

Reviewer n°3

Overview:

The manuscript „Spatial heterogeneity of GHG dynamics across an estuarine ecosystem” presents a nice data set of GHG data and related variables in an estuarine ecosystem in the northern Baltic Sea. The data set presents a spatial distribution within the onset of the of the salinity gradient, however, it represents just the late summer period. Nevertheless, the data set included next to the CO₂, Methane and N₂O as well. The main findings are that the estuarine system is heterogeneous, sinks and sources were found for CO₂ and N₂O, but methane were supersaturated in all samples and were emitted to the atmosphere.

The manuscript is well written and relatively easy to follow, even if you are not familiar with the study site. Although it is known that the coastal waters and estuaries are important for the GHG balance, comprehensive data set with all three most important GHG are still rare, and they are needed to understand these quite heterogeneous contributions.

Major comments:

If next to CO₂ and Methane also N₂O is included to understand the interaction between these three GHGs, it would be good to introduce next to the Carbon cycle also the Nitrogen Cycle and the interaction between them. At some points the mentioning of N₂O not good connected.

→ We modified the introduction. We can now read starting at L 65:

“N₂O is primarily produced via nitrification (ammonia oxidation) and denitrification (nitrate reduction) in sediments and water columns and is controlled by the availability of dissolved inorganic nitrogen and oxygen (Bange 2006). Eutrophication and hypoxia, often driven by excess nutrient and organic matter inputs, have been shown to promote N₂O emissions (Murray et al., 2015; Bräse et al., 2017). Coastal ecosystems are recognized as significant sources of N₂O to the atmosphere (Bange, 2006; Cheung et al., 2025; Resplandy et al., 2024), where denitrification, especially in sediments and on particles, often dominates N₂O production, even in well-oxygenated waters (Wan et al., 2023). However, coastal estimates remain uncertain due to sparse measurements and high spatial heterogeneity (Wan et al., 2023).”

One important variable to understand N₂O production and emissions is next to the oxygen supply the availability of nitrate and the other DIN, as the authors mentioned in the discussion. Can you present also at least nitrate concentrations and include them in the correlation matrix?

→ Unfortunately, we did not measure nitrate and other DIN during our sampling. Some measurements were taken in the study area during similar times, but our sampling was not conducted at the same time and/or exact location, making it difficult to use them to improve the interpretation of the N₂O data collected. Maybe our sentence was unclear; we modified it as follows:

L 257:

“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.”

L 355:

“Spatial variability of N₂O mirrors the findings of Aalto et al. (2021), who linked higher N₂O concentrations near the Karjaanjoki River to higher nitrate inputs and allochthonous carbon inputs.”

Somewhere in the manuscript the authors must explain what the potential sinks for N₂O are and present an explanation for the undersaturation of the N₂O. Do you assume that N₂O is consumed under anaerobic conditions in the sediments? Are the also processes in the water column which consumed N₂O.

→ The lack of nitrate measurements associated with our observations makes it difficult to explain the observed trend, but a study by Aalto et al. (2021) from the same area, along the same salinity gradient, suggested that sites located in the ‘offshore archipelago,’ where autochthonous (locally produced, e.g., phytoplankton-derived) organic matter is more common and nitrate concentrations are lower, promote DNRA as the main pathway for recycling nitrate to ammonium without producing N₂O. This process acts as a sink by suppressing N₂O formation. They also suggest that complete denitrification occurred in environments with a high organic carbon-to-nitrate ratio, such as those with abundant autochthonous organic matter.

We modified our manuscript and can now read from L 353:

“Spatial variability of N₂O mirrors the findings of Aalto et al. (2021), who linked higher N₂O concentrations near the Karjaanjoki River to higher nitrate inputs and allochthonous carbon inputs. They suggested that the ratio between nitrate and autochthonous organic carbon controls the balance between N-removing denitrification and N-recycling through Dissimilatory Nitrate Reduction to Ammonium (DNRA), as well as the end-product of denitrification (Aalto et al., 2021). Within the archipelago, where riverine influence is limited, DNRA can produce significant amounts of bioavailable ammonium, enhancing nitrogen recycling between sediments and surface water, especially in summer, when autochthonous biomass production and sedimentation are highest.”

The aim of the study which is formulated at the end of the introduction seems to be a bit too ambiguous. I would suggest orientating the aims a bit more on the structure of the discussion section.

→ We rephrased the last chapter of the introduction (L 77). It now reads:

“We investigate the dynamics of CO₂, CH₄, and N₂O (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 and discuss the roles of physical drivers and biological processes in the observed changes in GHG concentrations. In doing so, we aim to estimate the contribution of coastal ecosystems to GHG emissions and provide additional data that may be useful in improving global estimates of GHG emissions from the coastal ocean.”

The explanation of the importance of the sediments for the GHG production, without having direct measurements comes a bit out of the blue and contradicts the hypotheses that the GHGs are mainly just mixed from the river inputs.

→ We have tuned down the importance of the sediments for GHG production, as we don't have direct measurements. In the new section 4.3 Exposed and semi-sheltered vs sheltered sites, we can read at L 338:

“Freshwater mixing with seawater appears to control the concentration of all three GHGs at exposed and semi-sheltered 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.”

Further down, L 349, we can read:

“Anoxic degradation of organic-rich sediments (methanogenesis), exacerbated by warm late-summer waters (Roth et al., 2022; Yvon-Durocher et al., 2014), combined with short water residence times that limit oxidation in both sediment and the overlying water column (Reeburgh, 2007), creates favourable conditions for CH₄ production. Due to the sheltered nature of the sites and limited water exchange, the produced CH₄ can accumulate. Similarly, enhanced respiration of organic carbon in shallow ecosystems elevates CO₂ concentrations (Humborg et al., 2019).”

Some specific / minor comments:

Abstract: quite too long and can be more focused.

→ We tried to shorten it, taking into consideration comments from other reviewers.

L21: N₂O is missing

→ We are not sure about what the reviewer is referring to.

L 21 reads: “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.”

This sentence is not related to N₂O, and the previous sentence clearly refers to both CO₂ and N₂O.

L 28: Is Methane always a source and N₂O a sink?

→ The sentence has been changed as follows: “The overall budget of air-sea GHG exchanges was dominated by CO₂ fluxes, with CH₄ consistently acting as a source, and N₂O alternating between source and sink.”

L64. There is some literature that N₂O production and Oxygen depletion correlated, e.g. in the Elbe Estuary

→ We modified this section; see earlier response, where we mentioned studies on N₂O dynamics in the Elbe Estuary.

L 88: What are soft-sediment habitats

→ The sentence now reads (L 93):

“Sampling sites (N = 21) were selected to encompass a wide range of soft-sediment habitats (e.g., including both vegetated and non-vegetated sediments with grain size ranging from coarse sand to clay, silt, and mud) and to represent a spatial gradient (50 km) from the outer to innermost archipelago.”

L100. What was the partial sampling strategy? From fresh to salty? Each Stations just once, how much on one day....

→ We added the following precision (L 110):

“Sites were visited once during the study period, with sampling conducted every two to three days, depending on weather conditions and boat availability.”

L231: Did you measure DIN (Nitrate, ...)

→ Unfortunately, we did not measure nitrate and other DIN during our sampling. Some measurements were taken in the study area during similar times, but our sampling was not conducted at the same time and/or exact location, making it difficult to use them to improve the interpretation of the N₂O data collected.

L 306 ff. Here comes the main concrete results of the manuscript that can be one new chapter

→ We have not split section “4. Discussion” into four subsections:

- 4.1. Salinity gradient
- 4.2 Biological driver
- 4.3 Exposed and semi-sheltered vs sheltered sites (the new chapter as requested)
- 4.4 Air-sea flux densities