Exploring the CO₂ fugacity along the east coast of South America aboard the schooner Tara, Olivier et al, submitted to ESSD, 2024

Response to reviewer 1

This manuscript presents an innovative methodology and a timely study, leveraging the capabilities of the Tara schooner to monitor CO₂ fugacity (fCO₂) in a key region for the global carbon cycle. The work demonstrates the potential of such expeditions for regional carbon dynamics studies and contributes valuable observations to the limited dataset from this area. Moreover, this represents an excellent initiative to expand the scope of the Tara schooner's activities—traditionally centered on marine biology and ecology-toward geoscience observations, as exemplified by the dataset presented in this manuscript. The manuscript is well-written, well-structured, and includes high-quality figures. The article is worthy of publication and appropriate to support the publication of a data set, but the dataset itself exhibits significant shortcomings that must be first addressed. Important modifications are required to ensure the dataset meets the standards of openness, metadata completeness, and long-term usability. I recommend a major revision, primarily to address issues with the data product, as outlined below. Additionally, there are inconsistencies in the framing and presentation that detract from the overall clarity and impact of the work, but they should be easily ameliorated.

First, we would like to thank the reviewer for his positive comments on the paper, and for this detailed, complete and constructive review. We agree that the dataset presentation and associated metadata needed a little bit more structuring and work that now has been done. We believe that this review made the new version of the manuscript significantly better, so we thank the reviewer for taking the time to read the paper in depth and comment it. We will address each comment, and indicate in orange the changes made in the manuscript.

The current form of the data product significantly weakens the manuscript's suitability for publication in ESSD, a journal known for its rigorous standards in data quality and accessibility. The dataset lacks metadata, the data file itself it has an untraceable naming (*"CO2Tara.xlsx"* -sic-), fails to adhere to standardized variable names, and does not appropriately specify units. The dataset header lacks key information, such as details about the analytical methods used and the complete list of contributors. It is true that they are included in the Zenodo version, but the file should stand by itself. Additionally, quality control flags for variables should be assigned to enhance the dataset's reliability and usability. Metadata completeness is crucial for long-term usability and re-usability. The file format should be open source (rather than an Excel file) and it would be much better distributed as a NetCDF file as it is interoperable with other platforms. The use of proprietary or non-open-source formats is a critical limitation, so a conversion to a format compatible with community standards is necessary. Since the authors intend to submit this dataset to SOCAT, which I consider an excellent decision as it is the current reference database for fCO2 measurements,

it would be beneficial if the data product presented in ESSD could offer some added value or differentiation.

We completely agree with this comment, and we apologize for not having done it before the first submission. It is entirely true that the file should stand by itself, and should be in an open-source format. Here, we propose to include in Zenodo a full additional metadata file, describing the system and the uncertainties of each sensor, as well as the dates of calibration, as is necessary for the submission to the SOCAT database. In addition, we included a header in the dataset, as suggested, indicating the purpose of the dataset, the main contributors, the method of acquisition and the region/time-period sampled. We will change the format of the dataset to csv and netcdf to provide more variety in the formats (both open-source).

Regarding the differentiation, this is a good comment. We propose here to add the bottom depth and the measured wind speed, as both parameters are very useful for the interpretation of the dataset. The wind speed is essential for calculating the CO_2 flux, and the bottom depth is closely related to the fCO2 variability as analyzed in the document. The data have been submitted to SOCAT, the added value here is also the qualification and validation of the dataset as well as comparison to other in-situ data, well necessary in coastal environments.

Specific comments (section and/or lines):

Reframe the title to reflect the true geographic scope, as the analysis is primarily focused on the Amazon River area rather than the entire east coast of South America.

Although the primary focus of the paper is the equatorial area close to the Amazon plume and the estuary, the dataset and its description cover a much wider area, which is roughly 2/3 of the meridional length of South America, from the Little Antilles to the border of Uruguay. If the reviewer agrees, we would therefore prefer to keep the title as is to avoid making it too long. Otherwise, we would suggest: Exploring the CO₂ fugacity along the east coast of South America aboard the schooner Tara: the Amazon River and beyond

Abstract 26-29: the order of the description should be homogeneous. For example, from river to ocean.

Thank you for the good suggestion, we modified the abstract, starting from the river, then the river plume and finally the open ocean, moving south. Observations revealed a wide range of fCO2 values, from up to up to 3000 μ atm in the river to a minimum of 42 μ atm downstream of the plume, where values were notably lower than atmospheric levels. South of the estuary, the fCO₂ of the North Brazil Current's waters (0-9°S) exceeds 400 μ atm while along the Brazil Current (10-30°S), fCO₂ is around 400 μ atm and decreases with temperature and distance from the equator.

Abstract: North Brazil Current and Brazil Current are concepts not explained in the abstract. Not easy to follow.

We believe that these currents are accepted concepts, but we added the bands of latitudes concerned for clarity.

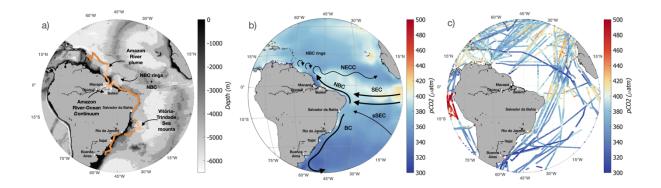
Intro. 40. agree with *These regions present much higher temporal and spatial variability*. Therefore, this highly valuable snapshot only informs about spatial variability of a single season. *Thank you, we fully agree.*

Intro 45. true sentence. The low number of observations in coastal waters is somewhat unexpected. Considering that coastal zones are, by definition, more accessible than the open ocean and offshore areas, it raises the question: why are these regions underrepresented in observational datasets? While addressing this issue is beyond the scope of this study, including a brief discussion or hypothesis to guide the reader would add valuable context.

We agree, and we find the low number of observations quite concerning. One explanation is that some of these coastal zones are not that easy to sample, either due to distance to major ports, or because of accessing permits to perform the measurements (since most of them are conducted in EEZ). We added this hypothesis in the conclusion. The limited number of observations could be due to the complicated access to some of these regions (distance from major port) and to the difficulty of obtaining sampling permits.

Figure 1 is highly effective and well-designed, offering a clear overview of the study area. However, the inclusion of Pacific data skews the color bar and detracts from the manuscript's focus on equatorial South America in the Atlantic Ocean. It would be more appropriate to exclude the Pacific data and revise the figure to better align with the study's regional scope.

Agreed, here is the new version of Figure 1 without the Pacific data. The colorbar was kept the same because it is centered on 400 µatm that is approximately the atmospheric value, so that the reader can easily identify visually potential sink and sources.



It represents one of the greatest environmental gradients on "the interface between" land and ocean in the world. *OK. added.*

64 as the "Amazon" rainforest sequesters... *OK, added.* The references to the ANACONDAS (Mu et al., 2021) and Camadas Finas III (Araujo et al., 2017) campaigns lack both date signatures and spatial context. As a result, these terms may be largely unfamiliar to readers who are not specialized in regional studies, potentially hindering the manuscript's accessibility. Providing additional information about the campaigns' timing and geographical scope would help contextualize these references.

Thank you for your perspective. We added the years of the cruise and their focus. On the other hand, oceanographic studies, carried out in particular during the ANACONDAS (in 2011, 2012 and 2013, Mu et al., 2021) and Camadas Finas III (October 2012, Araujo et al., 2017) campaigns that focused on the ARP development, maximum extension and early decay have shown the extent of CO₂ undersaturation in the ARP.

The manuscript mentions the link between these two systems, but it is unclear how this connection is made, as the schooner does not sail as far as Óbidos. If the link is indeed established, further clarification is needed, as it is not apparent from the current description. Could you please clarify whether the link is made, or revise the statement to reflect the actual coverage of the study?

It is very true that Tara did not sail as far as Obidos, but slightly inland of Macapa. However, the connection is made, not only because Macapa is fully inland with no salt water influence, but also because the previous and key study of Sawakuchi et al stopped at Macapa (they extended the river from Obidos to Macapa). Were are therefore adding the missing link, Macapa-Open ocean. To improve clarity, we added in the manuscript that the missing link is the amazon estuary, sampled by the schooner. *However, the* estuary, which is the link between these two systems is little known, if at all as riverine observations stopped in Macapá.

71 I would delete "extensively". OK, done.

75 in advance: The statement in paragraph 75 claiming that the Argo program could address the scarcity of fCO2 measurements in the medium term is not accurate. Currently, this is technically unfeasible, as the Argo program is designed primarily

for interior ocean monitoring. To measure fCO2, a surface-intensified approach would be required. The entire paragraph should be reassessed and revised to reflect the current limitations and the specific needs for fCO2 measurements. Thank you for this comment, this is a very interesting and debated issue in the community. The mention of the Argo program was certainly not done to signify that a surface-intensified approach was not deemed necessary, but to mention added capability to observe the near surface ocean (albeit indirectly in the case of BGC Argo float) that is being implemented. In data-scarce area, such as the Southern Ocean, using Argo floatderived CO₂ fluxes brought a new understanding of the area and showed contributed to identify limitations in our observations. We completely agree that a surface-intensified approached should be strongly encouraged when measuring fCO₂, and Argo floats enriches this information information by bringing complementary biogeochemical

parameters that are worth looking at. We therefore rephrased our paragraph. While measurements of biogeochemical parameters in the open ocean have increased in recent years owing to the development of the biogeochemical Argo program, it is not the case for biogeochemical measurement on the shelves and continental margins. Moreover, continuous surface fugacity of CO₂ (fCO₂) measurements carried out on ships remain the most accurate way to asses CO₂ fluxes and are still too sparse.

As this dataset is based on underway measurements, you use kilometers to express the magnitude of the data, which is a valid option. However, it would be helpful to include additional information regarding the timing of the observations. For example, how many days of data were collected? Furthermore, how many different biomes were crossed during the survey? Providing this contextual information would enhance the understanding of the dataset's temporal and spatial coverage. *We agree, thank you for the suggestion, we included the number of days (81 days).*

108-114. The port-to-port description could be better represented in a table format. This information, while useful, does not add significant value to the narrative and would be more concise and accessible in a tabular form.

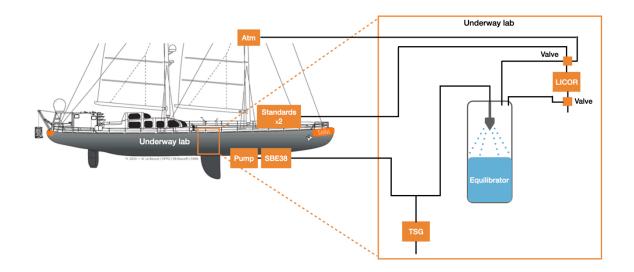
Agreed, thank you very much for the good suggestion. This section has been modified to include the table and is now: The dataset presented in this study focuses on the underway data collected during the legs 5, 6, 7, 8 and 9 of the Mission Microbiome (Table1). The dataset covers 14,000 km and stops on 25 November, as the authorization to sample in the exclusive economic zone of Uruguay was not obtained. Attempts were subsequently made to restart the system during leg 11, but these were aborted, as the conditions of the standard gas cylinders did not allow the same accuracy to be achieved.

In line 103, you mention 14,000 km, which is a considerable distance. However, the schooner sailed a total of 70,000 km. This discrepancy raises the question: why are the remaining 56,000 km not included in the analysis? While there may be valid reasons for excluding these data, offering an explanation would strength the manuscript's transparency.

The remaining 56,000 km are not included because the pCO2 system stopped working. While crossing the Drake Passage (stage 11), one of the gas cylinders used for calibration leaked and emptied, preventing us from calibrating the data correctly. Due to COVID and strict regulations, it was almost impossible to ship another gas cylinder in time to continue the measurements. We added a short version of this explanation to the manuscript, see modification in the previous comment.

Figure 2 does not accurately represent the full circuit, as it omits two branches. Please revise the figure to include these missing branches. *We are very sorry, but we don't see which branches are missing. It is true that the branches for the 0 and 502.3 ppm standards are merged into one under the name 'standards' to avoid overloading the schematic. Then there is the atmospheric air branch and the branch coming from the equilibrator, all connected to a valve that control the air sent to the LICOR analyzer. Thus, this adds up to*

four branches. We added the TSG exit branch, and made clearer that there are two standards.



However, the dataset lacks integration with existing efforts (e.g., SOCAT) and does not demonstrate sufficient added value over what is already available. It would strengthen the manuscript to articulate why this dataset is unique and necessary in the context of global fCO_2 monitoring.

We agree, thank you for pointing it out. We tried first to point out what this dataset brings out on top of the dataset submitted to SOCAT (ancillary data very useful for the interpretation and quality control of the data), and also to show how this dataset is unique (the first equilibrator-based system on a sailboat, unique region, diverse gradients) and necessary (overall lack of data etc...). In the manuscript (section 2.5), we included: In the dataset, ancillary data are added (wind speed at 10 m, bottom depth) to offer a more detailed interpretation of the data. Wind speed was measured by a Gill anemometer at the top of the mast (27 m), and then adjusted to 10 m using a logarithmic relationship (Tennekes, 1973). This dataset addresses the overall lack of data identified by SOCAT, by covering diverse environmental gradients with a high-resolution sampling. The use of the schooner highlights the potential of non-traditional platforms for collecting high-quality data in challenging environments, complementing traditional research vessels.

Section 2.2: You mention an important flow rate, which is often a bottleneck in underway systems on unconventional vessels. Could you please provide the model and specifications of the pump used? This information would be useful for understanding the system's limitations. Does the pump include a filter? Additionally, what is the maximum speed of the schooner at which the pump remains functional? Is the schooner's speed included in the dataset? If not, it should be, as this could be an important variable to consider. *We agree: on Tara to avoid the bottleneck there are two pumps feeding the underway system. The pump is a Shurflow probait master 4 from Penatair. The maximum flow rate is 12L/min. After the pump the circuit includes a*

debubbler and a large particles filter, we added this information to the manuscript: It then goes through a large particles filter and enters a debubbler to remove most of the bubbles that can be caused by such shallow water intake, especially in rough seas. Tara is not a very fast sailing sailboat, so we never reached a speed at which the pump couldn't work anymore. For example, Tara's average speed is 6kn, while a research vessel's speed is 10kn. One of the issues with sailing vessels and the shallow intake is excess bubbles entering the system when the sea is rough. Fortunately, these conditions were not encountered here.

Line 132: The term "accurately" could be removed. *Ok, removed.*

Line 138: It is unclear to me why you do not have this data. In line 140, you mention a temperature difference, are you not talking about that in line 138? Unfortunately, there was no temperature sensor in the equilibrator. This is why we used the TSG temperature, which, based on how the system was installed, should provide a rather good estimate of the equilibrator's temperature. In line 140, we talk about the temperature difference between the hull temperature sensor (SBE38, true SST) and the TSG temperature (SBE45). On a sailboat, the difference is very small, but on a research vessel the difference can be much larger than 0.1°C, and in this case the fCO_2 data needs to be discarded (according to the sampling best practices). We tried to make this clearer by modifying Figure 2, and including the SBE38 in the schematic so that it is possible to identify visually the two temperature sensors. In the manuscript: the temperature difference between the hull sensor (SBE38) and the TSG is small (always below 0.1 °C and averaging 0.07°C, Figure 2).

Line 150: The sentences need to be reordered for clarity. It would be more effective to first describe the atmospheric air, then the reference gases, and finally the seawater. This would improve the logical flow of the section. *We agree, thank you, we modified: Through a system of valves, four circuits are operated, one for the atmospheric air, one for each of the two reference gases, and one for the air equilibrated with seawater.*

Line 160: When stating that the system is "cleaned regularly," it would be helpful to include the periodicity of the cleaning process. Additionally, does the intake circuit feature any physical barriers or filters to prevent the introduction of large particles? This should be clarified for completeness. *This is also true. the system was cleaned at each stopover (5 times), and each time the boat exited a major river (two additional times leaving Macapá and Belém). There is a large particle filter on the line, this has been added to the description of the system following the comment on the pump. We propose to add in the manuscript: The equilibrator was cleaned at each stopover, and each time the ship exited a major river (so 7 times in total) to avoid the buildup of mud, and the system therefore recorded data during the whole time spent in the Amazon River.*

Line 185: You mention "yellow" in Figure 3, but no yellow is visible (at least to me) in the figure. Please revise the description to match the actual content of the figure. *We agree that it is not easy to describe this color, we changed yellow by light brown in both the text and the legend of the figure, hopefully it improved clarity.*

Figure 3: The straight line in the "Raw" data does not convey meaningful information and appears to be an artifact caused by the connection of data points in the time series. This should be corrected to ensure the figure accurately represents the data. *We agree and removed the connection between the points.*

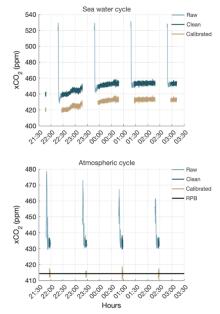


Figure 4: Please include a scatter subplot that illustrates the 1:1 relationship between the discrete samples and the underway measurements. Use the timing of the bottle closure from the CTD surface samples, applying a time window of 2-3 minutes for the underway. Also, include the uncertainty associated with the discrete samples (5.7 µatm) and the range of underway measurements. The current format of this Figure 4, which combines all values into one plot, makes it difficult to discern patterns due to the large range of values. It would be clearer if the figure were split into three subplots: one for high values, one for the central values around 400, and another for low values. Following your comment, we revised Figure 4. The figure now has 3 panels as suggested, but we kept the first two as previously, because they show the full range of values, both in the upper values of the Amazon River (top panel) and the lower values of the plume (2nd panel, now in the middle). To address the comment, the third panel focuses on the 350-450 fCO₂ range, which includes most of the underway and discrete measurements. On this panel, we also added the discrete samples uncertainty of 5.7 µatm as error bars. We included the scatter plot as a fourth panel. For the scatter plot, some interpretation needs to be considered. For stations 36abc, the system was calibrating while the sample was taken. In this variable region, we do not feel comfortable either extrapolating or using a value measured 15min before or later. Last piece of information, we analyzed the difference between the salinity of the bottle from a salinity sample and the salinity measured by the Rosette's CTD, the difference can be up to 3 pss from station 35 to 42, due to the high surface variability of the region. For all these reasons, we prefer to focus on stations 45 onwards to assess the accuracy. We integrated these explanations in a more concise form in the manuscript (legend of Figure 4), but we believed the reviewer might be interested in more details.

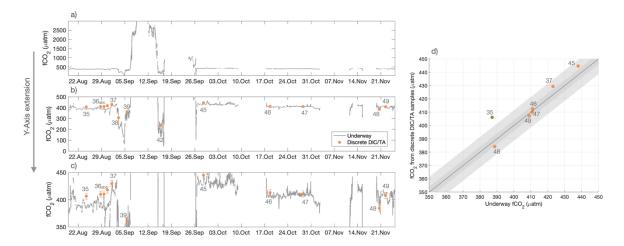
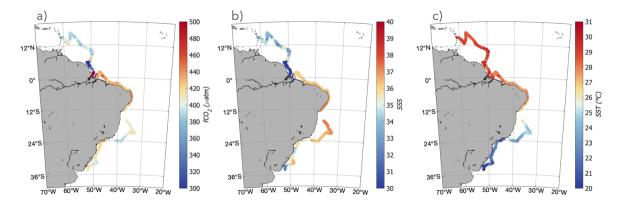


Figure 4 : Time-series of surface fCO_2 from 18/08/2021 to 25/11/2021, for the full range of values (a) for only oceanic values (b) for values between 350 and 450 µatm (c). The dots indicate the fCO_2 inferred from the DIC/TA water samples for stations 35 to 49, with error bars of 5.7 µatm to represent the uncertainty of the chemical formulas. Scatter plot of the underway fCO_2 and the fCO_2 inferred from the DIC/TA samples, for fCO_2 values ranging between 350 and 450 µatm (d). The green dot indicates a salinity difference between the CTD sensor and the sample from bottle of more than 0.5. The fCO_2 system was measuring the standards gases for calibration during stations 36abc and 39, these stations are therefore not represented in (d).

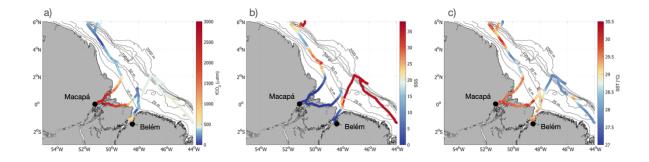
Figure 5: While I appreciated the broad context provided by Figure 1, I would recommend a closer zoom for Figure 5 to focus specifically on the underway track. The current version leaves a significant amount of blank space that could be better utilized. The figure should be revised to eliminate this excess space and highlight the relevant data more clearly. Additionally, the arrangement of the subplots is unclear, and the "pyramid" layout may not be the most effective. I suggest reconsidering the layout for better clarity and visual coherence before publication. *Thank you, we completely agree, here is a revised version of Figure 5.*



Overview section: Ensure that the variables are always presented in the same order: temperature, salinity, and then fCO2. *Thank you, we modified this section and try to*

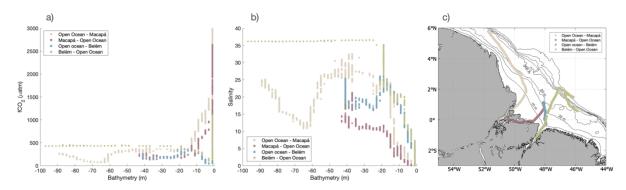
follow the order you suggested. However, when the fronts were driven by salinity, we preferred to start by salinity, then temperature and finally fCO2.

Figure 7: Please add the locations of Obidos, Belem, and Macapa to the figure. Additionally, label some isobaths of bathymetry for reference. *Thank you, done. We didn't add Obidos because it is not in the area represented on the map.*



Figures 8 & 9: It would be more efficient to include the area shown in Table 1 directly in the figures, thereby eliminating the need for the Table 1 itself. In my opinion, this will enhance the visual presentation and reduce redundancy.

Thank you for this good suggestion. We removed the table and added another panel to figure 9 (Figure 8 already had 4 panels) directly showing the areas on a map. Here is the revised Figure 9:



Bathymetry: The bathymetry data is sourced from ETOPO2v2 and is colocalized along the ship track. However, including bathymetry values at 0 m or depths of 1-2 m raises some questions, as this would imply the ship was at or near the seabed (which, of course, we hope did not occur!). It may be more appropriate to group these shallow measurements or explore alternative methods for representing this data in a way that better reflects the actual conditions. Another comment about bathymetry: I would strongly recommend adding the bathymetry data to the dataset. This would enable others to fully reproduce the analyses presented in the manuscript.

Thank you again for an interesting comment. We agree that the bathymetry ETOPO2v2 does not resolve well the river, and for further analysis of the river part of the dataset a dedicated

bathymetry should be used, such as the one described in Fassoni-Andrade et al., Comprehensive bathymetry and intertidal topography of the Amazon estuary, (2021). ESSD. <u>https://doi.org/10.5194/essd-13-2275-2021</u>. Nonetheless, this is a bit out of scope for this study and the grouping in Figure 9 is still relevant at 0-order, even though the uncertainties are large. We modified the manuscript to show this limitation of the dataset, and also refer to a more accurate one if the user is interested. In the discussion: Their "River Zone", for depth below 5 m, indeed corresponds to a salinity of 0. Nevertheless, we observe significant variability of fCO2 even if the salinity does not change anymore. This region was not investigated by these studies that focused further offshore of the mouth. For the region, the bathymetry used here is not adapted anymore, and a specific Amazon estuary bathymetry should be used for further studies (such as Fassoni-Andrade et al., 2021).

We agree with the suggestion of adding the bathymetry to the dataset. Both the bathymetry and the measured winds are important relevant variable, that are not included in the SOCAT database and that we will include in this dataset.