m or at 14 m. In contrast, the O_2 concentration was always highest at 3 m and lowest at 14 m in August. Given the lack of a consistent vertical gradient in CH_4 and N_2O at MID4, we expect that the effect of vertical tidal mixing on CH_4 and N_2O concentrations will vary with time and with season and be smaller than is observed for O_2.

Our observations at MID4 suggest that the drivers of variability in CH_4, N_2O, and O_2 are complex and cannot be correlated to light levels or tidal phase alone. Similarly, Duvall et al. (2024) found that at station EXRX, O_2 was influenced by both the diel variability in photosynthesis rates and in tides. Given the lower sampling frequency and duration of our observations at MID4 (every 4 h over 28 h) as compared to previous studies based on in situ mooring observations (e.g., every 15 min over several weeks), we are unable to perform quantitative correlations between the gas concentration data and tidal phase (or light levels). The data presented here provide the first insights into the influence of tidal dynamics and light on the distributions of CH_4 and N_2O in western LIS.

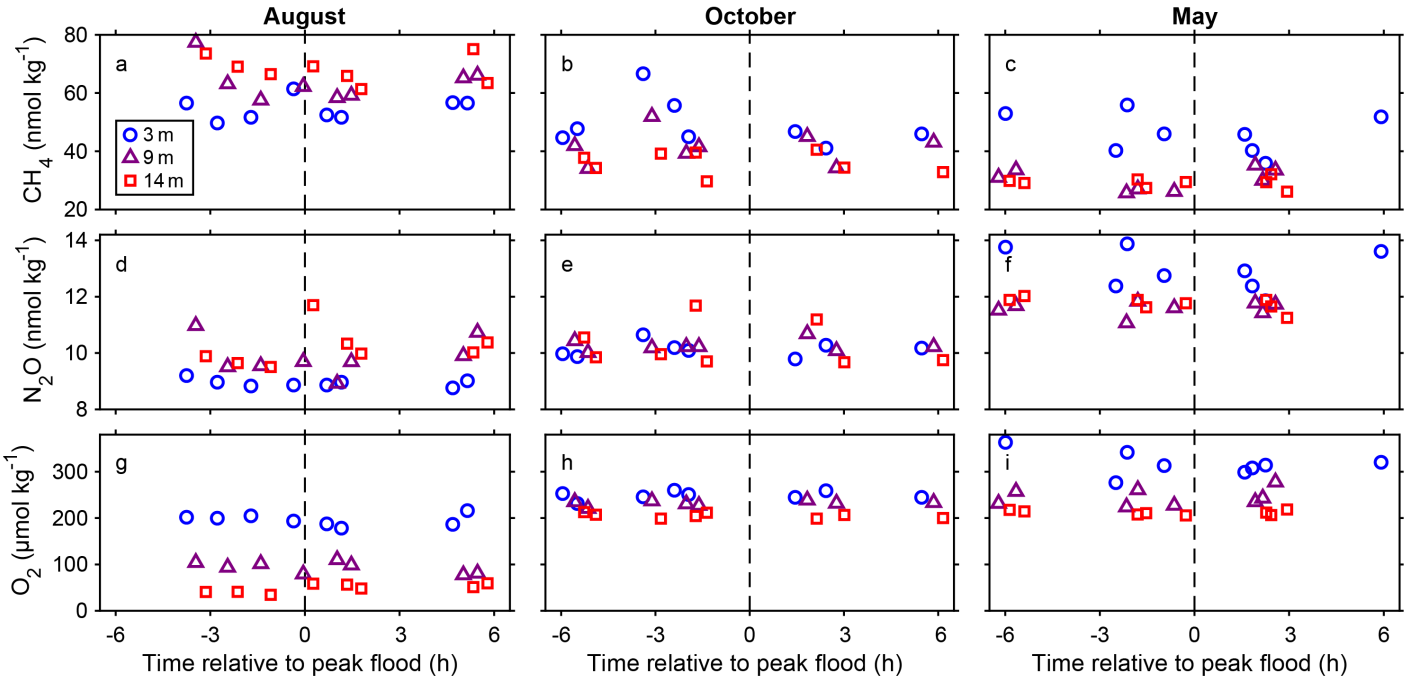

Figure 6. Dissolved gas concentrations at station MID4 relative to the timing of peak flood tide.
Concentrations of: a–c) CH_4 in nmol kg^{-1}, d–f) N_2O in nmol kg^{-1}, and g–i) O_2 in µmol kg^{-1} in August (left), October (center) and May (right column) at depths of 3 m (blue circles), 9 m (purple triangles), and 14 m (red squares).
Alt Text: Timeseries of dissolved gas concentrations (CH_4, N_2O, and O_2) at station MID4 for each cruise, visualized as a function of time relative to peak flood.

3.4 Sea–air fluxes of CH_4 and N_2O

We calculated sea–air fluxes of CH_4 and N_2O at each station in each season, following the 15-day weighting procedure described in Section 2.4, and averaged measurements for the two repeated stations (EXRX and MID4) to obtain one flux for each of these stations in each month. The surface saturation anomalies, concentrations, and weighted sea–air fluxes of both gases were consistently highest at the westernmost station (EXR1) and followed a general decrease toward the east (Figure 7 and Table 2). Across the seven stations, the mean sea–air CH_4 fluxes (μmol m^{-2} d^{-1}) were 154 in August, 133 in October, and 62 in May, and the mean sea–air N_2O fluxes (μmol m^{-2} d^{-1}) were 2.5 in August, 3.3 in October, and 4.8 in May. Thus, the CH_4 fluxes were highest in August, whereas N_2O fluxes were highest in May.

The gas transfer velocities were similar in all three months. Elevated temperatures (highest in August) and elevated wind speeds (highest in October) both increase the gas transfer velocity. The CH_4 gas transfer velocity averaged 1.4 m d^{-1} in August, 1.6 m d^{-1} in October, and 1.3 m d^{-1} in May, and the N_2O gas transfer velocity averaged 1.4 m d^{-1} in August, 1.5 m d^{-1} in October, and 1.2 m d^{-1} in May. We note that seasonal variability in levels of surfactants and turbidity may influence the gas transfer velocity but these variables are not incorporated into our flux calculation (see Section 2.4).

Seasonal variability in the calculated sea–air fluxes was driven primarily by changes in the surface saturation anomaly. For CH_4, August had the highest sea–air flux because the mean CH_4 surface saturation anomaly was 52% higher in August compared to October, even though the gas transfer velocity was 13% lower in August compared to October. For N_2O, the surface N_2O saturation anomaly was highest in May at every station (mean of 41%), leading to enhanced fluxes even though the gas transfer velocity was lowest in this month (Table 2).

To estimate annual fluxes, we used the weighted flux data from August, October, and May and applied a linear interpolation at daily frequency over 1 year. The annual mean CH_4 flux was 106 μmol m^{-2} d^{-1} (median of 66 μmol m^{-2} d^{-1}) and the annual mean N_2O flux was 3.7 μmol m^{-2} d^{-1} (median of 3.2 μmol m^{-2} d^{-1}). This approach has some uncertainty, because we did not collect data during November–April, and we did not utilize wind speed data outside of the 15 days prior to each cruise due to gaps in the mooring wind speed data discussed in Section 2.4. Nevertheless, it provides an initial annual estimate for comparison with results from other estuaries worldwide (Section 3.8).

Finally, we evaluated the effect of the sampling time on the calculated sea–air fluxes. For station MID4, the relative standard deviation of the weighted CH_4 flux from the 8 time points was 12%, 20%, and 21% in August, October, and May, respectively; for the weighted N_2O flux it was 14%, 32%, and 28% in August, October, and May, respectively. The variability in sea–air fluxes was driven primarily by concentration changes, as the weighted gas transfer velocity for both gases had a standard deviation of 4% in August and October and 10% in May. Instantaneous sea–air fluxes showed much stronger variability with the sampling time. For example, the relative standard deviation of the instantaneous gas flux at MID4 in May was 135% for CH_4 and 113% for N_2O due to large changes in wind speed during this cruise. This result demonstrates the advantage of using weighted gas fluxes, which incorporate variability in wind speed.

Table 2. Sea–air fluxes, surface concentrations, and surface saturation anomalies of CH_4 and N_2O from all seven stations, calculated using a 15-day weighting scheme, for each sampling month.

Parameter	August		October		May	
	Median[a]	Mean[b]	Median[a]	Mean[b]	Median[a]	Mean[b]
CH_4 flux ($\mu mol\ m^{-2}\ d^{-1}$)	69 (61, 455)	154 ± 147	72 (40, 287)	133 ± 103	59 (31, 104)	62 ± 25
CH_4 surface concentration ($nmol\ kg^{-1}$)	54 (44, 335)	114 ± 109	50 (28, 185)	86 ± 64	48 (28, 86)	51 ± 21
CH_4 surface saturation anomaly (%)	2200 (1800, 14000)	4700 ± 4600	1800 (900, 6800)	3100 ± 2400	1600 (900, 3000)	1800 ± 700
N_2O flux ($\mu mol\ m^{-2}\ d^{-1}$)	1.9 (1.3, 5.9)	2.5 ± 1.6	2.0 (1.7, 7.5)	3.3 ± 2.2	5.0 (1.9, 8.3)	4.8 ± 2.1
N_2O surface concentration ($nmol\ kg^{-1}$)	8.9 (8.4, 12.1)	9.4 ± 1.3	10.2 (9.9, 13.9)	11.1 ± 1.5	13.1 (10.6, 16.3)	13.1 ± 1.9
N_2O surface saturation anomaly (%)	20 (15, 28)	25 ± 16	14 (12, 54)	23 ± 16	42 (17, 73)	41 ± 18

[a] Values in parentheses represent the first and third quartile.

[b] Uncertainty is the standard deviation; n = 7 in all cases.

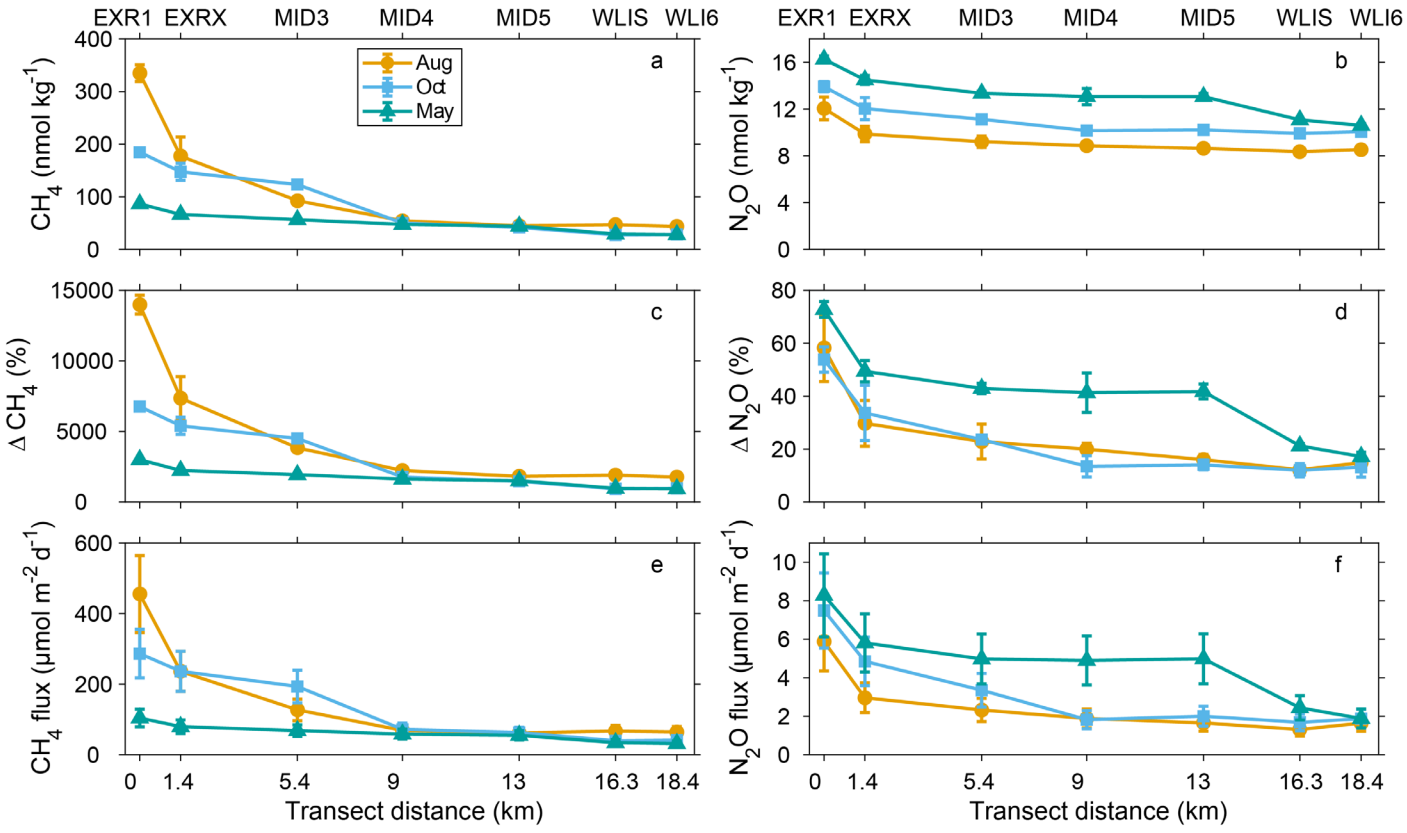

Figure 7. Surface concentrations, saturation anomalies and sea–air fluxes of CH_4 and N_2O along the sampling transect. Surface concentrations ($nmol\ kg^{-1}$) of a) CH_4 and b) N_2O, with saturation anomalies (%) of c) CH_4 and d) N_2O, and sea–air fluxes ($\mu mol\ m^{-2}\ d^{-1}$) of e) CH_4 and f) N_2O calculated using a 15-day weighting period for each of the seven stations. The transect distance corresponds to the position of each station along the transect (see Figure 1). August, October, and May are represented by yellow lines and circles, blue lines and squares, and green lines and triangles, respectively.

Alt Text: Surface CH_4 and N_2O concentrations, saturation anomalies, and sea–air fluxes. The data show that fluxes and concentrations generally decrease eastward, and that at station EXR1 CH_4 fluxes were highest in August, whereas N_2O fluxes were highest in May.

3.5 Potential sources and sinks of CH_4 in western LIS

Here we use the observed trends in CH_4 to motivate future studies. We suspect that East River discharge influences surface CH_4 concentrations in western LIS, given the elevated concentrations at the stations closest to the East River where salinity was lowest. Wastewater treatment facilities are significant sources of CH_4, including CH_4 directly released from the wastewater facility, emitted from wastewater effluent, and produced from the degradation of organic matter downstream of the facility (EPA, 2022). Studies of other wastewater facilities indicate that CH_4 concentrations can peak in wastewater effluent and/or downstream of wastewater plants (Alshboul et al., 2016; Jin et al., 2018; Peterse et al., 2024). The East River contains high dissolved organic carbon (DOC) concentrations (around 200 μmol kg^{-1}) which may serve as a substrate for aerobic or anaerobic CH_4 production (Buck et al., 2005). Photodegradation processes following the release of DOC may increase its bioavailability (Yin et al., 2021; Yu et al., 2025). Although DOC concentrations are relatively uniform throughout the East River and LIS (Buck et al., 2005), the wastewater effluent-derived DOC present in the East River will have distinct chemical characteristics compared to the terrestrial-derived DOC and the natural marine organic matter present farther east in the estuary, which may affect the production rate of CH_4 from the DOC (Maya-Altamira et al., 2008; Gonsalves et al., 2011; Amaral et al., 2021).

In October and May, CH_4 concentrations were generally higher at the surface than in the subsurface. In August, however, some stations displayed CH_4 maxima in the subsurface, for example, at station EXRX on August 3 we observed a maximum of 438 nmol kg^{-1} at 16.5 m depth, compared to 203 nmol kg^{-1} at 2.5 m depth. Subsurface peaks could reflect local sedimentary production that has been transported to the water column through diffusion and/or ebullition (Bange et al., 2010; Valentine, 2011). Sedimentary effluxes of CH_4, particularly in the form of bubbles, can be influenced strongly by pressure, with lower pressure increasing gas efflux (Maeck et al., 2014; Römer et al., 2016; Nylund et al., 2025). Therefore, changes in tidal stage and overlying water depth may drive effluxes of gases and contribute to some of the spatial variability we observed in near-bottom waters for CH_4. Mazur et al. (2021) performed sediment core incubations and found that stations EXRX and WLIS had on average net negative benthic CH_4 fluxes in summer, though fluxes were widely variable with some cores showing strongly positive fluxes and others negative fluxes. Sediment core incubations cannot account for tidally driven effluxes. As for N_2O (Section 3.6), we may have observed the effects of transient CH_4 fluxes from the seafloor interacting with the effects of tidal advection causing transient near-bottom peaks in CH_4.

3.6 Potential sources and sinks of N_2O in western LIS

Here we use the observed gas distributions and published literature on western LIS and the East River to speculate about potential N_2O sources and sinks and motivate future work, which could involve direct measurements of N_2O production and consumption. The highest N_2O concentration and saturation anomaly in our study was observed in the surface waters at station EXR1 in May, rather than in the stratified subsurface hypoxic waters of August, which we initially expected to have the highest concentrations. Our observations of enhanced N_2O concentrations in the fresh water in the far western LIS suggest that the N_2O is discharged to or produced within the East River, and/or the substrates that lead to N_2O production are released from the East River and rapidly converted to N_2O within western LIS. Studies in other estuaries and rivers have reported elevated N_2O concentrations in wastewater effluent and/or downstream of some wastewater treatment plants, though results are highly variable (Burgos et al., 2015; Peterse et al., 2024; Tang et al., 2024b).

Water column nitrification rates in oxygenated systems typically increase with reduced competition for NH_4^+ from phytoplankton and decrease with increasing light levels, though different ammonia-oxidizing organisms exhibit different light sensitivities (Ward, 2008; Smith et al., 2014; Proctor et al., 2023). In the East River, total ammonia ($NH_4^+ + NH_3$) concentrations are typically above 5 μmol kg^{-1} (and can exceed 40 μmol kg^{-1}), NO_2^- is typically above 2 μmol kg^{-1} (and can exceed 10 μmol kg^{-1}), and NO_3^- is typically above 2 μmol kg^{-1} (and can exceed 30 μmol kg^{-1}; Gobler et al., 2006; Li et al., 2018). Comparing conditions in the East River and western LIS, salinity is lower, chlorophyll *a* concentrations are lower, and dissolved inorganic N concentrations are higher in the East River (Bowman, 1977; Li et al., 2018; Wallace and Gobler, 2021), making the East River a net exporter of N to western LIS (Buck et al., 2005; Vlahos et al., 2020). These trends suggest that nitrifiers will experience reduced competition for NH_4^+ in the East River compared to western LIS due to the lower phytoplankton biomass and higher dissolved inorganic N. Euphotic zone depths in the East River are on the order of 4 m (reported range of 1–8 m), indicating rapid attenuation of light, which is driven by suspended solids rather than phytoplankton biomass and may limit phytoplankton growth in some seasons (Li et al., 2018). Somewhat deeper euphotic zone depths of 5–11 m have been reported for LIS (Anderson and Taylor, 2001; Goebel and Kremer, 2007). Given the elevated inorganic N supply and shallow euphotic zone depths in the East River, we expect water column nitrification to be prevalent in this system.

Nitrification has previously been reported in the East River from direct incubation measurements in the early 1970s (Chen et al., 1975). The authors found that nitrification rates increased when the salinity of the incubation water was decreased, suggesting nitrifying microbes in the East River are adapted to the fresh water released from the wastewater plants. Additionally, recent research has proposed that nitrification significantly influences chemical concentrations in the East River (Wallace, 2020; Wallace and Gobler, 2021). Specifically, Wallace and Gobler (2021) estimated aerobic respiration-driven changes in pH and O_2 by collecting diurnal profiles from late afternoon to sunrise and found respiration rates to be lower in the East River than in western LIS. They concluded that aerobic respiration could not fully explain the biogeochemical conditions observed in the East River (low total alkalinity, low O_2, low pH, and high pCO_2) and proposed that ammonification of wastewater-derived organic N followed by nitrification could contribute to these observed conditions. Sedimentary denitrification in the East River is another potential source of N_2O, given the high organic carbon supply. Due to rapid flushing and shallow bottom depths, the East River is not known to reach suboxic conditions in the water column (O'Connor, 1966). However, if denitrification in the East River were the primary driver, we would predict N_2O saturation anomalies to be highest later in the summer following more respiration within the system, rather than in early spring, the start of the productive season.

In western LIS, we observed subsurface peaks in N_2O at the four easternmost stations in August and hypothesize that these trends reflect sedimentary sources, either from denitrification or nitrification. These elevated N_2O concentrations did not display a consistent relationship with O_2. Such a relationship, if observed, could suggest a dominant subsurface source from nitrification below the mixed layer (Nevison et al., 2003). O_2 concentrations were consistently above the threshold for water column denitrification to occur, based on the minimum observed O_2 concentration in this study of 8 μmol kg^{-1} and an O_2 threshold ≤0.01 μmol kg^{-1} for denitrification (Zakem and Follows, 2017; Zakem et al., 2020). However, anoxic microenvironments within organisms, aggregates, and suspended/sinking particles may have provided sites for anaerobic metabolic processes to occur (Klawonn et al., 2015; Bianchi et al., 2018; Wan et al., 2023a; 2023b). Mazur et al. (2021) conducted sediment core incubations in western LIS and found sediments were on average a small net source of N_2O (mean of 8.6 nmol N_2O m^{-2} h^{-1}) but sediment–water fluxes varied widely (range of −32 to 68 nmol N_2O m^{-2} h^{-1}). Variability in sedimentary N_2O fluxes is consistent with our observation that stations with similar bottom-water O_2 concentrations had variable N_2O concentrations and vertical gradients in N_2O.

3.7 Role of CH_4 and N_2O in C and N budgets of western LIS and global warming potential of emissions

We assessed the contribution of CH_4 and N_2O to the overall C and N budgets for western LIS. CH_4 concentrations in our study were ≤0.5 μmol kg^{-1}, whereas DOC typically exceed 100 μmol kg^{-1} and dissolved inorganic carbon concentrations typically exceed 1600 μmol kg^{-1} (Vlahos and Whitney, 2017; Barrett et al., 2024). Dissolved N_2O concentrations did not exceed 0.016 μmol kg^{-1} in our study, whereas total inorganic N concentrations (excluding N_2 gas, which is not bioavailable to most organisms) in western LIS typically exceed 14 μmol kg^{-1} (Vlahos et al., 2020). Therefore, CH_4 and N_2O are not significant components of the total C and N budgets in western LIS.

We converted the CH_4 and N_2O fluxes to units of CO_2-equivalents (CO_2e) and compared these values to estimated fluxes of CO_2, the anthropogenic greenhouse gas that is the biggest contributor to global warming (Forster et al., 2021). The global warming potential (GWP) quantifies how much heat a greenhouse gas traps in the atmosphere over a specific time relative to the same mass of CO_2. We used a 100-year global warming potential (GWP-100) of 27 for CH_4 and 273 for N_2O (Forster et al., 2021). Because contemporaneous measurements of CO_2 were not collected, we used surface pCO_2 measurements by Wallace and Gobler (2021) collected in 2014 at stations MID4 and EXCR (named B3 and A4, respectively, in that study) to provide an initial and approximate evaluation of the relative importance of CO_2, CH_4, and N_2O emissions from western LIS. Using the wind speeds measured in 2023–2024 and the pCO_2 concentrations from June–September 2014 (range of 600–1300 μatm), the estimated CO_2 fluxes averaged 0.8 g CO_2 m^{-2} d^{-1} at MID4 and 2 g CO_2 m^{-2} d^{-1} at EXCR. Using our data from August, October, and May, we calculated an average CH_4 flux of 0.03 g CO_2e m^{-2} d^{-1} at MID4 and 0.08 g CO_2e m^{-2} d^{-1} at EXCR, and an average N_2O flux of 0.03 g CO_2e m^{-2} d^{-1} at MID4 and 0.05 g CO_2e m^{-2} d^{-1} at EXCR. Therefore, N_2O and CH_4 emissions from western LIS each likely generate ≤5% of the radiative forcing caused by CO_2 over 100 years. These results could be further refined through future studies measuring all three gases simultaneously.

3.8 Western LIS sea–air CH_4 and N_2O fluxes and concentrations in the global context

In general, the CH_4 and N_2O fluxes we estimated for western LIS fall within the range of prior studies which have concluded that estuaries play a small role in global CH_4 and N_2O budgets. Globally, CH_4 and N_2O concentrations and sea–air fluxes from estuarine systems are highly variable and have a positively skewed distribution, making global upscaling highly sensitive to the dataset and model used (Rosentreter et al., 2021; Zheng et al., 2022).

The sea–air CH_4 fluxes we estimate for western LIS (annual mean of 106 μmol m^{-2} d^{-1} and median of 66 μmol m^{-2} d^{-1}) are comparable to a recent global metanalysis by Rosentreter et al. (2021), who reported a mean estuarine CH_4 flux of 151 μmol m^{-2} d^{-1} and a median of 38 μmol m^{-2} d^{-1} (n = 53 sites), and a global metanalysis by Zheng et al. (2022), who reported a mean diffusive estuarine CH_4 flux of 780 μmol m^{-2} d^{-1} and a median of 120 μmol m^{-2} d^{-1} (n = 91 sites). The estuarine concentrations reported in Zheng et al. (2022) had a mean of 230 nmol kg^{-1} and a median of 110 nmol kg^{-1}: our surface measurements in western LIS are comparable (annual mean of 78 nmol kg^{-1} and median of 50 nmol kg^{-1}). The maximum estuarine concentration reported in the metanalysis was 2300 nmol kg^{-1} and the maximum diffusive flux was 27,000 μmol m^{-2} d^{-1} (Zheng et al., 2022). The fluxes we report are for diffusive processes only. Ebullitive fluxes can be a significant contributor to CH_4 emissions in aquatic systems <5 m deep, but in deeper systems such as western LIS,

diffusive fluxes dominate as the vast majority of bubbles released from the sediment will dissolve before reaching the surface (Joyce and Jewell, 2003; West et al., 2016). Globally, estuaries are thought to contribute emissions of 1–6 Tg CH_4 y^{-1} based on mean fluxes from global data compilations (Rosentreter et al., 2021; Zheng et al., 2022), which is ≤1% of global CH_4 emissions from both natural and anthropogenic sources, currently estimated at 540–865 Tg CH_4 y^{-1} (Saunois et al., 2025).

Our N_2O fluxes, estimated to have an annual mean of 3.7 μmol m^{-2} d^{-1} and median of 3.2 μmol m^{-2} d^{-1} are comparable to, though on the low end, of published typical ranges for estuaries. For example, the global metanalysis of Zheng et al. (2022) reported a mean estuarine N_2O water-air flux of 19 μmol m^{-2} d^{-1} and a median of 6 μmol m^{-2} d^{-1} (minimum of −7 μmol m^{-2} d^{-1}, maximum of 177 μmol m^{-2} d^{-1}) based on 83 studies. Our surface observations of N_2O concentrations (annual mean of 11.5 nmol kg^{-1} and median of 11.1 nmol kg^{-1}) also compare reasonably well to their mean estuarine N_2O concentration of 32 nmol kg^{-1} and median of 15 nmol kg^{-1} (minimum of 4 nmol kg^{-1}, maximum of 210 nmol kg^{-1}), though our data trend lower. Globally, N_2O emissions from inland waters, estuaries, and coastal vegetation were estimated for the year 2020 as 0.1 (range of 0–0.2) Tg N y^{-1} (Tian et al., 2024), whereas Zheng et al. (2022) estimated a higher flux of 0.25 Tg N y^{-1} from estuaries alone. Both values are small in comparison to total net N_2O emissions from all anthropogenic and natural sources, estimated at 18.5 Tg N y^{-1} (range of 10.6–27.0 Tg N y^{-1}) from bottom-up approaches that incorporate flux measurements, data-based nitrogen inventories, and models (Tian et al., 2024).

4. Conclusions

We have obtained the first measurements of CH_4 and N_2O in western LIS, a eutrophic urban estuary, and in three seasons. Although both gases can be generated under processes associated with organic matter remineralization and low-oxygen conditions in subsurface waters, we found that both CH_4 and N_2O often displayed higher concentrations at the surface compared to the subsurface. Both gases showed an along-estuary gradient in the near-surface, and concentrations in the upper 10 m were highest at the westernmost station (closest to the East River and New York City) in all three seasons. Conversely, near-surface O_2 concentrations were typically lowest at the westernmost stations and decreased eastward. Hypoxic conditions in August were associated with elevated CH_4 concentrations and sea–air fluxes. However, N_2O concentrations and fluxes were highest in May, indicating that biogeochemical processes associated with seasonal hypoxia are not the primary driver of N_2O dynamics in western LIS. Repeated measurements at station MID4 suggested that sub-daily variability in O_2, CH_4, and N_2O concentrations could not be correlated solely to daily changes in light or tidal phase. Sea–air fluxes of CH_4 and N_2O in western LIS were comparable with other estuaries worldwide.

Our dataset suggests that there is a persistent source of fresh surface water elevated in CH_4 and N_2O (or substrates that support production of these gases) to western LIS which enhances surface concentrations and sea–air fluxes in this region. Future work could focus on mapping the distributions of these gases in the East River and in proximity to wastewater inputs. To determine production and consumption mechanisms and rates, incubation experiments could be combined with metagenomic analyses (Karl et al., 2008; Uhlig and Loose, 2017; Euler et al., 2020; Bourbonnais et al., 2021; Rasmussen and Francis, 2022). Ongoing changes in western LIS include reductions in nutrient loading, increased water temperatures, reductions in O_2 solubility, and ocean acidification (Wallace and Gobler, 2021; Whitney and Vlahos, 2021). Continued monitoring along with targeted experiments evaluating the impacts of multiple stressors would improve predictions of how projected future changes will influence greenhouse gas emissions (Tang et al., 2024b).

Data accessibility statement: The following datasets were generated.
Manning, CCM; Payyambally, A; Mottram, J; Ward, K (2026): Methane and nitrous oxide dissolved gas concentrations from western Long Island Sound [dataset].
PANGAEA, https://doi.org/10.1594/PANGAEA.987944

Manning, CCM; Payyambally, A; Mottram, J; Ward, K (2026): Methane and nitrous oxide sea–air fluxes from western Long Island Sound [dataset]. PANGAEA, https://doi.org/10.1594/PANGAEA.987952

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The authors declare no competing interests.

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