Response to Reviewer Comments

Manuscript Title:

Marine emissions and trade winds control the atmospheric nitrous oxide in the Galapagos Islands

Manuscript Number:

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Responses to the reviewer comments are written in cyan in italics.
Changes to the manuscript associated with each comment are explained in orange in bold.

Reviewer #1 Comments

Comment 1 This study presents the first 15 months of in situ atmospheric N2O data from a newly established monitoring site on the Galapagos Islands. The site is situated between two hot spots of oceanic N2O emissions: (i) the Peruvian and Chilean and (ii) the Costa Rican upwelling systems, often referred to as the Eastern Tropical South Pacific and North Pacific, respectively. The new Galapagos site is much closer to these ETSP and ETNP hot spots than previously available data from NOAA or AGAGE. Overall, this is an exciting and innovative study that introduces a valuable new N2O monitoring site. The Introduction is also excellent, going beyond the usual statements about N2O and covering new ground relevant to the current study.

We thank the reviewer for the time spent assessing the manuscript, for their constructive comments, and for their interest in the content. Manuscript improvements based on the reviewer's comments are addressed below and tracked in the original manuscript document.

Comment 2 Sections 3.2 and 3.4 on diurnal variability and local Galapagos emissions are details that seem to digress from the big picture goals of this study but require much of the reader's concentration to follow. On the other hand, the diurnal variability is NOT small (e.g., the diurnal cycle of 0.8 ppb in March, 2024) with respect to the big picture variability (upwelling vs. Southern Ocean vs. NH influences) shown in Figure 8. At minimum, the last paragraph of the Introduction should provide a blueprint for the reader as to why so much attention is focused on diurnal variability and local emissions. Perhaps Section 3.4 could even be moved to the Supplement.

We thank the reviewer for their suggestion. Indeed, the diurnal variability is not negligible compared to the variability shown in Figure 8 and Section 3.5. Therefore, we still believe it is crucial to discuss this in the main manuscript. We edited the last paragraph of the introduction to motivate the readers on the importance of the analysis of local emissions and the diurnal cycle.

We have added the following sentence to the introduction (Lines 70-76): "Because such top-down analyses cannot resolve emissions for the grid cell in which observations are collected, it is necessary to identify periods during which local emissions are a possible dominant source of N_2O. Given the availability of concurrent CO measurements due to instrumental capabilities, we supplement the analysis of N_2O variability with CO data to examine the influence of local anthropogenic activities. Additionally, we analyze the stagnancy of sampled air masses using supplementary meteorological data to further refine the observations. Lastly, investigating the N_2O and CO diurnal cycles is necessary as they provide insights into how local trends in anthropogenic activities in the Galapagos impact short-term observations."

Comment 3 Also, when the values of I are presented in Figure 2, please provide some forewarning of why Region 3 is included, i.e., to filter local emissions. Otherwise, it is puzzling why that region was considered in the same league as the NH and ETSP upwelling regions.

We agree that the motivation for including Region 3 in Figure 2 might not be as clear as originally intended. Please see our response and description of changes in Comment 8 below.

Comment 4 In general, this study would be more satisfying if a Figure 5-like set of results could be presented that connected logically to Figure 6.

We thank the reviewer for the suggestion. We have added various statements in section 3.3 to connect the results in Figure 5 and 6 in a more logical manner. The detailed comments are given below in response to line-by-line comments.

Comment 5 Line 59. Since the Introduction has focused entirely on N2O, a line explaining why CO is also included in the study would be useful, e.g., is this due to common physical properties of N2O and CO that allow the two gases to be measured with the same instrumentation or is it because CO serves as a useful indicator of combustion activity?

We thank the reviewer for their insightful comment. The Picarro Inc. G5310 is designed to measure both N_2O and CO due to the overlap in their near-IR absorption spectra, making concurrent measurements possible and necessary. Additionally, we include CO measurements in our analysis as a means to filter out local combustion activities that could otherwise bias the attribution of observed N_2O enhancements to marine emissions from the ETSP.

We have added the following statement in the Introduction (Line 73): "Given the availability of concurrent CO measurements due to instrumental capabilities, we supplement the analysis of N_2O variability with CO data to examine the influence of local anthropogenic activities." We also included the following explanation in Methods Section 2.2 (Line 107) to describe the instrumental properties enabling simultaneous CO and N_2O measurements: "Due to overlapping spectral features of N_2O and CO absorption in the near-IR range and their relevance to climate and air quality monitoring, the Picarro Inc. G5310 CRDS provides concurrent measurements of both gases (Adkins et al., 2021; Nie et al., 2024; Zellweger et al., 2019)."

Comment 6 Line 111-112. The repeatability of 0.04 ppb for N2O measurements is impressive. It would seem most relevant to compare this to the repeatability of the NOAA and AGAGE measurements for the sites shown in Figure 1. For example, Lan et al., 2024 report an "uncertainty" in NOAA N2O data of 0.16 ppb following the replacement of the GC-ECD system with a TILDAS system [Lan et al., 2024]. How are uncertainty and repeatability, as defined here, related?

We thank the reviewer for their question on the repeatability. While repeatability represents the precision of repeated measurements, uncertainty includes instrumental noise and calibration bias as well. We estimate our repeatability by calculating the long-term precision of four calibration cylinders, as shown in Figure S2. In the most recent version of the NOAA CCGG flask measurement product, Lan et al., 2024 report that the repeatability based on a single high calibration tank measurements ranges between 0.01 and 0.02 ppb for the TILDAS instrument. This value is comparable to our repeatability estimate (see Section 7 in their README[1] file for the most recent repeatability values for NOAA flask measurements.

We added the following sentence in Line 126 to include the repeatability comparison between data presented in Figure 1: "Similarly, N_2O flask measurements from the NOAA Global Greenhouse Gas Reference Network have repeatability ranging between 0.01 and 0.02 ppb based on repeated measurements of the high calibration tank (Lan et al., 2024)."

Comment 7 Line 138. Please clarify what is meant by, "the surface layer in which the fluxes occur is defined as 0-100 m" Some particle dispersion models assign a flux only if the footprint comes from the bottom half of the surface layer. Is this the case here? Also, how does the 100m surface layer correspond to the 529 m boundary layer at GAL cited on line 197?

[1] `https://gml.noaa.gov/aftp/data/trace_gases/n2o/flask/surface/README_n2o_surface-flask_ccgg.html`

We thank the reviewer for highlighting the need for clarification. In FLEXPART v10.4, the footprints assigned to fluxes, i.e., the source-receptor relationship, are averaged between two user-selected altitudes above sea level, typically 0 – 100 m. In this context, "the surface layer" refers to this specific altitude range. In our study, air-sea gas exchange occurs within the first meter, and there are no known point sources of anthropogenic emissions above 100 m in the Galapagos, except for aviation. We acknowledge that referring to this layer as the "surface layer" could be confused with the surface boundary layer discussed in later sections. The surface boundary layer mentioned in Line 529 specifically refers to the well-mixed boundary layer over the Galapagos in the context of local anthropogenic and terrestrial emissions.

We revised the sentences in Line 152 as follows: "The footprints (F; $s\ kg^{-1}\ pmol\ mol^{-1}$), i.e., the source-receptor-relationship, within the 0 – 100 m range above sea level over the full domain were used for further analysis (Henne et al., 2016; Pisso et al., 2019; Seibert and Frank, 2004; Stohl et al., 2009)"

Comment 8 Line 152. Please explain in more detail the significance of the histograms in Figure S5, e.g., what is the reader to understand from the broad histogram of Region 1 compared to the narrower distribution of Regions 2 and 3? In general, given that the three regions chosen are extremely disparate in terms of their areal extent, can they be compared in a meaningful way?

We thank the reviewer for their suggestion regarding Figure S5. While the areal extent of the three regions differs significantly, they serve as analytical tools for estimating the sources/mechanisms driving N_2O variability over the Galapagos. We propose that the observed N_2O enhancements are influenced by three primary factors: (i) marine emissions from coastal upwelling regions, (ii) increased transport of northern hemispheric air masses, which have higher mean N_2O, and (iii) local anthropogenic or terrestrial emissions from San Cristóbal Island. By presenting the histograms of these regional influence metrics, we aim to assess the role of each mechanism in shaping N_2O variability. Histograms contextualize our further analysis in Sections 3.4 and 3.5, where we establish the critical threshold for local influence and high-influence and low-influence regimes for Regions I and II.

To address the lack of explanation regarding the motivation for selecting these regions, we added the following sentence in Section 2.3 (Line 161): "While the areal extent of the three regions differs significantly, they serve as analytical tools for further analyzing which mechanisms could explain the observed variability in N_2O over the Galapagos." Additionally, we added the following statement in the results Section 3.4 (Line 307)to further interpret Figure S5 (c): "Due to the dominance of strong trade winds in the region throughout the observational period, the air masses are transported rapidly from the South American coast to the Galapagos. Therefore, the localness metric, I_{local}, is low, with a median of 4.4 % and strong right-skewed distribution." We also added the following statements in Section 3.5 (Line 327) to further comment on the histograms in Figure S5 (a) and (b): "The I_{NH} is low with a median of 1.2 % and a strongly right-skewed distribution because the transport of northern hemispheric air masses to the Galapagos is not common and only limited to the wet season. On the other hand, I_{upw} is normally distributed with a median of 30.0 %. "

Comment 9 Line 43 and Line 152. On a related note, the Introduction mentions the Costa Rican upwelling (aka ETNP) yet Region 2 is defined as the entire NH. How does this allow the distinction of air masses specifically from the ETNP vs. from the entire NH, which, due to N2O's well-known N-S gradient, is expected to be 1 ppb higher than air coming from the SH? If it doesn't, perhaps the motivating reference to Costa Rica on line 43 should be toned down.

We agree with the reviewer that the motivating statements about the Costa Rican Upwelling System and ETNP could be toned down to prevent confusion. Figure 6 clearly shows that air mass transport from the ETNP to the Galapagos is very limited. Therefore, we focused on the impact of seasonality in the ITCZ and sampling of northern hemispheric air on setting the variability and not the impact of ETNP in the rest of the manuscript.

We revised the following sentence in the introduction (Line 47) to align with rest of the manuscript: "Located in the eastern tropical Pacific Ocean, the Galapagos Islands are situated in proximity to the hot spots of oceanic N_2O emissions: the Peruvian and Chilean upwelling systems (Fig. 1a)."

Comment 10 Figure 3 and line 158: Why are the SIO CGO data shown as monthly means when the in situ data are available at much higher temporal resolution? Could they be shown at higher than monthly resolution without detracting from the GAL data (since CGO is offset by 1.3 ppb relative to GAL)?

A shorter time scale averaging of the CGO data (SIO scale) could show the synoptic variability at Kennaook/Cape Grim, Australia, due to regional emissions and local pollution events, and not be appropriate for a proper comparison as the station's distance from the Galapagos. Although other stations, such as SMO, could be more appropriate to present at higher resolution due to proximity and general circulation patterns, SMO high-frequency data was unavailable during this period due to infrastructural problems at that site. Therefore, after an in-depth conversation about this comment with the collaborators in the CGO and AGEGE network, we decided to keep the monthly mean observations for all the comparison stations, including CGO.

Comment 11 Figure 3. What is the distinction between GEMS and GAL? Why is GAL used in Figure 3 but GEMS used elsewhere? Similarly, why is GSC used sometimes in the text and how is it distinguished from GEMS?

We thank the reviewer for the question. GSC refers to the Galapagos Science Center, which is a research institution that operates the building in which our instrument is located. On the other hand, GEMS refers to our project and the monitoring efforts. Lastly, the 3-letter GAL is used by convention, similar to other atmospheric monitoring stations named within GAW, AGAGE, or NOAA networks.

Since the acronym GEMS is not essential in the manuscript, we changed all the GEMS acronyms to GAL for simplicity throughout the manuscript. Please see the tracked changes document for more details. However, we keep the mention of "Galapagos Emissions Monitoring Station" in line 68 as it still reflects our project and the station housed in the GSC.

Comment 12 Line 213: Please define the duration of the 2023-24 El Nino event including approximate start and end months.

We thank the reviewer for the suggestion. The start and end months are added.

The line 230 is changed to "It is important to note that the mean observed temperature in March 2024 (Fig. S6) is approximately 1 ℃ higher than the March climatology reported by Paltán et al. (2021), likely due to the El Niño event, lasting from June 2023 to May 2024".

Comment 13 Line 240: Please define GSC earlier in the methods before presenting here.

We thank the reviewer for the suggestion, and the change is made.

We added the GSC acronym after the Galapagos Science Center in line 84.

Comment 14 Figure 5. In panels c and f, the angle of the N2O measurement doesn't correspond to the angle of the wind direction of the ERA5 or GSC data. Please explain more clearly.

We thank the reviewer for their comment. The bar heights in panels (c) and (f) were determined by the mean wind speed measured at the GSC, whereas they were determined by the frequency of different wind speeds in the other panels. For example, the wind speeds between 45-135 degrees in panel (e) are dominated by wind speeds well below 0.5 ms^{-1}. Therefore, the bar heights in panel (f) are quite small to the degree that they are not visible. For a better comparison, we now use the same wind speed frequency at each bin to set the bar height in panels (c) and (f). This way, the readers can compare the wind speeds vs. the N_2O anomaly more clearly.

We have changed the bar height metric in panels (c) and (f) to make the data more visible and comparable to other panels in Fig. 5. We also edited the caption to reflect this change.

Comment 15 Line 246-251: The logic of these statements is confusing and "Nevertheless" is a puzzling choice of conjunction.

We agree with the author about the confusing nature of these statements. Given the changes in Figure 5 and the mentioned confusion, we have rewritten this section in response to this comment and comment 17 below.

Lines 265 – 274 now read: "Fig. 5 (c) & (f) suggest that there is no significant relationship between the N_2O mole fractions and the observed wind direction and speed during September due to a minor anomaly. On the other hand, the observed N_2O anomaly is correlated with the wind direction and speed during March. Due to the southward shift of the ITCZ to the latitude of the Galapagos in the eastern Pacific during the wet season, air masses are more stagnant over the Galapagos, which allows for the accumulation of some local N_2O emissions. This is evident as the easterly winds transporting air masses over the land contain more N_2O, compared to air masses transported over the ocean via westerly winds. While the analysis of local winds could support the analysis of local impacts on the N_2O variability, they do not contain any information about the history of sampled air masses. Therefore, footprints calculated using the FLEXPART model are a better tool than the observed wind directions to examine the variability in the N_2O mole fraction anomalies as they represent the history of air masses over the different surfaces where emissions occur.

Comment 16 Figure 6. This figure raises questions about why September 2024 was chosen as the contrast for March 2024 (which clearly has the strongest NH source strength)? Based on September, 2023, there is still a NH source component in September. The lowest NH contribution appears to be in June 2024.

We thank the reviewer for their question. We chose these months as they are in the middle of each wet/dry season. One could also choose them based on the highest and lowest northern hemispheric influence, as noted by the reviewer. The goal of this figure is to motivate the audience to understand the appropriateness of ERA5 meteorology for footprint calculations and to contrast the wind patterns between wet and dry seasons. Therefore we believe that the choice of March and September is more appropriate.

We added a more clear reasoning behind our choice of the month in Line 254: "To investigate the impact of seasonal changes in winds on the observed N_2O, we examined both observed and reanalysis wind data during the middle of each season (wet, March 2023; dry, September 2024) in Fig. 5. "

Comment 17 How do the results shown in Figure 5 relate to the information shown in Figure 6? Why is there no wind rose showing winds coming from the north or northeast and the associated N2O values? Is this the basis of the argument in Lines 246-251 (i.e., that FLEXPART is more useful than simple wind data?)

We thank the reviewer for their comment. Indeed, Figure 5 is used to discuss the local trends in the winds over San Cristóbal island. First, we aimed to show the appropriateness of ERA5 meteorology for our footprint calculation. Second, we aimed to assess the seasonality of winds and their impact on the variability in N_2O. However, local meteorological observations do not provide any information on long-term transport of the sampled air masses. On the other hand, Figure 6 shows the long-term transport history and highlights the importance of larger regional circulation and differential marine emission sources in setting the variability in the observed N_2O other than the local meteorology. Therefore, as the reviewer suggests, Figure 5 naturally motivates the use of footprints in further analysis in the following section.

To make the transition from local meteorological observations to air mass footprints clear, we edited paragraph 2 of Section 3.3 as given in the response to comment 15 above.

Comment 18 Figures 6 and 8, please explain the unit (s kg-1 pmol/pmol). In particular, what does 's' refer to?

FLEXPART v10.4 calculates the footprints, or the source-receptor response, as the sensitivity of mole fraction observations at a station to fluxes from the land or ocean surface or point sources. Thus, the units represent how much the N_2O mole fraction (in $pmol\ mol^{-1}$ units for this case) is changed per 1 $kg\ s^{-1}$ N_2O flux. Therefore, 's' refers to the time dimension of the fluxes.

We added the following statement in the methods section 2.3 (Line 145) to further clarify what the units mean: "Footprints represent the sensitivity of measured N_2O mole fractions at GAL (in $pmol\ mol^{-1}$) to fluxes across some land or ocean surface (in $kg\ s^{-1}$)."

Reviewer #2 Comments

Comment 1 The manuscript by Cinay and colleagues presents the first set of N2O (and CO) measurements of a newly stablished atmospheric monitoring site at Galápagos Islands. Based on their data, the authors conclude that the observed trends mostly result from the interplay between the seasonal shifts of the ITCZ and emissions from marine N2O hotspots in the Eastern South Pacific. An atmospheric monitoring station for N2O in the region represents a clear advance for the field because it allows an improvement of both top-down and bottom-up estimates of marine air-sea fluxes of N2O. Up to know, groups who did not have the instrumentation to conduct at-sea surveys of atmospheric N2O in the region had to rely on information from distant stations to compute the fluxes. While the zonal distribution of many trace gases tends to be rather homogeneous, several studies have shown that oceanic trace gas production and emissions might indeed have an imprint in the overlying atmosphere. Although the changes in atmospheric N2O observed by Cinay et al might, at first, not appear particularly large, it is precisely the monitoring of such small changes over long periods what one aims for to detect significant trends (which I would expect for this gas). Based on the evidence provided in this manuscript, it is my opinion that the resolution and accuracy at the station are suitable for this purpose.

We appreciate the reviewer's time and constructive feedback and are gratified by their interest in the study. We also agree that the data from the station could better inform future marine N_2O flux studies. Improvements based on the reviewer's comments are noted below and tracked in the original manuscript.

Comment 2 Overall, the manuscript is well written and structured, and figures and tables are adequate for publication. Besides some clarifications (which I list below under "Specific comments"), the only criticism I have is the inclusion of CO data throughout the manuscript. I myself work with CO and therefore recognize the immense value of such a time series. CO is a potent, yet indirect, greenhouse gas on its own right, whose atmospheric dynamics are worth looking at. In this region in particular (and because of its short lifetime) I would expect CO to be useful to investigate e.g. tropospheric convection (although land pollution did not seem to play much of a role yet). Nevertheless, it is obvious that the manuscript is focused on N2O, and therefore the appearances of CO are rather distracting. For instance, in lines 220 – 224, the authors themselves acknowledge that CO does not provide any significant hints of an alternative driver for the observed N2O mixing ratios. I would kindly suggest the authors to consider placing all the information on CO (including plots) in the supplementary because its connection with N2O is not direct (and in this case not that relevant, as also indicated in e.g. line 185). One exception of this would be the analysis done in section 3.4, where CO mixing ratios, wind stagnation and local regional influence ("Ilocal") were used to evaluate small-scale N2O emission sources.

We would like to thank the reviewer for their comments regarding the inclusion of the CO data in the main manuscript. In addition to section 3.4 and Figure 7, we believe that the CO diurnal cycle is also crucial for analyzing diurnal variability in N_2O. Since the CO diurnal cycle is clearly influenced by local combustion events, as shown in Figure 4b, it serves as an excellent reference to support our assertion that such combustion events do not significantly affect N_2O, except during periods of high stagnation, as indicated in Figure 7. Moreover, we believe that including the full CO mole fraction timeseries in Figure 3 is critical for the study, as it contextualizes the analyses and results in Figure 4b and Figure 7. High-resolution CO mole fractions are an important addition to the data collected at the Galapagos and could further motivate future studies. Therefore, we decided to retain the CO panels in Figures 3 and 4 discussions.

Comment 3 l.24–25: The accuracy of marine estimates is not only due to temporal and spatial gaps. There is also an important methodological issue in getting the fluxes "right". Here the differences between using the traditional gradient method with a given air-sea gas exchange parameterization vs. top-down estimates and direct flux measurements is also a challenge.

We agree with the reviewer that different methods of flux estimates can be difficult to compare given differences in the methods and assumptions.

We added the following sentence in Line 25: "Moreover, different techniques for emission estimation, such as direct flux calculations based on air-sea concentration gradients versus flux calculations using atmospheric inverse modeling, are difficult to reconcile due to inherent methodological biases and varying assumptions, such as the gas transfer velocity parametrization (Wanninkhof, 2014)."

Comment 4 l.28–29: As shown by (e.g. Ji et al), strong thermal-driven stratification during El Niño events results in accumulation of N2O below the mixed layer, as long as waters are not completely oxygen depleted.

We agree that El Niño events could lead to subsurface accumulation of N_2O as reported by Ji et al., 2019.

We added the following statement in Line 32 to include more details on the impact of El Niño conditions: "The isolation of low-oxygen surface environments from the surface due to increased stratification during an El Niño event could lead to subsurface accumulation N_2O (Ji et al., 2019). However, the effect of subsurface accumulation on subsequent surface fluxes still needs to be explored."

Comment 5 l.95–97: If the analyser still measures H2O it means that there is still humidity, just in the form of water vapour. The idea of drying the samples is to reduce the extent of the water correction performed by the analyser. In my opinion this sentence needs a bit of clarification as it might lead to confusion later in the text when the authors explain that there is a water correction.

Indeed, the Nafion^{TM} tubing in our setup is used to minimize the water vapor in the system during the measurements as the instrument water corrections are not accurate for higher humidity.

We rewrote the sentence in Line 109 as follows to prevent any confusion in the section: "The air samples are dried prior to measurement to minimize the biases in the dry air mole fraction calculations performed by the native Picarro G5310 software, as described in previous studies (Rella, 2010; Reum et al., 2019; Zellweger et al., 2019). No further water vapor corrections are performed as the mean measured H_2O mole fraction was 775 $\pm$ 100 ppm due to the inline Nafion™ tubing dryer."

Comment 6 l.305–306: While forcing is similar in the Peruvian and Chilean upwelling systems, clustering them as one region has a clear bias because while upwelling off Peru is a perennial feature, upwelling off Chile has a much stronger seasonal component. Moreover, the extent of the emissions is also different. I would not expect this to change the conclusions of the study, but it certainly adds to the uncertainty of this estimate, and I would therefore recommend at least mentioning it.

We thank the reviewer for their suggestion. We agree that clustering both the Peruvian and Chilean upwelling systems together in Figure 8 and Section 3.5 is a simplification. However, it is challenging to differentiate the influence of the Peruvian and Chilean upwelling systems using the current method because most air masses transported over the Peruvian upwelling system are also transported over the northern Chilean upwelling system. Therefore, further inverse modeling is required, but this is beyond the scope of this current study. Thus, we decided to include a statement discussing these potential biases as outlined by the reviewer rather than changing our plan analyses.

We added the following sentence in Lines 332: "This approach could mask the unique temporal variability and spatial extent of N_2O emissions from each upwelling system. While the grouped footprint influence metric is helpful in attributing variability to the heterogeneous spatiotemporal structure of marine fluxes, further attribution to each upwelling system is only possible with a future top-down inverse modeling study."

Additional Changes

Change 1 **Due to the additional availability of the final version of the ERA5 data for July 2024 - September 2024, we expanded the data plotted in Figure 7 (c). Additionally, this allowed for the inclusion of more data points for analysis in Figure 8 and Section 3.5. Therefore, mean and standard deviation values of various regional influence regimes were updated. However, this update does not alter any of the conclusions of our study. We also removed the following sentence from Section 3.2: ”Air mass footprints are calculated until 30 June 2024 as the ECMWF ERA5 reanalysis product's final release is only available with a latency of 2 – 3 months.”**