Reviewer n°1:

Overview

This manuscript (egusphere-2025-5068) presents a valuable dataset on greenhouse gas (GHG) dynamics across 21 sites in a temperate estuary. The study's primary strength lies in providing concurrent measurements of all three major GHGs across a spatial gradient from the river mouth to the outer archipelago. The spatial coverage, which captures contrasting habitats (sheltered vs. exposed sites), provides a useful map of GHG hotspots and sinks. However, the manuscript has several methodological flaws and some overinterpretation of results. The authors claim that benthic processes drive observed patterns, despite the lack of direct benthic measurements.

The authors have assembled impressive fieldwork and an extensive measurement campaign. Reframing the manuscript to emphasize its strengths (comprehensive spatial coverage, simultaneous GHG measurements) while providing more details for the method section and acknowledging some limitations (no benthic measurements, discrete sampling) will strengthen the work considerably.

Thank you for your constructive comments. We have addressed them below.

Major Concerns

1. The manuscript repeatedly mentions "benthic processes" and "methanogenesis", but there are no direct benthic measurements. The authors' attempt to deconvolve contributions using Apparent Oxygen Utilization (AOU; Figure 6) is insufficient because AOU reflects the net result of all processes (pelagic, benthic, and advective) and cannot isolate the benthic contribution. The authors observe deviations in surface water GHG concentrations from expected salinity-driven patterns and infer benthic processes, but are not really convinced.

→ This is correct; we don't have direct measurements of benthic processes and/or methanogenesis. To avoid misunderstanding, we have now modified both the abstract and the introduction to place less emphasis on these unmeasured processes. We do, however, still use Apparent Oxygen Utilization (AOU) to discuss the potential importance of benthic processes relative to pelagic contributors. We recognize that AOU may not be perfect because it reflects all processes that affect O_2 concentration in the water column. Nonetheless, we believe AOU can provide valuable insights, given the poor correlation ($R^2 = 0.03$) between chl-a and AOU. Using chl-a as a proxy for pelagic primary production, this suggests that primary producers from the pelagic realm have a limited impact on the AOU. If pelagic processes alone cannot explain the observed changes in GHGs, we suggest that processes beyond the pelagic realm, such as benthic community production and organic-matter degradation, are likely contributing to the observed surface-water pCO_2, CH_4, and N_2O concentrations. This is further supported by studies from Attard et al. (2019) and Roth et al. (2023) (performed at similar water depth and in the same area), who highlight how benthic processes such as community production, organic matter degradation, and sediment-water interactions are likely to influence both CO_2 and CH_4 dynamics.

The discussion has been adjusted to better reflect our approach while maintaining a more tempered tone in both the discussion and the conclusion.

2. Unclear gas transfer velocity and fluxes calculation. The authors measured CO_2 and CH_4 fluxes directly using floating accumulation chambers. However, for the final CO_2-equivalent budget in Figure 7, they state they "chose to use the estimated fluxes" (line 350-354). The authors adopted a gas transfer velocity (k) wind parameterization, despite having direct measured flux data, water-phase partial pressure and partial pressure data. These three data points are what are needed to derive their own site-specific gas transfer velocity. With these measurements, the authors would have generated a novel, site-specific parameterization, a valuable contribution for gas transfer velocity parameterizations. The authors' justification that Randers Fjord is most comparable (line 148) is insufficient. Additionally, several paragraphs in the discussion are more closely related to the method section.

→ Thank you for this comment. You are absolutely right that, based on our direct measurements of surface water pCO_2 and pCH_4 and the corresponding air–sea exchange, we could theoretically derive a site-specific gas transfer coefficient (k). However, it is important to note that we conducted only a small number of chamber measurements at each site. The reported values, therefore, represent average air–sea fluxes. We have clarified this in the manuscript, which now states at line 149:

"Reported fluxes correspond to the mean of two to three individual measurements conducted at each site."

As noted in Borges et al. (2004a) and mentioned in the manuscript, the formulation of k is often site-specific. Consequently, deriving a k within the scope of this study would require estimating one for each site we visited. However, we currently lack direct site-specific wind measurements, which are essential for deriving a robust k. The limited number of air–sea exchange measurements we collected is hence insufficient to support a reliable estimation. Finally, water turbulence is known to be a key parameter controlling k (Borges et al., 2004a; 2004b), and this variable was not measured. For all these reasons, we believe that estimating k under these conditions would not be meaningful.

We are aware of several estimates of k in estuarine environments: i) Borges et al. (2004a) for Randers Fjord, the Scheldt, and the Thames; ii) Borges et al. (2004b) for the Scheldt; and iii) Jiang et al. (2008) for the Georgia estuaries. As previously mentioned, k is highly dependent on water turbulence (Borges et al., 2004a; 2004b), which can be amplified by tidal currents. Among these studies, only Randers Fjord experiences minimal tidal influence. One specific aspect of working in the Baltic Sea is the absence of tides. Therefore, since we do not experience tides at our sites, we used the k value established for Randers Fjord. This reasoning is mentioned in the manuscript on lines 156–166.

Borges Alberto Vieira Delille Bruno Schiettecatte Laure-Sophie Gazeau Frédéric Abril Gwenaöl Frankignoulle Michel , (2004a), Gas transfer velocities of CO2 in three European estuaries (Randers Fjord, Scheldt, and Thames), Limnology and Oceanography, 5, doi: 10.4319/lo.2004.49.5.1630.

Borges, A.V., Vanderborght, JP., Schiettecatte, LS. et al. Variability of the gas transfer velocity of CO2 in a macrotidal estuary (the Scheldt). Estuaries 27, 593–603 (2004b). https://doi.org/10.1007/BF02907647

Jiang Li-Qing Cai Wei-Jun Wang Yongchen , (2008), A comparative study of carbon dioxide degassing in river- and marine-dominated estuaries, Limnology and Oceanography, 53, doi: 10.4319/lo.2008.53.6.2603.

3. The authors describe "in situ" measurement using a custom flow-through system (line 104) but then detail a protocol where they stopped at 21 discrete sites, waiting "until equilibrium was reached (up to 45 minutes)". This equilibration time is quite long for the LI-7810 analyzer, which has a response time of 2 seconds. Please provide more details on the "custom-built flow-through system" and why it is turning a high-resolution instrument into a 21-point discrete sampler.

→ Indeed, we used a custom-built flow-through system where water is pumped through multiple sensors. At each site, water was continuously circulated, and all parameters were measured. While most parameters could be recorded quickly, gas measurements, especially for CH_4, took noticeably more time. Our setup relies on continuous measurement of the gas phase, which equilibrates with water through an equilibrator. Therefore, the speed of measurements depends, among other factors (such as the size and type of the equilibrator), on the gas solubility. While CO_2 equilibrium was reached within minutes, CH_4 solubility caused equilibration to take much longer, particularly at high concentrations, such as those observed at Site 1, where xCH_4 values reached up to 282 ppm.

This issue occurs not only when moving from low to high concentrations but also when shifting from high to low concentrations. Since our study examines the spatial variability of GHG concentrations, it was important to ensure that each measurement truly reflected an equilibrium state. Therefore, to ensure high-quality data, we allowed enough time—up to 45 minutes—for the system to reach complete equilibrium with the water.

Finally, the 2-second response time mentioned by the reviewer is correct and appears in the instrument manual (https://www.licor.com/support/LI-7810/topics/specifications.html#top). However, this response time applies only once the gas is already in the detector and only within the range of 0–2 ppm CH_4. In our case, we first had to extract the gas from the water using the equilibrator, a process controlled by gas solubility, and our concentrations were well above the range specified in the manual.

We added this precision in the manuscript at line 120:

"Equilibration between the seawater and gas phases was monitored in real time using a laptop connected to the IRGA. Equilibrium was considered reached when both CO_2 and CH_4 concentrations stabilized at a clear plateau. Depending on the concentration gradient between sites, this equilibration period could vary substantially. While CO_2 typically reached equilibrium within a few minutes, CH_4 required longer times (up to 45 minutes) to reach a stable plateau."

Specific Comments

Line 8: "Estuaries remain understudied for GHGs" is overstated. Please moderate language to acknowledge the growing body of estuarine GHG research. Recent literature demonstrates substantial research on estuarine GHG emissions, as shown below.

→ We changed the sentence, taking also into consideration the input from reviewer 2 mentioning that "Detailed studies of GHG dynamics across the land-ocean continuum are, despite the admittedly increasing attention of the topic over the last decade, still scarce. From that perspective, there is a great value in having such a comprehensive survey of distribution and air-sea fluxes of all three gases simultaneously."

Line 8 now reads:

"Although they have gained more attention in the past decade, detailed studies of GHG dynamics across the land-ocean continuum, including shallow-water estuaries, remain relatively scarce even though they are active sources of the three most potent greenhouse gases (GHGs): carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O)."

Line 29: "CH_4 and N_2O contributed differently as a source and a sink". This phrasing is wrong. Data show CH_4 was consistently supersaturated. Only CO_2 and N_2O acted as both source and sink.

→ We changed the sentence as follows (L29):

"The overall budget of air–sea GHG exchanges was dominated by CO_2 fluxes, with CH_4 consistently acting as a source, and N_2O alternating between source and sink."

Line 115: Quite a complete setup, but not sure why there is a complete absence of pH measurements, which significantly limits the validation of carbonate chemistry calculations.

→ Indeed, it would have been valuable to include pH measurements. Unfortunately, we did not have the capability to measure pH at the time. However, we collected discrete water samples for TA and DIC, which allow us to better characterize and understand the carbonate system dynamics during the sampling period.

Lines 125-130: Were these floating chambers anchored or drifting (following the current)?

→ The manuscript reads:

"Air-sea exchanges of CO_2 and CH_4 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."

Because the chambers needed to stay connected to the IRGA, the chamber was kept 'anchored' to the boat. We used 1.5 m of Tygon tubing to connect the chamber to the IRGA, allowing the chamber to float freely on the water surface while remaining close enough to ensure safe measurements for the IRGA (e.g., preventing water from entering the IRGA), especially when other boats passed nearby. The air volume of the tubing was included in the flux calculations.

We modified the text as (L140):

"Air-sea exchanges of CO_2 and CH_4 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 with 1.5 m long Tygon tubing, which allows the chamber to move freely on the water surface."

Line 134: The choice to use Borges et al. (2004) parameterization instead of deriving site-specific values is unjustified. I suggest comparing the K600 derived from the floating chamber with the K600 by Borges et al. (2004).

→ Please refer to our response provided earlier on our decision to use the k estimated by Borges et al (2004) for the Randers fjord.

Line 160: If the system was stopped for 45 minutes at each station (line 118), why would there be 'sharp concentration changes' or 'data from transition periods between stations'? This statement is really confused about the actual sampling protocol.

→ We modified L 160 as follows:

"The recorded data from the IRGA for both seawater and air-sea flux measurements were filtered to remove measurements taken during the transition between stations and when switching between ambient air and seawater measurements, as the IRGA requires time to respond to sharp concentration changes. Additionally, data affected by improper functioning (i.e., seawater flow < 1.5 L min–1) were discarded."

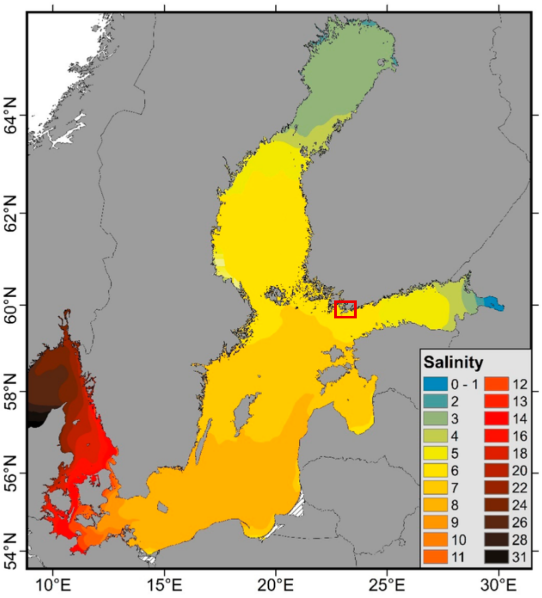
This implies that the IRGA was used for both seawater and air–sea flux measurements. Consequently, when switching the system from the seawater flow-through setup to the air–sea flux measurements, in which atmospheric concentrations were recorded, large changes in gas concentrations were observed. Please refer to our earlier response describing our system.

Lines 210-2015: The Results section for GHGs is very thin on statistical description. The Kendall correlation analysis is currently in the Discussion, but is a presentation of results. It should be moved to the Results section.

→ We have moved the statistical description from the Discussion to the Results section.

Figure 5: The "seawater endmember" has a salinity of only 6.36. This is very low for a seawater endmember. What is the salinity range in that region?

→ Salinity in the area ranged from approximately 0 (near the river inputs) to about 6.5 toward Hanko, as described in the manuscript (Fig. 1). This salinity range is expected for the area and is consistent with the values reported in Lehmann et al. (2022). Below is a visual representation of the sea surface salinity (1.5 m depth), illustrating the pronounced salinity gradient across the Baltic Sea. This map is based on hydrodynamic model data from Lehmann et al. (2022).



The map is from Jaspers, C.; Bezio, N.; Hinrichsen, H.-H. Diversity and Physiological Tolerance of Native and Invasive Jellyfish/Ctenophores along the Extreme Salinity Gradient of the Baltic Sea. Diversity 2021, 13, 57. https://doi.org/10.3390/d13020057 (https://www.mdpi.com/1424-2818/13/2/57). The red square represents our research area.

Lehmann, A., Myrberg, K., Post, P., Chubarenko, I., Dailidiene, I., Hinrichsen, H.-H., Hüssy, K., Liblik, T., Meier, H. E. M., Lips, U., and Bukanova, T.: Salinity dynamics of the Baltic Sea, Earth Syst. Dynam., 13, 373–392, https://doi.org/10.5194/esd-13-373-2022, 2022.

Lines 249-256 (Mixing Model) and Line 268 (nTA/nDIC): Details about theoretical pCO_2 calculations from conservative mixing and alkalinity/DIC normalization procedures belong in Methods, not Discussion.

→ The lines related to the mixing model read:

"Assuming that changes in SSS reflect a mixing ratio between the Karjaanjoki River and the seawater endmembers 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 pCO_2 (blue dashed line, Fig. 5a) using CO2SYS v3 (Sharp et al., 2023), applying the carbonic acid dissociation constants (K1 and K2) of Millero et al. (2006) and the KHSO4 formulation of Dickson (1990)."

Lines related to nTA/nDIC read:

"Therefore, to discard the impact of freshwater inputs, TA and DIC were normalized to the average surface seawater salinity of 5 (denoted as nTA and nDIC, respectively) using the normalization of Friis et al. (2003)."

We believe that moving this information to the Methods section would be inappropriate because it would require the reader to infer why these steps are included. Keeping this information in its current location does not disrupt the manuscript's flow and remains sufficiently concise.

Some GHG research papers for estuarine systems:

Yeo, J. Z. Q., Rosentreter, J. A., Oakes, J. M., Schulz, K. G., & Eyre, B. D. (2024). High carbon dioxide emissions from Australian estuaries driven by geomorphology and climate. Nature communications, 15(1), 3967.

Zheng, Y., Wu, S., Xiao, S., Yu, K., Fang, X., Xia, L., ... & Zou, J. (2022). Global methane and nitrous oxide emissions from inland waters and estuaries. *Global Change Biology*, *28*(15), 4713-4725.

Nguyen, A. T., Némery, J., Gratiot, N., Dao, T. S., Le, T. T. M., Baduel, C., & Garnier, J. (2022). Does eutrophication enhance greenhouse gas emissions in urbanized tropical estuaries?. *Environmental Pollution*, *303*, 119105.

Borges, A. V., Abril, G., & Bouillon, S. (2018). Carbon dynamics and CO_2 and CH_4 outgassing in the Mekong Delta. *Biogeosciences*, *15*(4), 1093-1114.