

Reviewer's comments for Drivers of the spatiotemporal distribution of dissolved nitrous oxide and air-sea exchange in a coastal Mediterranean area

This study investigates the spatiotemporal distribution of dissolved N₂O and air-sea exchange in the coastal waters of the Balearic Islands. The authors identify temperature, salinity, and chlorophyll *a* as key drivers influencing N₂O variability, using machine learning approaches to analyze their relationships. Their findings contribute valuable data on N₂O fluxes in a Mediterranean coastal system, an area where such measurements remain limited. However, several aspects of the study warrant further clarification and discussion. Below are my comments and suggestions for this manuscript.

We sincerely thank the reviewer for the thorough and constructive evaluation of our manuscript "*Drivers of the spatiotemporal distribution of dissolved nitrous oxide and air-sea exchange in a coastal Mediterranean area.*" We appreciate the recognition of the novelty and relevance of our contribution, particularly regarding the scarce N₂O observations in the Mediterranean Sea. We carefully considered all comments and suggestions, which have led to significant improvements in the manuscript.

In the revised version, we have clarified the methodological approach, strengthened the discussion on mechanistic drivers of N₂O variability, included supporting literature, and provided more precise information about sampling design, environmental context, and site-specific features such as the presence of seagrass meadows. Below, we provide point-by-point responses to each of the reviewer's comments, including detailed explanations of the revisions made and the corresponding locations within the manuscript.

The title suggests that the study identifies drivers of the spatiotemporal distribution of dissolved N₂O and air-sea exchange. However, the manuscript does not clearly demonstrate how the measured parameters (drivers) directly influence these variations over time and space. Additionally, why were these specific parameters chosen as drivers? For instance, why was NH₄⁺ not included.

We thank the reviewer for highlighting these critical points. We acknowledge the importance of clearly justifying both the selection of environmental parameters and their relationship to the observed N₂O dynamics across time and space.

To identify the most influential variables, we first conducted a broad exploratory analysis that included a wide range of physical, chemical, and biological parameters measured during the study—such as NH₄⁺, PO₄³⁻, turbidity, and others. We applied variable importance metrics (e.g., based on random forest models and correlation analyses) and tested multiple model configurations to evaluate their predictive strength and consistency across sites and seasons.

This data-driven approach resulted in the selection of a final set of variables that consistently explained the greatest variation in dissolved N₂O concentrations and saturation. These include:

- Temperature and salinity, which influence gas solubility and microbial kinetics;
- NO₃⁻ and NO₂⁻, as key substrates or intermediates in nitrification and denitrification;
- DOC, which supports heterotrophic microbial activity;
- Chlorophyll *a* serves as a proxy for primary production and potential oxygen variability, as well as for organic matter.

Although NH₄⁺ was initially considered, its influence in the model was relatively low, and in some cases, its inclusion reduced the overall predictive power due to missing data or noise in certain sites. Therefore, it was excluded from the final analysis to ensure robustness and comparability across the entire spatiotemporal dataset. We have now clarified this process in the revised

Methods section Lines 223-225 and expressly acknowledge the exclusion of NH_4^+ as a limitation and an opportunity for future, targeted studies.

Additionally, we have revised the Results and Discussion to explain more explicitly the mechanistic pathways through which the retained variables influence N_2O production, accumulation, and fluxes. This includes:

- The role of temperature and salinity in modulating solubility and stratification; Lines 312-325.
- How NO_3^- enrichment reflects anthropogenic inputs and potential for enhanced nitrification; Lines 345-348.
- And the contribution of DOC and Chl-a to oxygen availability and microbial dynamics. Lines 336-342.

Finally, we have ensured that the title and narrative more clearly align with the structure of the analysis, emphasizing the identified environmental associations with N_2O distributions.

In addition, the study area appears to be relatively shallow. Were sediment N_2O fluxes considered? If not, could the lack of sediment contribution explain the weak relationships observed in the study?

We appreciate the reviewer's pertinent observation regarding potential benthic contributions to the N_2O budget, particularly in shallow coastal areas such as those studied here.

At the time of this study, no direct measurements of sediment–water N_2O fluxes were available, as the required instrumentation (e.g., benthic chambers or microprofiling sensors) and logistical support were not yet in place. For this reason, our analysis focused exclusively on water column N_2O dynamics and air–sea exchange.

We fully acknowledge that sediment-derived N_2O fluxes may play a role in shaping dissolved N_2O concentrations, especially under low-oxygen or organic-rich conditions, and that the absence of these data may contribute to the moderate explanatory power of some of our observed relationships. However, the predominantly oxygenated conditions observed throughout the study period, along with negative AOU values, could suggest limited sedimentary N_2O production in our sites.

Importantly, we are currently conducting a dedicated follow-up study designed to quantify benthic N_2O fluxes using sediment core incubations and in situ benthic chambers in the same sampling locations. These measurements will allow us to better assess the relative contribution of sediment processes to the coastal N_2O budget in future analyses.

We have now included a sentence in the Results and Discussion section to acknowledge this limitation and highlight the importance of benthic flux measurements in future efforts. Lines 346-348.

Line 21: Consider providing the average air-sea flux with standard deviation for clarity and comparison.

We thank the reviewer for this helpful suggestion. As recommended, we have included the average air–sea N_2O flux along with its standard deviation in the Abstract to enhance clarity and facilitate better comparison with other studies. Line: 22

Line 36: Briefly introduce nitrification and denitrification, including the conditions under which these processes occur.

We appreciate the reviewer's insightful suggestion. In response, we have added a concise overview of the nitrification and denitrification processes, including the environmental conditions

in which they take place, to the Introduction section (Lines: 38-42). This enhancement improves the contextual understanding of the microbial pathways that lead to N₂O production in marine systems.

Line 86: Time sampling timeline is unclear. Please specify when the samples were collected.

We thank the reviewer for pointing this out. The sampling timeline has now been clarified in Section 2.1 – Study Area, where we specify the exact time periods and seasonal coverage of the data collection.

Line 136 - 143: Please specify the bottle type, volume, and collection frequency for DO, Chl *a*, nutrient, DOC and N₂O samples.

We appreciate the reviewer's attention to methodological detail. As suggested, we have now added the bottle type, volume, and collection frequency for DO, Chl *a*, nutrients, and DOC in the Materials and Methods section. For N₂O, we considered that all relevant sampling information, including handling and analytical procedures, was already sufficiently detailed in the original submission.

Line 202: This section lacks descriptions of basic environmental parameters, such as surrounding nutrient and oxygen variations. While these results are presented in Section 3.2, that section mainly focuses on their impact on N₂O rather than describing the environmental parameters themselves. To improve clarity and provide a better understanding of local environmental conditions, consider including these descriptions here.

We thank the reviewer for this valuable suggestion. As recommended, we have now added a brief summary of key environmental parameters—including oxygen, nitrate, nitrite, and DOC concentrations—at the end of Section 3.1 (Lines 261-269). This addition provides a clearer and more complete overview of the local environmental conditions, independently of their influence on N₂O dynamics, which are further explored in Section 3.2.

Line 205: Is it BP or PB? The abbreviation appears inconsistent. Please check for consistency, including in the Methods section.

We apologize for this inconsistency. The station abbreviation has been thoroughly reviewed and corrected throughout the manuscript, including the Methods section, to ensure consistent usage.

Line 226-234: The table is unclear. It states significant seasonal, yearly, monthly, or station differences for some parameters, but these are not evident in Table 1. Please clarify or update the table accordingly.

We appreciate the reviewer's observation. To avoid confusion, we have removed references to Table 1 where statistical differences were not clearly supported. Additionally, we have revised and clarified Table 1 to indicate significant differences where applicable explicitly. For example, we have now marked when N₂O % saturation values significantly differ from 100%, as suggested in a previous comment, to improve clarity and interpretability.

Line 254: Unit?

We apologize for the oversight. The unit has now been included in the revised manuscript to ensure clarity.

Line 265: The not shown results could be included in the supplementary material.

We thank the reviewer for this observation. Due to the strong visual and statistical similarity between this relationship and the one already shown in Figure 5 (temperature vs. Sat%N₂O), we considered that including an additional figure or supplement would be redundant. For this reason, we have chosen to report the statistical results directly in the text, providing the exact correlation strength and significance for transparency.

Line 285: The study found low NO₃⁻ and NO₂⁻ concentrations, weak nitrification signals, and no correlation between AOU and N₂O. Based on these findings, the authors propose that photosynthetic organisms-driven NO reduction could be a source of N₂O in their system. This presents an interesting alternative pathway to nitrification and denitrification. However, based on these data, this hypothesis remains uncertain. Please provide a more detailed explanation of how this mechanism works.

We appreciate the reviewer for this insightful comment. We concur that the hypothesis related to N₂O production through NO reduction by photosynthetic organisms is indeed speculative in our study, given the indirect evidence presented. Our goal was not to claim this as the primary pathway, but to point out that it could be a viable complementary mechanism to consider under the specific conditions observed—particularly, low NO₃⁻/NO₂⁻ availability, well-oxygenated waters, and the seasonal correlation between N₂O and Chl *a* peaks.

To clarify this mechanism, we have expanded the explanation in the Results and Discussion section (Lines: 348-362). Briefly, recent studies have shown that certain photosynthetic microorganisms, including marine phytoplankton and cyanobacteria, can reduce intracellular nitric oxide (NO) to N₂O as part of a detoxification or signaling pathway (e.g., Burlacot et al., 2020). This pathway may be more active under high-light conditions or when nitrite accumulates transiently, leading to intracellular NO production. Although our data do not directly capture these intracellular processes, the temporal alignment between Chl *a* and N₂O concentrations, combined with the lack of evidence for pelagic nitrification, supports the consideration of this emerging mechanism in productive surface waters.

We have revised the manuscript to clarify the tentative nature of this interpretation and to improve the description of the underlying mechanism and its supporting literature.

Line 296: The explanation in Section 3.2 is largely based on the GBM and CVB results; however, it lacks a deeper discussion on the relationships between parameters and N₂O, as well as a literature review for comparison. Expanding on these aspects would strengthen the section.

We thank the reviewer for this helpful suggestion. As recommended, we have expanded Section 3.2 to include a more detailed discussion on the mechanistic relationships between N₂O concentrations and the main environmental variables identified (e.g., temperature, salinity, Chl *a*, DOC, NO₃⁻), as well as their potential interactive effects. We have also incorporated relevant literature for comparison with other coastal and estuarine systems. These additions can be found in the revised manuscript in lines 384-392.

Line 312: I agree that coastal air-sea N₂O exchange is an important parameter in the context of GHG emissions. However, this section lacks comparisons with similar studies or coastal systems, making the discussion somewhat limited.

We value the reviewer's perceptive feedback. In response, we have updated Section 3.3 to include comparisons with other coastal and estuarine systems from around the globe. This update specifically includes reference values from recent studies on N₂O fluxes in various environments, including both vegetated and non-vegetated shallow coastal areas, estuaries, and seagrass meadows. These enhancements provide context for the magnitude and direction of the observed fluxes in the Balearic Sea and reinforce the discussion about the regional and global significance of our findings. Please see lines 421-426 and 443-446 in the updated manuscript.

Lines 329-339: The description of the study sites is insufficient. It is unclear which areas are open regions and which have seagrass. This lack of detail in the study location section makes their sudden appearance in the discussion feel abrupt. In addition, please explain the mechanism and process by which vegetation acts as a sink for N₂O.

Thank you for pointing this out. We have revised Section 2.1 to include more precise descriptions of the physical and benthic characteristics of each sampling site. Specifically, we now clarify that PB is located in an open embayment without seagrass influence, CA is surrounded by dense *Posidonia oceanica* meadows, and CS includes shallow waters with patchy vegetation. This information has been added at the end of Section 2.1 (Lines 122-128), ensuring a smoother transition and improved contextual understanding of the discussion that follows in later sections.

We agree with the reviewer and have now included a paragraph in Section 3.3 (Lines 437-442) explaining the mechanisms by which seagrass meadows can act as sinks for N₂O. This includes enhanced denitrification in oxygenated sediments, reduced nitrogen availability due to high primary production, and microbial community processes favored by seagrass root systems. This addition supports our interpretation of the lower fluxes observed at vegetated sites and provides stronger mechanistic insight.

Line 340: Please provide references for European seagrass constitute.

Thank you for the suggestion. We have now added a reference to substantiate the statement regarding the contribution of European seagrasses to the global extent. The reference has been included in Section 3.3 (Line 448), supporting the ecological relevance of Mediterranean seagrass meadows in the context of coastal N₂O fluxes.

Line 344: The Methods section does not describe the presence, extent, or coverage of seagrass meadows at the study sites. Since seagrass is later discussed as a factor influencing N₂O dynamics, please provide details on seagrass distribution and area to support these claims.

Thank you for your valuable observation. In response, we have updated Section 2.1 (Study area) to explicitly describe the presence and ecological context of seagrass meadows at each station. Specifically, we now state that the CA site is located within a dense *Posidonia oceanica* seagrass meadow, the CS site includes shallow waters with patchy vegetated coverage, and the PB station is situated in an open bay without seagrass. These additions clarify the relevance of seagrass presence in the interpretation of N₂O dynamics and improve the connection between site characteristics and the discussion provided in Section 3.3.

Line 353: The estimation of N₂O GWP is based on a 1 km offshore distance and 1,428 km of coastal length. What is the basis for this area calculation? Additionally, uncertainty should be provided for this conversion. Does this area calculation include both seagrass meadows and bare sediments?

We appreciate the reviewer's thoughtful observation. The 1 km offshore distance combined with the 1,428 km of coastal length was used as a first-order approximation of the potentially active N₂O exchange area in the Balearic coastal zone. This estimation is based on previous methodological approaches applied in similar large-scale GHG assessments, including Resplandy et al. (2024) and Rosentreter et al. (2023), which use coastal buffer zones (typically 1–3 km) to estimate regional coastal fluxes.

While this approach does not differentiate between vegetated (seagrass) and non-vegetated (bare sediment) areas, it provides a conservative estimate of the potential footprint for N₂O exchange in the region. We have clarified this point in Section 3.3, noting that this surface likely

encompasses a mix of substrates, and that more refined spatial mapping would be required for precise habitat-specific flux quantification.

Additionally, the uncertainty of the GWP estimate is reported ($\pm 5.7 \times 10^{-7}$ Pg CO₂-eq y⁻¹) and reflects variability in flux measurements across sites and time.

Line 361: Line 361: Ensure unit consistency—sometimes 'nM' is used, while other times 'nmol L⁻¹' appears. Please standardize throughout the text

Thank you for pointing this out. We have reviewed the manuscript thoroughly and standardized the units, using 'nmol L⁻¹' consistently throughout the text to ensure clarity and uniformity.

There seems to be inconsistent use of r and R². Please ensure consistent notation throughout the text.

Thank you for your careful observation. We have reviewed the manuscript and standardized the correlation notation throughout the text.