



Spatial heterogeneity of GHG dynamics across an estuarine ecosystem

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Abstract.

Coastal ecosystems are critical components of the global carbon cycle, exerting a disproportionate influence on the carbon budget despite their limited spatial extent. Estuaries remain understudied despite being dynamic sources of the three most potent greenhouse gases (GHGs): carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). Such shallow coastal ecosystems are highly heterogeneous, shaped by strong physical, biogeochemical, and biological gradients. Combined with spatial variability in coastal biodiversity, these gradients strongly shape carbon cycling at both local and global scales. However, large uncertainties persist due to limited and spatially patchy measurements, highlighting the need for improved constraints on GHG budgets and their sensitivity to biodiversity loss and climate change.

We measured surface seawater partial pressure of CO₂ (pCO₂), CH₄, and N₂O concentrations, along with seawater physical and biogeochemical properties, and air-sea gas exchange, at 21 sites in southwest Finland (Baltic Sea). Sampling followed a transition from estuarine inner bays to the outer archipelago, covering diverse soft-sediment habitats, from sheltered to exposed areas, across a salinity gradient. Surface water pCO₂ and N₂O concentration ranged from undersaturated (160 ppm and 9 nmol L⁻¹, respectively) to supersaturated (2521 ppm and 25 nmol L⁻¹, respectively), compared to the atmosphere, resulting in an uptake of -36 and -0.0021 mmol m⁻² d⁻¹, and a release up to 220 and 0.0383 mmol m⁻² d⁻¹, respectively. CH₄ concentrations were consistently supersaturated (19 to 469 nmol L⁻¹) compared to the atmosphere, resulting in a net source to the atmosphere from 0.014 to 1.39 mmol m⁻² d⁻¹.

Freshwater input from the Karjaanjoki River and its mixing with seawater mainly determined the overall spatial patterns of GHGs. However, deviations from this salinity-driven control were observed. In sheltered sites within the archipelago, elevated pCO₂, CH₄, and N₂O concentrations likely reflected benthic processes, including enhanced organic matter respiration and methanogenesis in warm, late-summer shallow waters, where limited oxidation favoured CH₄ accumulation. At exposed sites, mixing processes had a stronger control, resulting in lower GHG concentrations. Our results show that both physical mixing and benthic processes influence coastal GHG dynamics, with benthic ecosystems playing a key but still poorly constrained role. Air-sea GHG exchanges were dominated by CO₂, while CH₄ and N₂O contributed differently as a source and a sink. The balance between production and consumption processes, particularly within benthic habitats, is therefore critical for understanding coastal contributions to the global carbon budget.



1. Introduction

Coastal ecosystems are increasingly recognized as critical components of the global carbon cycle (Bauer et al., 2013). Although covering only about 7% of the oceanic area, they play a disproportionately large role in biogeochemical cycling due to their location at the land–sea interface (Gattuso et al., 1998; Wollast, 1998). These environments act as hubs of exchange across biomes (Resplandy et al., 2024), contributing to the global oceanic uptake of anthropogenic carbon by absorbing carbon dioxide (CO₂) from the atmosphere and either burying, transforming, or releasing the carbon that land ecosystems deliver to coastal waters (Regnier et al., 2022). Due to intense inputs of nutrients and carbon from land and open ocean at continental margins, combined with high rates of biological production and degradation, coastal waters are among the most biogeochemically active regions of the biosphere (Wollast, 1998). Shallow coastal waters such as mangroves, salt marshes, and seagrass meadows effectively sequester large amounts of atmospheric carbon through vegetation growth and long-term sediment accumulation, making significant contributions to long-term carbon storage (Lovelock and Duarte, 2019; Macreadie et al., 2021; Mcleod et al., 2011). These so-called “blue carbon” ecosystems have been proposed as nature-based solutions for short-term climate change mitigation (Hoegh-Guldberg et al., 2019; Lovelock and Duarte, 2019).

Vegetated blue carbon ecosystems exemplify the value of healthy habitats in long-term carbon storage. Still, they cover a small part of the coastal oceans (thebluecarboninitiative.org), and measurements from other key habitats remain scarce and largely neglected in carbon cycling budgets (James et al., 2024). Estuarine areas are characterized by strong physical and chemical gradients and host transitional biodiversity that bridges terrestrial and marine ecosystems (Elliott and Whitfield, 2011) and are recognized as hot spots for carbon cycling and GHG exchange with the atmosphere (Borges et al., 2005; 2016; Cai et al., 2013; Frankignoulle et al., 1998; Humborg et al., 2019; Rosentreter et al., 2021). The global oceans absorb roughly 25% of anthropogenic CO₂ emissions annually (Watson et al., 2020). While coastal waters contribute to this sink by taking up atmospheric CO₂ (Chen and Borges, 2009; Regnier et al., 2022), many nearshore systems like estuaries have been recognized as net heterotrophic ecosystems with negative net ecosystem production (Gattuso et al., 1998; Testa et al., 2012), leading to the production and release of both CO₂ and methane (CH₄) (Abril and Borges, 2005; Bonaglia et al., 2025; Borges et al., 2018). Despite their small size, emissions from near-shore ecosystems such as estuaries could nearly balance the carbon uptake by marginal seas (Borges et al., 2005; Chen and Borges, 2009). Global CO₂ emissions from estuaries range from 0.1 to 0.6 PgC per year (Borges et al., 2018), an amount equivalent to 5-30% of the oceanic CO₂ sink of ~ 2 PgC per year (Le Quéré et al., 2016), while CH₄ emissions range from 1 to 7 Tg per year, mainly driven by organic matter accumulation, anaerobic decomposition in sediments, and production in submerged plants (Borges et al., 2018; Rosentreter et al., 2018). However, CH₄ emissions are probably underestimated due to difficulties in accounting for ebullition and gas flaring (Borges et al., 2016; Humborg et al., 2019). The complexity of these pathways, combined with a lack of systematic, high-resolution, and long-term measurements, hampers robust global assessments of coastal CH₄ emissions (Roth et al., 2022). Besides CO₂ and CH₄, coastal ecosystems are important but poorly constrained sources of nitrous oxide (N₂O), a potent greenhouse gas with a global warming potential 273 times higher than CO₂ over 100 years (IPCC 2023). N₂O in oceanic environments is formed as a byproduct



during nitrification and as an intermediate during denitrification, both of which depend strongly on oxygen concentration and are microbial processes that occur in the water column, in sediments, and within suspended particles (Bange, 2006). Coastal ecosystems are recognized as significant sources of N_2O to the atmosphere (Bange, 2006; Cheung et al., 2025; Resplandy et al., 2024). However, coastal estimates remain uncertain due to sparse measurements and high spatial heterogeneity. Given the strong warming potential of N_2O , understanding its fluxes from estuaries is essential for a complete picture of coastal greenhouse gas dynamics and determining how these emissions, along with those of CH_4 (with a warming potential of 27; IPCC 2023), offset the coastal uptake of CO_2 (Resplandy et al., 2024; Rosentreter et al., 2018; Roth et al., 2023). This questions the efficiency of blue carbon ecosystems in mitigating the rise of GHG concentrations in the atmosphere and their related radiative effects (Kristensen et al., 2025; William and Gattuso, 2022).

This study investigates the dynamics of CO_2 , CH_4 , and N_2O (GHGs) along a salinity gradient and across contrasting coastal habitats within an estuary. We combined detailed field measurements of surface seawater physical and biogeochemical properties with both *in situ* measurements and calculated estimates of air–sea GHG exchange. This approach allowed us to capture spatial variability, identify the underlying biogeochemical drivers, and examine interactions with coastal habitats. In doing so, we aim to disentangle the biogeochemical controls of GHG dynamics in estuarine environments and contribute to improving global estimates of the coastal ocean’s GHG emissions.

2. Materials and methods

2.1 Study area

This study was conducted within a 30 km radius of the Tvärminne Zoological Station (TZS), located at the southwestern tip of mainland Finland. The study area encompasses the coastal waters extending from the cities of Hanko, Tammisaari, and Pohja (Fig. 1), where the coastal environment is characterized by strong spatial heterogeneity due to the intricate bathymetry and geomorphology of the archipelago system (Asmala and Scheinin, 2024) and enhanced human impact. The studied area receives substantial freshwater from the Karjaanjoki river (in Pohja, runoff $0.59 \text{ km}^3 \text{ yr}^{-1}$, Räike et al., 2012), delivering relatively large amounts of allochthonous carbon and nutrients to the system, resulting in eutrophication and elevated concentrations of organic carbon in the water column across the inner archipelago area (Fleming-Lehtinen et al., 2015). Sampling sites ($N = 21$) were selected to encompass a wide range of soft-sediment habitats and to represent a spatial gradient (50 km) from the outer to innermost archipelago, encompassing exposed to sheltered bays. Exposed sites are characterized by a higher degree of exposure to wave, wind, current energy, and greater water exchange (sites 1–4 and 14–21), while sheltered sites are more enclosed and experience more limited water circulation (sites 5–13). Exposed sites in the outer archipelago (between Hanko and TZS, sites n°14–21, Fig. 1) are characterized by sandy sediments (96.2–100% sand) with low organic matter content (0.3–1.3%). These sites host both marine and freshwater plant species (Gustafsson and Norkko, 2019; Lammerant et al., 2025), and their faunal biomass is dominated by bivalves and polychaetes (Gammal et al., 2019; Mäkelin et al., 2024). Sheltered sites within the archipelago (sites n°5–13) are characterized by sediments containing high proportions of



clay/silt (20.8-64.3%) and organic matter (2.4-13.2%; Lammerant et al., 2025). At these sites, fast-growing fresh- and brackish-water macrophytes are often found, while faunal biomass is dominated by gastropods (Mäkelin et al., 2024). In Pojoviken Bay, a 14 km inlet between Tammisaari and Pohja (sites n°1-4), dense vegetation occurs down to ~2 m depth but becomes sparse at greater depths (>3 m) due to light limitation (Lammerant et al., 2025). Deeper sites are characterized by high organic matter content (>13%) in the sediment and low faunal biomass (Gammal et al., 2019). Sampling was conducted from 14 August to 18 September 2023.

2.1 Sampling procedure

Physical and biogeochemical properties of surface seawater, including the partial pressure of dissolved CO₂ (pCO₂) and CH₄ concentration, were measured *in situ* using a custom-built flow-through system. Seawater, from a depth of 50 cm, was pumped onboard using a submersible pump and directed into two separate flow-through systems.

The first water flow (3 L min⁻¹) was dedicated to gas extraction using a double showerhead equilibrator (Sunburst) equipped with a temperature probe (Hex fitting thermistor, ThermX, 0.1°C accuracy) and a barometric pressure sensor (BARO-A-4V, All Sensors). From the equilibrator, a continuous air flow (2 L min⁻¹) circulated in a closed loop to an infrared gas analyser (IRGA, LI-COR, LI-7810). The analyser measured the dry mole fractions of CO₂ and CH₄, denoted as xCO₂ and xCH₄, respectively, as the gas passed through a Peltier cooler to remove the excess water before entering the IRGA. Both gas concentration and temperature were recorded every second until an equilibrium was reached (up to 45 minutes). The measured xCO₂ was later converted into pCO₂ and corrected for *in situ* temperature using the Matlab CO2SYS v3 (Sharp et al., 2023). Surface seawater CH₄ concentration (in nmol L⁻¹) was computed from xCH₄, *in situ* temperature, salinity, and the solubility coefficients from Wiesenburg and Guinasso (1979).

The second water flow (2 L min⁻¹) was directed through a thermosalinograph (SeaBird, TSG045), a fluorometer for chlorophyll *a* (chl-*a*), turbidity, and phycocyanin concentrations (Chelsea, TriLux), a fluorometer for coloured dissolved organic matter (CDOM, Chelsea, UviLux), and an optode for dissolved oxygen concentration and saturation (Aanderaa 4531). Each sensor was factory-calibrated before deployment, and data were logged at 1-second intervals until equilibrium for xCO₂ and xCH₄ was reached (up to 45 min). A 5-second average was then recorded.

Discrete surface water samples were collected for total alkalinity (TA), dissolved inorganic carbon (DIC), methane (CH₄), and nitrous oxide (N₂O) concentration using a peristaltic pump (Cole Palmer, Masterflex Environmental Sampler) equipped with Tygon tubing. Seawater samples were collected into 12 mL gas-tight vials (Exetainers, Labco High Wycombe, UK) for DIC, 60 mL borosilicate vials for TA, and 60 mL serum bottles for dissolved CH₄ and N₂O concentrations. Samples were preserved by adding 1% of the sample volume of a saturated mercuric chloride (HgCl₂) solution. Samples were stored in the dark at room temperature until analysis.

Air-sea exchanges of CO₂ and CH₄ were measured using the accumulation chamber technique (Frankignoulle, 1988). The chamber consists of a polyethylene container (internal diameter: 34 cm, height: 14 cm, total volume = 11.4 L) connected in a closed loop to the IRGA. The air partial pressure of CO₂ (pCO₂) and CH₄ (pCH₄) within the chamber was recorded every



second for 10 minutes. The flux was computed from the slope of the linear regression of pCO₂ and pCH₄ against time ($R^2 >$
130 0.99) following the method of Frankignoulle (1988), accounting for the air volume enclosed within the chamber. The
uncertainty of the flux calculation, based on the standard error on the regression slope, was approximately 3% on average.
Direct measurements of N₂O air-sea exchanges were not possible during our survey. Therefore, the air-sea exchange of N₂O,
as well as CO₂ and CH₄ (i.e., F_X , where X represents N₂O, CO₂, or CH₄, respectively) was parameterized using the bulk formula:

$$F_X = kK_{0(X)}(pX_{(sw)} - pX_{(atm)}) \quad (1)$$

135 where k (m s⁻¹) is the gas transfer velocity, K_0 (mol m⁻³ atm⁻¹) is the temperature and salinity dependent gas solubility
determined from Weiss (1974) for CO₂, Wiesenburg and Guinasso (1979) for CH₄, and Weiss and Price (1980) for N₂O, and
 $pX_{(sw)}$ and $pX_{(atm)}$ are the measured partial pressure of gas in the surface seawater and the air, respectively.

This approach strongly relies on selecting an appropriate parameterization for the gas transfer velocity, k . Numerous
theoretical, laboratory, and field studies established that k depends on a variety of parameters, including capillary and breaking
140 waves, boundary layer stability, air bubbles, surfactant surface films, evaporation and condensation, precipitation, water
currents (including tides), as well as turbulence at the air-water interface (Borges et al., 2004). The parameterization of k is
most often expressed as a function of wind speed. This relationship is well established for the open ocean, where wind stress
is the main source of turbulence (e.g., Wanninkhof, 2014). In estuarine environments, significant regression functions between
 k and wind speed have also been reported (Borges et al., 2004; Raymond et al., 2000). However, such formulations have been
145 proven to be site-specific and may not fully account for other controlling processes, such as turbulence at the air-water interface
(Borges et al., 2004). Since no k -wind relationship has been developed for our study area, we adopted the formulation proposed
for the Randers fjord by Borges et al. (2004), as its physical characteristics, particularly tidal amplitude and freshwater
discharge, are most comparable to those of our site:

$$k = 1.2 + 2.3u \left(\frac{Sc_{(balt)}}{660} \right)^{-0.5} \quad (2)$$

150 where u is the wind speed (m s⁻¹) and $Sc_{(balt)}$ is the Schmidt number at the sampling site, based on local temperature, salinity,
and gas molecules. $Sc_{(balt)}$ is extrapolated from freshwater and seawater ($S = 35$) coefficients from Wanninkhof (2014) for the
salinity observed at the sampling site (Roth et al., 2023).

Wind speed (in m s⁻¹, METEK, uSonic-3 Scientific) and air temperature (in °C, Vaisala, HMP155) are measured at the 3.2
and 2 m height above sea level at the newly established Integrated Carbon Observation System (ICOS) coastal site at TZS
155 (ICOS code FI-Tvm; Fig. 1). Daily averaged wind speed, extrapolated to a height of 10m using the relationship from Hsu et
al., (1994), assuming a near-neutral atmospheric stability conditions, was used to calculate the air-sea exchanges of GHGs.
Atmospheric concentrations of CO₂ and CH₄ were measured at each site before the air-sea flux measurements. For N₂O, we
used the monthly average atmospheric concentration of 0.3367 ppm, measured at Pallas-Sammaltunturi, GAW Station, Finland
(PAL, <https://gml.noaa.gov/dv/iadv/graph.php?code=PAL&program=ccgg&type=ts>).



160 The recorded data on the IRGA for both seawater and air-sea flux measurements were filtered by removing measurements taken during the transition period between stations and ambient air sampling, as the IRGA requires time to respond to sharp concentration changes. Additionally, data affected by improper functioning (i.e., seawater flow $< 1.5 \text{ L min}^{-1}$) were discarded.

2.3 Sample analysis

TA was determined by Gran titration (Gran, 1952) using an AS-ALK2 titration system (Apollo SciTech), where a 15-ml
 165 sample was titrated with a standard 0.1 M HCl solution. DIC was measured on a DIC analyser (Apollo SciTech) by acidification of a 0.75 ml subsample with 1 ml 10% H_3PO_4 , and quantification of the released CO_2 with a non-dispersive infrared CO_2 analyser (LI-COR, LI-7000). Results were then converted from $\mu\text{mol L}^{-1}$ to $\mu\text{mol kg}^{-1}$ based on sample density, calculated from salinity and temperature at the time of the analysis. Accuracies of ± 3 and $\pm 2 \mu\text{mol kg}^{-1}$ were determined for TA and DIC, respectively, from routine analysis of certified reference materials (A.G. Dickson, Scripps Institution of
 170 Oceanography, San Diego, CA, USA).

Discrete seawater samples for CH_4 and N_2O concentrations were measured via the headspace equilibrium technique (25 ml N_2 headspace in 60 ml serum bottles) and measured with a gas chromatograph (SRI 8610C) with flame ionization detection, and electron capture detection calibrated with CH_4 : CO_2 : N_2O : N_2 mixtures (Air Liquide) of 1.0, 10, and 30 ppm CH_4 and 0.2, 1.0, and 6.0 ppm N_2O . The measurement precision was 8 % for CH_4 and 4 % for N_2O .

175 3. Results

3.1 Atmospheric forcing and seawater physical properties

During the survey period, atmospheric temperatures remained relatively stable, averaging 18.0°C ($\text{SD} = 1.5$, $n = 1989$; Fig. 1a). A short warm event occurred on the 7th of August, when the air temperature peaked at 26.3°C . In contrast, short cold spells were observed on 5 and 7 September, with temperatures dropping to 13.7 and 11.5°C , respectively. With relatively stable
 180 atmospheric temperature, surface seawater temperature (SST) showed limited variation, ranging from 17.2 to 19.5°C (mean = 18.4°C , $\text{SD} = 0.66$, $n = 21$; Fig. 1c). The Karjaanjoki River, being the main source of freshwater input to the area, created a pronounced salinity gradient, from nearly fresh surface seawater salinity ($\text{SSS} = 0.07$) at the river mouth (in Pohja) to a SSS of 6.36 in Hanko (Fig. 1d).

3.2 Seawater biogeochemical properties

185 Surface seawater chlorophyll-*a* (chl-*a*) concentration ranged from 3.7 to $37.7 \mu\text{g L}^{-1}$ (mean = 14.4 , $\text{SD} = 8.1$, $n = 21$, Fig. 1e), with the highest concentration observed in the sheltered bay around Tammisaari (S5 and S6). Turbidity ranged from 5.0 to 8.4 FTU (mean = 6.1 , $\text{SD} = 0.8$, $n = 21$, Fig. 1f), with the highest values observed in sheltered bays within the archipelago (S8, S9, and S11). Coloured dissolved organic carbon (CDOM) ranged from 3.0 to $10.6 \mu\text{g L}^{-1}$ (mean = 5.9 , $\text{SD} = 2.6$, $n = 21$, Fig. 1g) and exhibited a salinity-driven gradient, with the highest concentrations observed towards Pohja and the lowest towards



190 Hanko. However, one site in the archipelago (S8) and near Hanko (S19) exhibited elevated CDOM concentrations compared to other locations in their respective area, reaching up to 10.0 and 10.6, respectively. Dissolved oxygen (DO) saturation levels ranged from 74.3 to 112.7 % (mean = 94.1, SD = 9.6, n = 21, Fig. 1h), with most of the sites undersaturated in O₂, excepted for two sites closed by Tammisaari (S3 and S4) and four sites in closed vicinity of TZS (S14, S15, S18, and S19). Surface water pCO₂ ranged from strong undersaturation (160 ppm) to a significant supersaturation relative to the atmosphere (average atmospheric concentration measured during this survey = 406 ppm) at S2 (1702 ppm) and up to 2521 ppm at the river mouth (triangle on Fig. 2a). Surface water CH₄ concentrations were consistently supersaturated (up to 14609 %, data not shown) compared to the atmosphere (average atmospheric concentration measured during this survey = 2.05 ppm), with concentrations ranging from 19 to 469 nmol L⁻¹ (Fig. 2b). Undersaturated pCO₂ (from 160 to 403 ppm) and low CH₄ concentrations (from 19 to 34 nmol L⁻¹) were mostly observed at open sites between TZS and Hanko (S14 to S21), except for 200 S17, where pCO₂ and CH₄ reached 485 ppm and 48 nmol L⁻¹, respectively. Seawater pCO₂ and CH₄ concentrations increased across the archipelago and Pojoviken Bay, reaching their maximal values at the mouth of the Karjaanjoki River. Local lows were observed in Pojoviken Bay (S3 and S4), where pCO₂ was undersaturated (192 and 238 ppm, respectively), and CH₄ concentrations were relatively low (83 and 67 nmol L⁻¹, respectively). N₂O concentration ranged from 9 to 25 nmol L⁻¹, with higher concentrations observed at the mouth of the Karjaanjoki River (Fig. 2c). South of Tammisaari, surface waters were 205 either undersaturated in N₂O (S8, S13, and S16) or close to the atmospheric equilibrium (S6 and S12, data not shown). TA and DIC ranged from 668 to 1631 and from 720 to 1550 μmol kg⁻¹, respectively, with minimum TA and DIC concentration measured at the mouth of the Karjaanjoki River. Both TA and DIC exhibited conservative behaviour with changes in salinity (Fig. 3a).

3.3 Air-sea exchanges of greenhouse gases

210 The area presented contrasts in terms of sink and source of CO₂ and N₂O, but was clearly a source of CH₄. Measured air-sea exchanges of CO₂ ranged from -36 to 150 mmol m⁻² d⁻¹, where negative values indicate net uptake of atmospheric CO₂ (Fig. 2d). In contrast, the study area acted as a net source of CH₄ to the atmosphere, with fluxes ranging from 0.014 to 1.39 mmol m⁻² d⁻¹ (Fig. 2e). Overall, the calculated fluxes showed a similar in term of pattern and range compared to the observed values, ranging from -26.4 to 220.3 mmol m⁻² d⁻¹ for CO₂ (Fig. 2f) and from 0.03 to 1.1 mmol m⁻² d⁻¹ for CH₄ (Fig. 2g). Calculated 215 fluxes of N₂O ranged from -0.0021 to 0.0383 mmol m⁻² d⁻¹, with sites in the archipelago and towards TZS acting as a slight sink of N₂O (Fig. 2h).

4. Discussion

Surface water pCO₂, CH₄, and N₂O concentrations showed significant spatial variation, spanning several orders of magnitude (Fig. 2). Humborg et al. (2019) reported pCO₂ and CH₄ levels following the salinity gradient driven by the Karjaanjoki River, 220 with values reaching up to 1583 μatm and 70 nmol L⁻¹, respectively. However, these measurements were conducted along the



deeper part of the main channel of the archipelago, and they did not explore Pojoviken Bay, whereas our study focused on shallow (< 4m depth) nearshore ecosystems. Asmala and Scheinin (2024) observed a similar range of pCO₂ and CH₄ concentrations across a 2000 km² coastal region surrounding the Hanko Peninsula, with the large magnitude of both gases associated with excessive organic matter loads, elevated primary production, trapping and accumulation of allochthonous organic matter, and sedimentary conditions favourable to CH₄ production. Focusing on nearshore shallow (< 4m depth) coastal habitats around the island of Askö (Sweden, northern Baltic Sea), Roth et al. (2023) reported strong spatial variability in surface water pCO₂ and CH₄ concentrations and emphasized that their dynamics were strongly habitat specific. The N₂O concentrations we observed were in the same range as those observed by Aalto et al. (2021) in the same area, with concentrations ranging from 25 to 50 nmol L⁻¹ within Pojoviken Bay and from 10 to 30 nmol L⁻¹ within the archipelago. Aalto et al. (2021) reported that higher N₂O concentrations were associated with higher nitrate concentrations and inputs of allochthonous carbon, while lower N₂O concentrations were associated with efficient internal recycling of N.

The Kendall's τ coefficient has been calculated to investigate the correlation between surface water pCO₂, CH₄, and N₂O concentration, as well as between physical and biogeochemical parameters and all three GHGs (Fig. 4). Surface pCO₂ and CH₄ concentrations show a moderate ($\tau = 0.5636$) and statistically significant ($p = 0.0165$) positive relationship (Fig. 4a), suggesting that processes driving high pCO₂, such as respiration and organic matter degradation, are likely also contributing to elevated CH₄ levels. N₂O is not correlated with pCO₂ and shows a moderate correlation with CH₄ ($\tau = 0.4182$), although this relationship is only marginally significant ($p = 0.0866$). Among all tested biogeochemical variables, SSS and O₂ saturation show strong and significant negative correlations with pCO₂ and CH₄ (Fig. 4b). N₂O is only strongly negatively correlated with salinity ($\tau = -0.8182$, $p = 0.00013$) and shows a marginal correlation with CDOM ($\tau = 0.4545$, $p = 0.060$). CDOM is positively correlated with CH₄ ($\tau = 0.4952$, $p = 0.0013$) while chl-*a* is moderately and significantly correlated with CH₄ ($\tau = 0.4095$, $p = 0.009$). SST and turbidity show weak and non-significant relationships with the three gases.

4.1 Drivers for variability in surface water pCO₂, CH₄, and N₂O concentration

The Karjaanjoki river is the main source of freshwater into the studied area, delivering large amounts of allochthonous carbon and nutrients to the system (Fleming-Lehtinen et al., 2015). Changes in SSS have been suggested to strongly influence the concentration of all three GHGs (Fig. 4b), with terrestrial runoff likely contributing to elevated CH₄ concentrations in the area (Asmala and Scheinin, 2024). At a first glimpse, only N₂O exhibited a strong relationship with salinity ($R^2 = 0.95$), while pCO₂ ($R^2 = 0.58$) and CH₄ ($R^2 = 0.39$) exhibited weaker correlations (Fig. 5, dotted black line). However, when focusing exclusively on exposed sites, the correlation with salinity strengthened considerably, reaching values up to 0.79 for pCO₂, 0.94 for CH₄, and 0.96 for N₂O (Fig. 5, dashed red line). The impact of water mixing on surface-water pCO₂ can be assessed by estimating the variation in pCO₂ resulting only from the physical mixing of Karjaanjoki River water ($S = 0$, $TA = 668 \mu\text{mol kg}^{-1}$, $DIC = 720 \mu\text{mol kg}^{-1}$) with a seawater endmember (black symbol in Fig. 3, $S = 6.42$, $TA = 1635 \mu\text{mol kg}^{-1}$, $DIC = 1586 \mu\text{mol kg}^{-1}$). The seawater endmember was collected on 18 September 2023 at 59.77393 °N, 23.2607167 °E, about 7.5 km south of TZS. This calculation excludes the effects of biological activity, gas exchange, and potential precipitation or dissolution of calcium



carbonate. Assuming that changes in SSS reflect a mixing ratio between the Karjaanjoki River and the seawater endmembers
255 and based on the observed linear relationships between salinity and both TA and DIC (Fig. 3a), representing conservative
mixing between the two water masses, TA and DIC can be estimated based on salinity. The estimated TA and DIC are then
used to compute $p\text{CO}_2$ (blue dashed line, Fig. 5a) using CO2SYS v3 (Sharp et al., 2023), applying the carbonic acid dissociation
constants (K_1 and K_2) of Millero et al. (2006) and the KHSO_4 formulation of Dickson (1990). While TA and DIC behaved
conservatively during mixing, $p\text{CO}_2$ showed a pronounced nonlinear response, similar to the one observed for exposed sites
260 (Fig. 5a). Such behaviour has already been reported in estuaries (Abril et al., 2021; Cai et al., 2013). This suggests that the
input of CO_2 , CH_4 , and N_2O supersaturated water from the Karjaanjoki River is a major source for all three GHGs across the
study area, with dilution playing a dominant role in GHG dynamics at exposed sites. While changes in SSS appear to explain
most of the variability observed in $p\text{CO}_2$, CH_4 , and N_2O concentrations, deviations from the expected salinity-driven pattern,
such as those observed within the archipelago, at sheltered sites, likely reflect additional local processes.

265 Many processes affecting the carbonate system are best described by examining the associated changes in DIC and TA (Zeebe
and Wolf-Gladrow, 2001). However, most of the changes in TA and DIC in surface seawater appeared to be driven by salinity
changes, with estimated endmember ($S=0$) values of 662 and 712 $\mu\text{mol kg}^{-1}$ for TA and DIC, respectively (Fig. 3a). These
estimates closely match the measured TA and DIC at the mouth of the Karjaanjoki River (668 and 720 $\mu\text{mol kg}^{-1}$, respectively).
Therefore, to discard the impact of freshwater inputs, TA and DIC were normalized to the average surface seawater salinity of
270 5 (denoted as $n\text{TA}$ and $n\text{DIC}$, respectively) using the normalization of Friis et al. (2003). In Figures 3b, c, and d, the dotted
lines illustrate the expected responses of TA and DIC to different biogeochemical processes. Biological activity
(photosynthesis/respiration) affects both TA and DIC in a ratio of -0.16 (Lazar and Loya, 1991), air-sea exchange of CO_2 only
affects DIC, and the precipitation-dissolution of calcium carbonate affects TA and DIC in a 2:1 ratio. However, the effect of
calcifying primary producers in the carbon pool can be neglected in the Baltic Sea, except in the benthic zone (Tyrrell et al.,
275 2008). The sampling sites are compared to the seawater endmember ($S = 6.42$, $\text{TA} = 1635 \mu\text{mol kg}^{-1}$, $\text{DIC} = 1586 \mu\text{mol kg}^{-1}$,
black symbol in Fig. 3). Figures 3b and c, show how exposed sites, undersaturated in $p\text{CO}_2$ and low CH_4 concentrations, follow
the theoretical trend of photosynthesis and CO_2 release. However, an uptake of CO_2 was both measured and estimated for
those sites (Fig. 2), suggesting that gas exchange as release towards the atmosphere could not explain the observed changes in
the carbonate system. In contrast, sheltered sites, with supersaturated $p\text{CO}_2$ and elevated CH_4 concentrations, were more
280 scattered around the theoretical respiration line and CO_2 uptake. Gas exchange, as CO_2 uptake, can also be ruled out, as both
measured and estimated air-sea fluxes pointed to a net release of CO_2 into the atmosphere. Altogether, this suggests that
biological processes—primary production at undersaturated $p\text{CO}_2$ sites and respiration at supersaturated sites—mainly
influence the carbonate system, while the direct role of air-sea exchange of CO_2 appears to be minor in shaping the inorganic
carbonate dynamics across the study area. The similar pattern observed for both $p\text{CO}_2$ and CH_4 concentrations illustrated the
285 positive relationship between the two gases (Fig. 4), where processes responsible for higher $p\text{CO}_2$, such as respiration and/or
organic matter degradation, also contribute to higher CH_4 concentrations (Reeburgh, 2007). No clear pattern could be observed
between the $n\text{TA} : n\text{DIC}$ ratio and N_2O concentration, as expected by the poor Kendall's coefficient of correlation (Fig. 4).



Elevated *chl-a* concentrations (up to $37.7 \mu\text{g L}^{-1}$, Fig. 1) in surface seawater were reported across the studied area. *Chl-a* measurements are typically considered as a proxy for pelagic primary production (Cloern et al., 2014). Therefore, elevated *chl-a* could indicate active photosynthesis production, resulting in pelagic O_2 production and pelagic CO_2 uptake. To investigate the relationship between photosynthetic activity and surface water pCO_2 , CH_4 , and N_2O concentrations, apparent oxygen utilization (AOU), calculated as the difference between oxygen saturation and measured oxygen concentration, was examined with *chl-a* concentrations. No clear relationship was observed between *chl-a* and AOU (Fig. 6a). Negative values of AOU, indicative of net photosynthesis, were associated with relatively low *chl-a* concentrations within the observed range. These negative AOU values corresponded to undersaturated pCO_2 and low CH_4 concentrations (Fig. 6b, c). In contrast, positive AOU values, representing net respiration, were associated with supersaturated pCO_2 and elevated CH_4 concentrations, both of which increased with higher AOU. A strong correlation exists between AOU and surface water pCO_2 (Fig. 6b), suggesting that pelagic primary production is the main process affecting the carbonate system, as already indicated by the nDIC: nTA ratio (Fig. 3). This relation is weaker for CH_4 and N_2O , as respiration is not ultimately associated with CH_4 production. Therefore, if *chl-a* concentration is considered as a proxy for pelagic primary production (Cloern et al., 2014), this suggests that primary production within the pelagic realm is not solely responsible for the change of pCO_2 . The influence of the pelagic realm is likely limited, as phytoplankton biomass is constrained by the shallow water column, and its productivity is low at the end of the summer bloom (Uth et al., 2024). Therefore, processes beyond pelagic production, such as benthic community production and organic matter degradation, are highly likely to influence the observed pCO_2 and CH_4 dynamics. No clear relationships between AOU and N_2O could be observed, as expected from the Kendall's correlation coefficient.

The inputs of freshwater supersaturated in CO_2 , CH_4 , and N_2O represent a major source of GHGs to the study area. Freshwater mixing with seawater appears to control the concentration of all three GHGs at exposed sites, as much of the variability in surface seawater concentrations can be explained by salinity. In sheltered sites of the archipelago, deviations from the salinity-driven pattern indicate the influence of additional processes. Biological activity is likely the key driver, with pCO_2 undersaturated associated with primary production, while pCO_2 supersaturated linked to respiration. However, pelagic production alone is unlikely to be the main contributor to the observed changes. Benthic processes such as community production, organic matter degradation, and sediment-water interactions are likely to contribute to both CO_2 and CH_4 dynamics (Attard et al., 2019). For CH_4 , riverine inputs and subsequent dilution largely determine large-scale patterns, but elevated concentrations within the archipelago reflect localized production and limited oxidation. Large amounts of carbon are turned over in the habitats from the studied area during the summer months (Attard et al., 2019), and macrophyte tissue becomes a direct component of local sediment organic matter pools that favour local CH_4 production (Roth et al., 2022; Wallenius et al., 2021). Anoxic degradation of organic-rich sediments (methanogenesis), exacerbated by warm late-summer waters (Roth et al., 2022; Yvon-Durocher et al., 2014), together with short water residence times that restrict oxidation in both sediment and the overlying water column (Reeburgh, 2007), create favourable conditions for CH_4 accumulation. Similarly, enhanced respiration of organic carbon in shallow sediments elevates CO_2 concentrations (Humborg et al., 2019). While macrophyte growth during summer can draw down pCO_2 through photosynthetic CO_2 uptake, the subsequent decomposition of deposited tissues may



instead enhance CO₂ and CH₄ release. Spatial variability of N₂O mirrors the findings of Aalto et al. (2021), with higher concentrations near the Karjaanjoki River linked to allochthonous carbon inputs and elevated nitrate availability. Aalto et al. (2021) suggested that within the archipelago, reduced riverine influence and enhanced sedimentary processes, such as dissimilatory nitrate reduction, likely sustain high ammonium availability and promote active nitrogen recycling between sediments and surface waters, particularly in summer, when autochthonous biomass and sedimentation are highest.

4.2 Air-sea fluxes

Given the strong spatial variability observed in GHG concentrations across the study area, strong variations were also observed in the corresponding air-sea fluxes. In exposed sites between Hanko and TZS, where surface seawater was undersaturated in CO₂ and low in CH₄ concentration, an uptake of atmospheric CO₂ associated with small releases of CH₄ was observed. In contrast, within the archipelago and across Pojoviken Bay, where surface waters were supersaturated in CO₂ and exhibited elevated CH₄ concentrations, releases of both CO₂ and CH₄ were observed. Sites 3 and 4 represented exceptions, being the only locations undersaturated in CO₂, thus acting as a CO₂ sink. Daily CH₄ emissions of $\geq 0.1 \text{ mmol m}^{-2}$ across all habitats are comparable to, or even higher than, CH₄ fluxes reported from similar (Lundevall-Zara et al., 2021; Roth et al., 2023) or other vegetated coastal ecosystems (Al-Haj and Fulweiler, 2020; Rosentreter et al., 2021). Regarding N₂O, Pojoviken Bay is estimated to act as a source to the atmosphere. In sheltered sites of the archipelago and exposed sites near TZS, N₂O concentrations close to or slightly below atmospheric equilibrium result in small emissions and occasional uptake, respectively. Our estimated air-sea exchanges overall mirrored the spatial trends of chamber-based fluxes and exhibited a similar range of air-sea exchange. Both chamber-based and estimated fluxes may underestimate the air-sea fluxes, as possible ebullition events are not considered. Humborg et al. (2019) suggested that air-sea CH₄ flux is likely dominated by frequent bubbling from the sediment. While this process could be dominant in shallow coastal environments, as shallow seafloor depth promotes a short residence time for CH₄ in the water column, preventing its potential full oxidation as observed in the deep open ocean (Reeburgh, 2007), it was not observed during our chamber-based measurements.

The overall contribution of the study area to atmospheric GHG budgets can be assessed by combining the air-sea flux of CO₂ with the CO₂-equivalent fluxes of CH₄ and N₂O. These equivalents are calculated using their respective sustained-flux global warming potential (SGWP), as a greenhouse gas metric to describe the relative radiative impact of a standardized amount of gas over a defined time horizon. Specifically, over a 100-year time horizon, the SGWP of CH₄ and N₂O is 27 and 273 times, respectively, greater than that of CO₂ (IPCC 2023), on a mass basis, based on:

$$F_{\text{CO}_2\text{-eq}(X)} = F_{(X)} \text{SGWP}_{(X)} \quad (3)$$

where the CO₂-eq flux of X (CH₄ or N₂O), $F_{\text{CO}_2\text{-eq}(X)}$, is the product of the flux of the gas ($F_{(X)}$) and its respective SGWP (i.e., 27 or 273) over the time horizon of 100 years. As direct measurements of air-sea N₂O fluxes were not available at the time, and to ensure consistency across all three gases, we chose to use the estimated fluxes rather than the chamber-based measurements.



Overall, the study area acted as a net source of GHGs to the atmosphere, with an average release of $1.6 \text{ g of CO}_{2\text{-eq}} \text{ m}^{-2} \text{ d}^{-1}$ over the study period, and ranging from $-1.0 \text{ g of CO}_{2\text{-eq}} \text{ m}^{-2} \text{ d}^{-1}$ at S14 to $10.6 \text{ g of CO}_{2\text{-eq}} \text{ m}^{-2} \text{ d}^{-1}$ at the mouth of the Karjaanjoki River (Fig. 7d). Exposed sites between Hanko and TZS generally acted as GHGs sink, primarily due to the substantial CO_2 uptake compensating for CH_4 emissions. An exception was S21, where the small uptake of CO_2 ($-0.008 \text{ g of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$) was offset by the release of CH_4 ($0.016 \text{ g of CO}_{2\text{-eq}} \text{ m}^{-2} \text{ d}^{-1}$), resulting in a net source. In Pojoviken Bay, the river mouth and S2 were acting as a strong source of GHGs to the atmosphere, with N_2O fluxes in the same order of magnitude as those of CH_4 . However, S3 and S4, both sites undersaturated in pCO_2 , remained net GHG sinks, despite releasing similar amounts of CH_4 and N_2O . In the archipelago, all sheltered sites remained a net source of GHGs to the atmosphere. If, from a climate mitigation perspective, it may seem sufficient to focus on CO_2 (as Figure 7a and d are pretty similar), as in the blue carbon approach, it has been shown that CO_2 uptake can be offset by CH_4 emissions (Roth et al., 2023). Our findings demonstrate that, if CH_4 matters in coastal, nearshore environments, so does N_2O , since N_2O fluxes are not only of the same order of magnitude as CH_4 fluxes but can either reinforce the warming effect of CH_4 or partially counterbalance it.

4.3 Conclusions

Shallow coastal ecosystems are highly heterogeneous, with their spatial structure and temporal dynamics of benthic communities shaping ecosystem functions (Snelgrove et al., 2014). This heterogeneity drives strong spatial variability in coastal biogeochemical processes, which exert an important influence on the carbon cycle at both local and global scales (Ward et al., 2020). Yet, despite their importance, identifying the locations and processes regulating coastal CO_2 , CH_4 , and N_2O fluxes remains uncommon, and global estimates still fail to capture the heterogeneous and dynamic nature of these environments. In particular, northern temperate coastal habitats are poorly represented in current GHG budgets, despite their relative importance: shallow waters ($<5 \text{ m}$) in the Baltic Sea cover $\sim 30,000 \text{ km}^2$ (HELCOM, 2013), an area comparable to 20% of the global distribution of mangroves (Bunting et al., 2018) or seagrass meadows (McKenzie et al., 2020). Across the study area, freshwater inputs from the Karjaanjoki River and subsequent mixing with seawater largely determined the overall spatial patterns of surface water pCO_2 , CH_4 , and N_2O concentrations. However, important deviations from this salinity-driven control were observed at the local scale. In sheltered sites within the archipelago, elevated CH_4 concentrations and supersaturated pCO_2 likely reflected benthic processes, including enhanced organic matter respiration and methanogenesis in warm, late-summer shallow waters, where limited oxidation favoured CH_4 accumulation. By contrast, in more exposed sites, mixing processes exerted stronger control, leading to lower GHG concentrations. N_2O patterns followed riverine influence with higher concentrations near the river mouth associated with inputs of allochthonous carbon and elevated nitrate availability, and lower concentrations within the archipelago reflecting reduced riverine input and active nitrogen recycling between sediments and surface waters (Aalto et al., 2021). Together, these results underline the dual importance of large-scale physical mixing and local benthic processes in shaping the spatial heterogeneity of GHG dynamics. Our findings suggest that benthic ecosystems likely play a pivotal role in regulating GHG dynamics, especially in shallow coastal environments, not only through



production but also through consumption pathways, which remain insufficiently constrained in current budgets (Rodil et al., 2021; Roth et al., 2022; Wallenius et al., 2021).

When translated into CO₂-eq, air–sea GHG fluxes were dominated by CO₂, while CH₄ and N₂O contributed comparably but in different ways. CH₄ consistently acted as a source, whereas N₂O partially offset the CH₄ release through uptake. This interplay emphasizes that the balance between production and consumption processes, particularly within benthic habitats, is critical to understanding coastal contributions to the global carbon budget. Given their extent, northern temperate coastal ecosystems represent a relevant but overlooked source of GHGs, with the potential to amplify the global ocean carbon budget. Our results highlight the urgent need for research that integrates GHG with biodiversity, benthic–pelagic interactions, and microbial processes, and that resolves temporal variability across seasonal cycles. Such knowledge is essential to improve predictions of how coastal ecosystems will mediate carbon–climate feedback under future environmental change.

Data availability

The complete dataset will be made publicly available upon acceptance of the manuscript.

Author contribution

NXG, AN, and AV designed the hypothesis field sampling. Field measurements were conducted by NXG and AV, laboratory and data analyses were performed by NXG, BD. NXG prepared the manuscript with contributions from all co-authors. All authors approved the final version of the manuscript for submission.

Competing interests

The authors declare no competing interests.

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Figure 1: Atmospheric conditions: 30-min averaged **a)** air temperature ($^{\circ}\text{C}$) and **b)** wind speed (m/s) recorded at the ICOS station FI-Tvm established at the Tvärminne Zoological Station (TZS). Spatial variation of **c)** surface seawater temperature (SST, $^{\circ}\text{C}$), and **d)** salinity (SSS), **e)** chlorophyll-*a* (Chl-*a*, $\mu\text{g L}^{-1}$) concentration, **f)** turbidity (FTU), **g)** colored dissolved organic carbon (CDOM, $\mu\text{g L}^{-1}$), and **h)** dissolved oxygen saturation (%) across the sampling area. Triangles represent the surface water conditions at the mouth of the Karjaanjoki River.

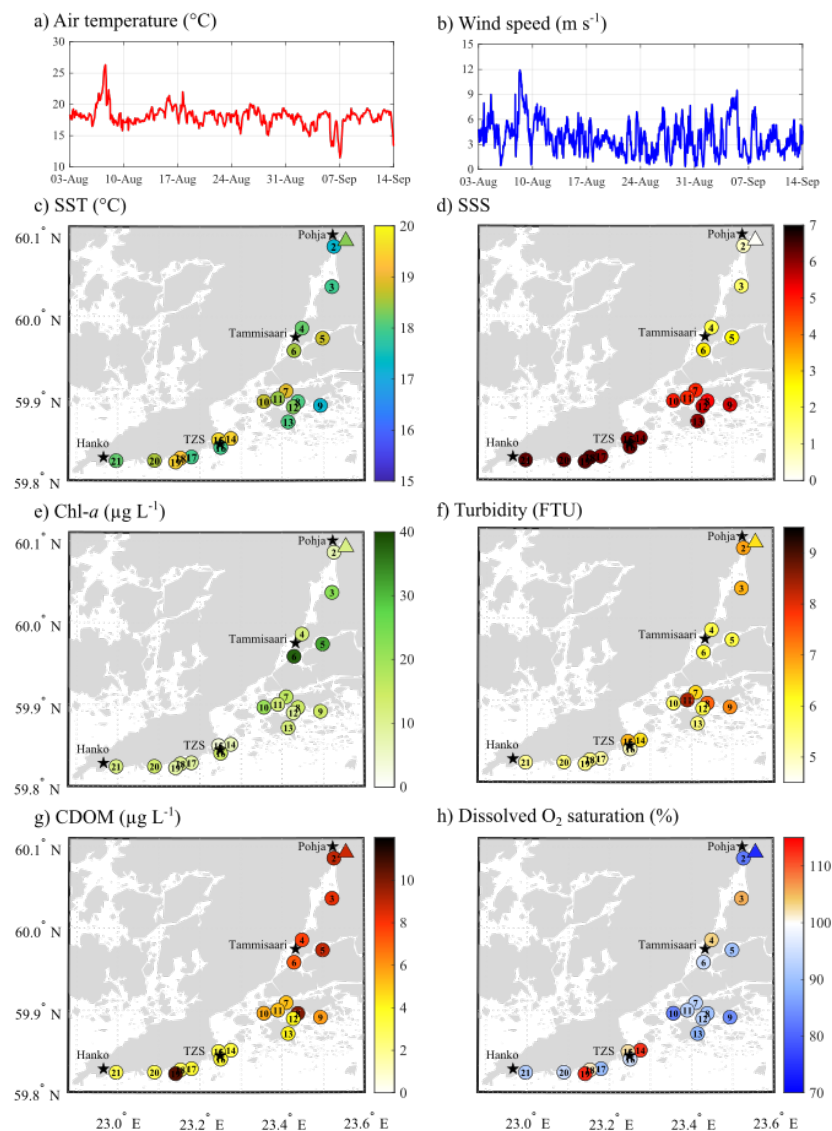




Figure 2: Left column presents the spatial variation of surface seawater **a)** pCO_2 (ppm), **b)** CH_4 (nmol L^{-1}), and **c)** N_2O concentration (nmol L^{-1}). The middle column presents measured air-sea fluxes of **d)** CO_2 ($\text{mmol m}^{-2} \text{d}^{-1}$) and **e)** CH_4 ($\text{mmol m}^{-2} \text{d}^{-1}$). The right column presents the calculated air-sea fluxes of **f)** CO_2 ($\text{mmol m}^{-2} \text{d}^{-1}$), **g)** CH_4 ($\text{mmol m}^{-2} \text{d}^{-1}$), and **h)** N_2O ($\text{mmol m}^{-2} \text{d}^{-1}$). Positive values indicate a release from the sea to the atmosphere, while negative values represent an uptake by the sea. Triangles represent the surface water conditions at the mouth of the Karjaanjoki River.

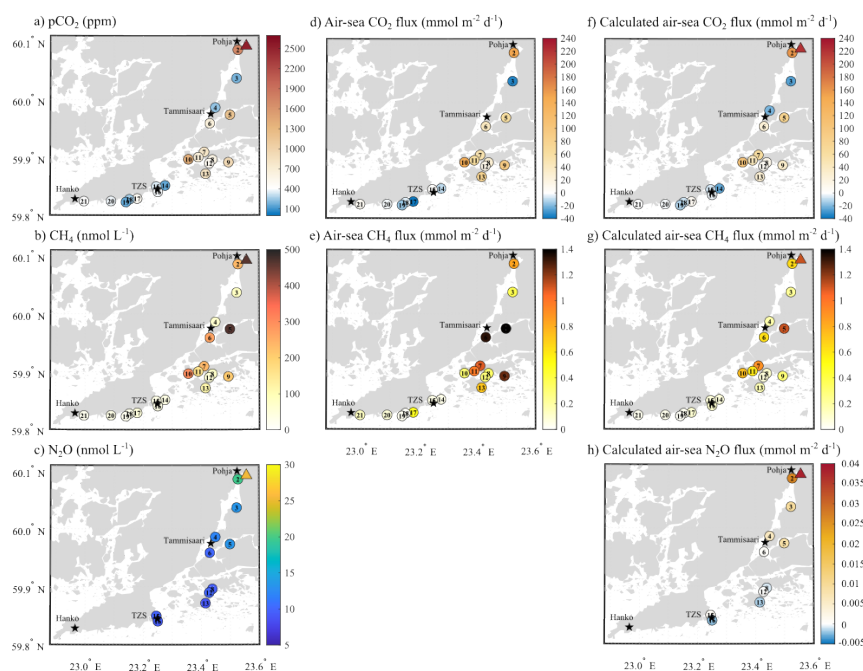




Figure 3: **a)** Relationship between salinity, TA ($\mu\text{mol kg}^{-1}$, upward triangles) and DIC ($\mu\text{mol kg}^{-1}$, downward triangles). Relationship between nDIC and nTA, and their association with **b)** pCO_2 (ppm), **c)** CH_4 (nmol L^{-1}), and **d)** N_2O (nmol L^{-1}) concentrations. Black symbols represent the seawater endmember. Circles denote exposed sites, and squares denote sheltered sites.

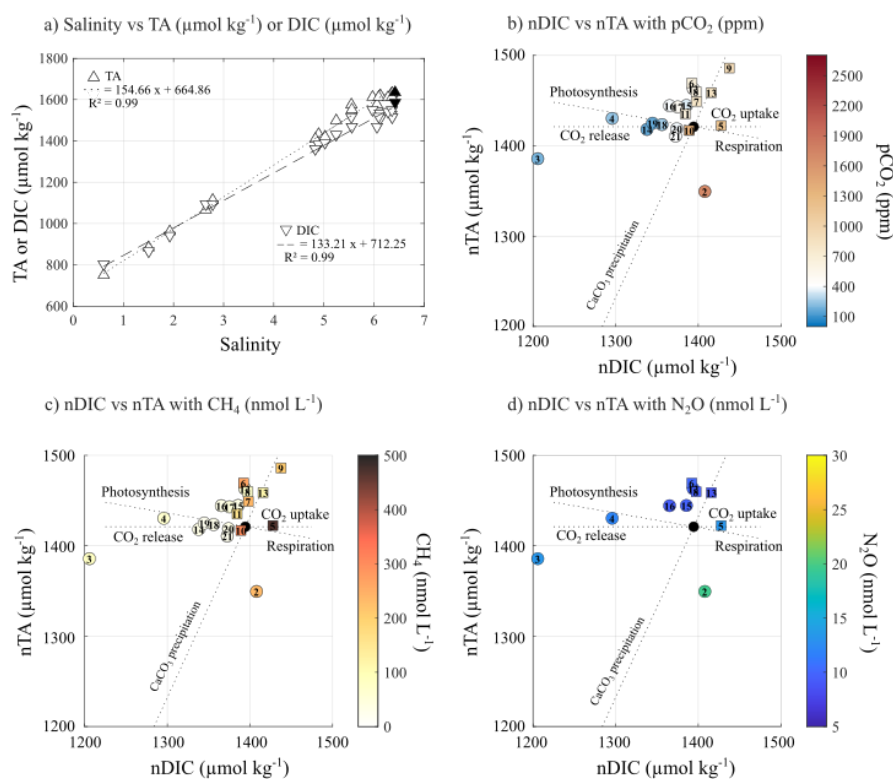




Figure 4: Heatmap of Kendall correlation coefficient **a)** between surface water pCO₂, CH₄, and N₂O concentration, and **b)** between main seawater biogeochemical properties (SST, SSS, chl-*a* concentration, colored dissolved organic carbon, turbidity, and O₂ saturation) and pCO₂, CH₄, and N₂O concentration.

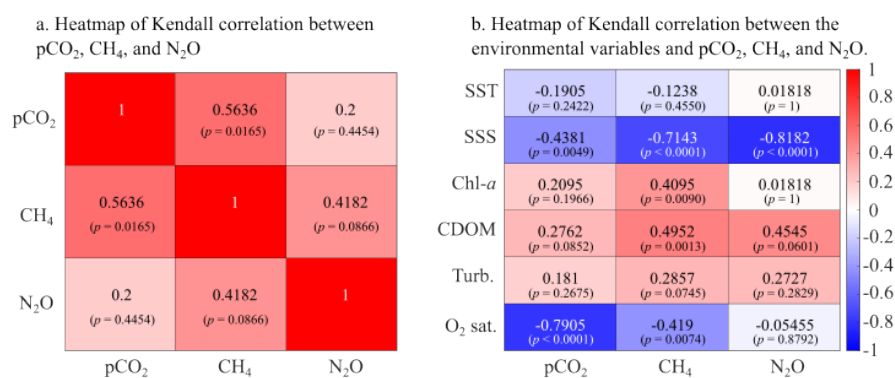




Figure 5: Relationship between surface seawater salinity and **a)** pCO₂ (ppm), **b)** CH₄ (nmol L⁻¹), and **c)** N₂O (nmol L⁻¹) concentrations. In each panel, the dotted line represents the regression across all sites, while the red dashed line shows the regression limited to “exposed” sites only. The blue line in panel **a)** represents the estimated pCO₂ resulting only from the mixing of the Karjaanjoki River water (S = 0) with seawater (S = 6.42).

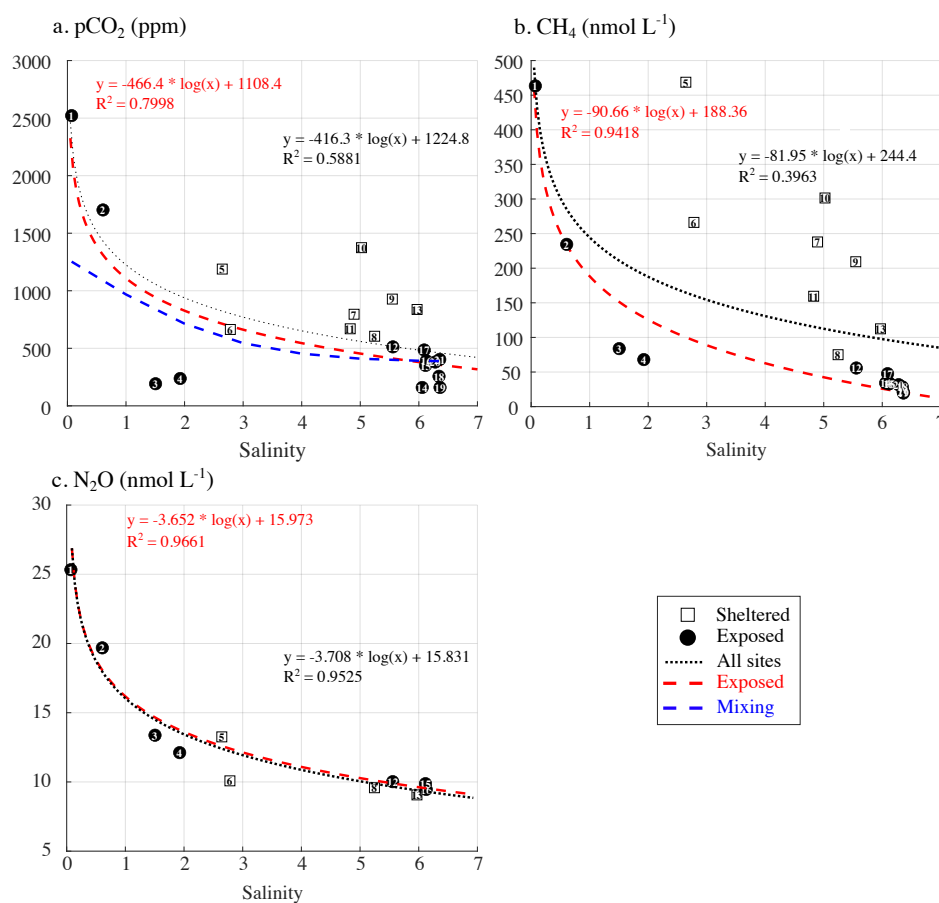




Figure 6: Relationship between the apparent oxygen utilization (AOU) and **a)** surface water Chl-*a* concentration ($\mu\text{g L}^{-1}$), **b)** surface water pCO_2 (in ppm), **c)** CH_4 (nmol L^{-1}), and **d)** N_2O (nmol L^{-1}) associated with the Chl-*a* concentration ($\mu\text{g L}^{-1}$). The triangle in each panel corresponds to the mouth of the Karjaanjoki River. Circles denote exposed sites, and squares denote sheltered sites.

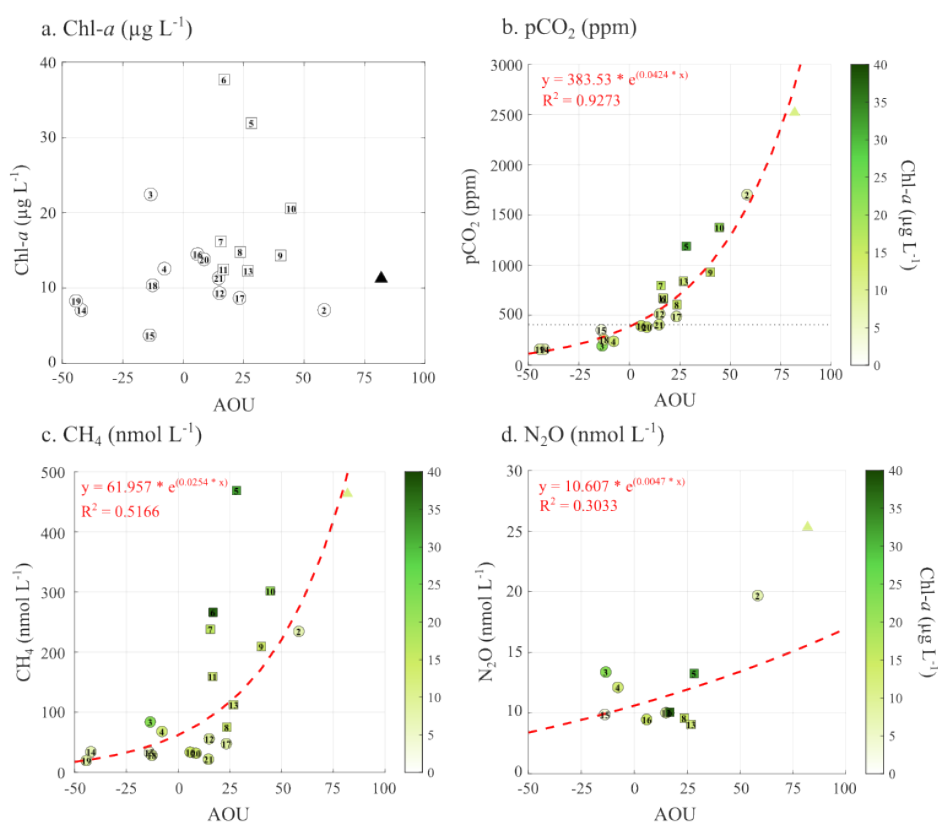




Figure 7: Air-sea fluxes of **a)** CO_2 ($\text{g m}^{-2} \text{d}^{-1}$), and CO_2 -equivalent fluxes of **b)** CH_4 ($\text{g m}^{-2} \text{d}^{-1}$), and **c)** N_2O ($\text{g m}^{-2} \text{d}^{-1}$) estimated using their respective sustained-flux warming potential (SGWPs) over a 100-year time horizon ($\text{CH}_4 = 27$; $\text{N}_2\text{O} = 273$, relative to $\text{CO}_2 = 1$, IPCC 2023), and **d)** the overall budget for all three GHGs ($\text{g m}^{-2} \text{d}^{-1}$).

