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 2

Dear Reviewer,

Thank you for taking the time to carefully review our manuscript. We appreciate your detailed comments, which provide valuable insight to improve the quality of our work. We will address each comment, and indicate in orange the changes made in the manuscript.

The manuscript presents CO₂ fugacity data measured during the Tara expedition in the Tropical and Southwest Subtropical Atlantic Ocean, with a focus on the Amazonas River and the Brazilian coast. However, the manuscript contains several inconsistencies between figures and text, along with errors in names and terminology, which need to be corrected throughout. Key regional references are lacking, and the authors show limited understanding of the area. Additionally, the authors rely on outdated literature, some over 30 years old, which may no longer reflect the current local status and climatology.

Although the dataset covers the Caribbean to Argentina, the authors primarily focus the results and discussion on the Amazonas River plume and the North Brazil Current in the Equatorial Atlantic, with minimal discussion of the rest of the Southwest Atlantic Ocean. This narrow focus, combined with the lack of relevant references, leads to an over-interpretation of some parts of dataset and findings. Many of the findings and conclusions have already been published by other researchers in the same region, but this is not addressed clearly. Furthermore, there are several unsupported assumptions throughout the manuscript that need to be addressed.

We acknowledge the importance of ensuring consistency between figures, text, and terminology. We have thoroughly reviewed the manuscript and corrected any discrepancies or errors in naming conventions and terminology.

We appreciate your suggestion to include more regional references. While we agree that incorporating relevant and recent literature is essential, we have carefully evaluated the references provided in your comments and included those that enhance the context of our work. However, some of the suggested references do not align directly with the focus of this study. We aim to ensure that the manuscript reflects a balanced and pertinent citation of the literature.

The data collected in the Southwest Atlantic Ocean are indeed less novel, and we provided less scientific background for them. However, they are an integral part of the same dataset, validated using the same methodology, and therefore fully belong in this manuscript.

We agree that the most significant contribution of our dataset is to the study of the Amazon River plume and the land-sea continuum. While we acknowledge that we could have included a broader range of references on this topic, many of the suggested publications provide limited insights into actual pCO_2 variability in the Amazon River plume. Additionally, there remains a scarcity of published, accessible pCO_2 data in this region, particularly during the late flood season, with a stronger focus on the North Brazil Current and the Pará River plume.

Regarding data quality, the ESSD aims to ensure that high-quality and reproducible research data sets are included in permanent repositories. The authors mention issues with standard (STD) gases used for calibration but have not provided key data (e.g., pCO2air for STD calibration, in situ DIC and alkalinity data, or cruise metadata) for review. A major concern is the limited calibration with only two gases, one of which (502.3 ppm) is much lower than the values found in the river-ocean continuum (~2000 uatm), which falls outside the range, recommended in the SOCAT CookBook (2018). This raises doubts about the uncertainty of the data beyond the STD calibration range. Additionally, the authors report using only 13 discrete samples to calibrate measurements over 14,000 km, which is statistically insufficient. This raises concerns, especially since only six in situ samples were taken during the longest part of the cruise. No statistical metrics are provided to support the calibration's accuracy and validation.

We acknowledge that not all data can meet the highest quality standards, even within SOCAT guidelines, which explicitly accept data of varying quality levels. In regions with large variability, such as the Amazon River–ocean continuum and plume, a slightly reduced precision does not significantly impact the dataset's scientific value.

The choice of reference gases was constrained by availability but was also made to optimize accuracy for the most common oceanic surface water conditions in the study area. While we recognize that this calibration approach introduces higher uncertainty at the extreme *pCO*₂ values observed in the river–ocean continuum, it remains within an acceptable range for scientific interpretation. Unfortunately, we currently lack the means to quantitatively assess the uncertainty specifically at these high pCO_2 levels. However, we have reported uncertainty estimates for a more typical oceanic range, that is the majority of the dataset. Regarding independent validation with DIC and TA measurements, we acknowledge the limited number of usable samples. The discrepancy between the 13 retained and the 17 collected is due to unsatisfactory sample quality in some cases (e.g., riverine waters) and the absence of simultaneous pCO_2 measurements. While we recognize that 13 samples are fewer than ideal, logistical constraints and the practical challenges of recommended sampling protocols made broader coverage difficult across the Southwest Atlantic expedition legs. Nonetheless, these values, combined with the pCO_2 air measurements, provide an additional layer of validation to support our accuracy assessment. It is an added value, as SOCAT for example does not require comparison with DIC/TA samples.

The authors claim there are no comparable datasets, focusing solely on the SOCAT database which excludes river measurements. I suggest they explore additional references to find relevant studies that might help:

• For the River-ocean continuum see: Valerio et al., 2018 (doi: https://doi.org/10.1364/OE.26.00A657) and the pre-print of Less et al., 2018

(https://doi.org/10.5194/bg-2018-465) - although the manuscript was withdrawn there is valuable information that authors can use.

• For Amazonas River Plume and North Brasil Current see: Monteiro et al., 2022 (doi: https://doi.org/10.1029/2022GB007385), Valério et al., 2021 (doi: https://doi.org/10.1016/j.csr.2021.104348), and others that authors should consult, for example, Ibánhez et al., 2016; Lefèvre et al., 2014, 2017 and 2020.

• Other references about CO2 fluxes, ocean pCO2 and fCO2 in the Brazilian coast can be found in the review paper Oliveira et al., 2022 (doi: http://dx.doi.org/10.21577/0100-4042.20170970).

• For the Vitória-Trindade Seamounts: Dynamics see: Napolitano et al., 2020 (doi: https://doi.org/10.1029/2020JC016731) and Silveira et al., 2020 (doi: https://doi.org/10.1007/978-3-030-53222-2_2). pCO2 data: request to Marinha do Brasil (Brazilian Navy).

We appreciate the reviewer's suggestion to explore additional references; however, we respectfully clarify that our manuscript does not focus on riverine pCO_2 measurements alone. Instead, it emphasizes the river–ocean continuum and the Amazon River plume, with only limited data collected within the river itself. Therefore, while some of the suggested references provide valuable insights into riverine processes, they do not directly align with the scope of our study.

Regarding the suggested references:

- River-focused studies (e.g., Valerio et al., 2018; Less et al., 2018) primarily investigate seasonal variability in river properties. We appreciate the reviewer's suggestion and have cited Valerio et al. (2018) in our manuscript. Their discrete measurements, taken in April 2017, provide valuable context, though a direct comparison with our data from September 2021 is not possible. While these studies offer important insights by extending to the river mouth, they do not explore the connection with the Amazon River Plume beyond the estuary.
- Amazon plume studies: Valerio et al. (2021) utilizes pCO₂ data from three Anacondas cruises to develop a model based on an early version of SMOS sea surface salinity (SSS). However, it is not a data paper (unlike Mu et al. 2021, which we already reference). Additionally, the Anacondas cruises do not overlap with our dataset temporally or spatially—the closest observations to the estuary were from July 2012, outside our study period, and most data were collected much farther downstream off French Guiana in September–October. Thus, this study does not provide a direct comparison for our results.
- Monteiro et al. (2022) presents an interesting analysis based on the SOCAT database, which we reference in our manuscript. However, this dataset includes very few measurements in the area and season relevant to our study, limiting its applicability to our findings.
- Other suggested references: Some of the suggested works (e.g., Ibanhez et al. 2016, Lefèvre et al. 2017) are already cited in our manuscript. Lefèvre et al. (2014) provides

data at 38°W off French Guiana with one August crossing, which, while valuable, does not significantly enhance the contextual relevance of our dataset due to limited overlap. Lefèvre et al. (2020) focuses on the NECC at 8°N, an entirely different region. For the Southwest Atlantic, the references provided are of limited relevance to our study:

- Oliveira et al. (2022) is written in Portuguese, provides a general overview of Brazilian shelf datasets but lacks clear data coverage details beyond publicly available SOCAT sources.
- Napolitano et al. (2020) and Silveira et al. (2020) focus on ocean dynamics near the Vitória-Trindade Seamounts, which, while scientifically interesting, are not central to our dataset. While these processes were one motivation for Tara's sampling in the region, there is no direct evidence that these phenomena influenced the pCO₂ measurements collected. We therefore included them in the introduction to provide context.
- Silveira et al. (book chapter) presents a summary that includes model reanalysis but does not contribute substantially to the analysis of in situ pCO₂ observations.

Regarding the data from Marinha do Brasil, we acknowledge that these datasets could be valuable. However, since they are not publicly available (requests for access have not been granted), we are unable to incorporate them into our analysis.

In summary, while we appreciate the reviewer's suggestions, many of these references do not directly address the pCO_2 variability in the Amazon River–plume continuum or the specific oceanic regions and seasons covered by our dataset. Nevertheless, we will carefully reconsider our reference list and ensure that we include any additional relevant studies where appropriate.

We now provide a response to the detailed comments.

Review by line:

Fig 1. Needs a geopolitical map, with countries borders, as in the manuscript refers to at least 4 different countries. Indicate where Martinique is. Correct the city name "Salvador" (not only in the figures but in all document). Increase figure axes font. I suggest to include different colours in the Tara path according with the Leg numbers presented in section 2.1.

Thank you for the helpful suggestions. We have corrected the city name to Salvador throughout the manuscript. In figure one, we indicated where Martinique is, and corrected "Salvador da Bahia" in Salvador. Regarding the addition of country borders we followed the explicit recommendation of the journal: "In order to depoliticize scientific articles, authors should avoid the drawing of borders" (ESSD submission guidelines, section maps & aerials: <u>https://www.earth-system-science-data.net/submission.html#figurestables</u>). Thank you for your suggestion regarding the use of different colors for the Legs. However, since our analysis does not focus on interpreting the data leg by leg, we believe that adding this information to the figure would unnecessarily clutter it without serving a specific purpose in the manuscript.



Figure 1: Revised version of Figure 1

54-55: "There are several reasons for this, including the reduced solubility of CO2 at high temperatures, and the upwelling of deep waters rich in dissolved inorganic carbon (DIC) in the equatorial upwelling and along the coast." - Include reference. *Thank you, we included a reference to a paper showing and studying the* CO₂ *outgassing in tropical waters, and the role of the equatorial upwelling: Andrié, C., Oudot, C., Genthon, C., and Merlivat, L.: CO2 fluxes in the tropical Atlantic during FOCAL cruises, Journal of Geophysical* Research: Oceans, 91, 11741–11755, *https://doi.org/10.1029/JC091iC10p11741, 1986.*

58-59: "It represents one of the greatest environmental gradients on land and ocean in the world." - Include reference.

Thank you, we added a reference to Araujo et al., (2017).

59-61: The Amazonas River plume is not constant in area and position along the year. Therefore, in this paragraph it would be good to have more information about seasonal variation of the Amazonas River discharge, which is intimately related with the rainy season and Intertropical Convergence Zone (ITCZ) position, as well as El Niño and La Niña years. This is important once you're analysing a period of transition between seasons. Literature suggestion: Kang et al., 2013 (doi: https://doi.org/10.1007/s13131-013-0269-5) Lefèvre (doi: and et al., 2014 https://doi.org/10.1002/2013/C009248).

Thank you for this suggestion. We fully acknowledge the seasonal and interannual variability of the Amazon River plume, however, as this manuscript is primarily a data paper rather than a process-focused analysis, we have kept the discussion concise, referring readers to Olivier et al. (2024) and references therein for a more detailed analysis of the 2021 conditions and broader climatological context. That said, we now explicitly state that the cruise took place during a period of decreasing Amazon outflow, following one of the largest Amazon flood events on record, a bit later in the manuscript's introduction: This novel dataset presents 14,000 km of fCO2 measurements over 98 days between August to end of November 2021, primarily along the South American coast, and marking the first repeated sampling of the AROC. The cruise took place in a period of decreasing rive outflow, following one of the largest Amazon flood events on record. Freshwater transport was strongly directed toward the Caribbean, with comparatively less Amazon-derived freshwater reaching the NECC and central Atlantic (Olivier et al., 2024b).

We appreciate the references provided and reviewed them to ensure that relevant aspects of seasonal variability are appropriately acknowledged.

62: Needs to describe the influence of salinity too as it was observed by other authors as one of the most important drivers to this area act as sink of CO2. See recommended literature.

Thank you, we added this influence of salinity: combined with low salinities (Ibánhez et al., 2016; Lefévre et al., 2010)

63-64: "Opposing this, the Amazon River outgasses nearly as much CO2 as the rainforest sequesters on an annual basis." - Include reference. Do you have the numbers?

We included a reference to Sawakuchi et al., 2017 and Richey et al., 2002. We also recommend, seeing your interest in the question, this communication from the journal frontiers:

<u>https://www.frontiersin.org/news/2017/05/15/frontiers-in-marine-science-study-finds-amazon-river-carbon-dioxide-emissions-nearly-balance-terrestrial-uptake</u>

71-72: Although there is a need to better integrate the observations in the river and in the ocean, there are some studies that have been dedicated addressing these areas. Therefore, the references used here can be outdated. I suggest rephrasing or deleting this sentence. Please, also check the recommended references, and the project Carbon in the Amazon River Experiment (CAMREX).

Thank you for bringing the CAMREX references to our attention, we find the project very interesting. While these studies are indeed valuable, they primarily focus on riverine waters and do not extend to the transition zone between the river and the ocean. As we highlight in our manuscript, there is still a lack of recent surveys that fully capture the river-ocean continuum, particularly during this season, and this is the main focus of this paragraph. In particular, few studies have documented the transition from high pCO₂ river waters to the low surface values observed in the Amazon River Plume. We have reviewed the suggested references and will incorporate any relevant insights to ensure our discussion is as up-to-date as possible.

52-74: I suggest a full review of this paragraph in view as key references are missing.

We reviewed the paragraph, made some modification and included a reference suggested. However, the estuary, which is the link between these two systems is little known, if at all (Sawakuchi et al., 2017; Ward et al., 2017). Valerio et al., (2018) collected discrete samples for CO₂ partial pressure all the way to the river mouth in April 2017 but does not address the Amazon River CO2 flux budget. Chen et al. (2013) studied the CO₂ in the world's coastal seas by evaluating the air-sea exchanges of CO₂ in 165 estuaries, but no data were available in the Amazon estuary, despite being arguably one with the strongest impact. Since then, Araujo et al., (2017) collected discrete DIC and total alkalinity (TA) samples at the mouth of the Pará-Tocantins River system, near the town of Belém.

76-78: Are you referring to Argo or BCG-Argo floats? How much of the data gap in the surface ocean fCO2 was covered by the BCG-Argo floats in the open ocean? Can you put this in numbers? Do you know why there are no BCG-Argo floats in these coastal areas?

While the statement is true for both normal and BGC-Argo floats, it is more relevant to talk about BGC-Argo floats, so we replace the sentence by: While data gaps in the open ocean have begun to narrow, partly due to advancements such as the Argo biogeochemical float program, it is not the case for biogeochemical measurement on the shelves and continental margins.

The number of BGC-Argo floats worldwide is limited, and most are equipped only with oxygen sensors (and occasionally nitrate). Few have pH sensors necessary for indirectly deriving pCO₂. Additionally, like most Argo floats, they are programmed to remain at depths greater than 1,000 m, making them unsuitable for coastal measurements, except for specific programs, like the study of the Southern Ocean's shelves. Furthermore, Brazil does not currently contribute to the BGC-Argo program, despite being well-positioned to deploy floats in its coastal waters. For the contribution of BGC-Argo floats to surface ocean recommend Southern fCO₂, we can this paper in the Ocean: https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2019GB006176

In this paper, we agree with the other reviewer that we should insist on the fact that while Argo floats are helpful, we should aim at increasing the direct fCO2 surface measurements as they are the most accurate, especially in extreme conditions where approximating total alkalinity with salinity and temperature is highly uncertain. We therefore modified the paragraph in the paper: 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.

78-81: I suggest you reorganize these sentences. There is a global decrease in the uploaded dataset of ship observations into SOCAT that is an interesting discussion to be included here. Start addressing why this might be happening and which region is more affected, then comment about the Brazilian coast. This raises an important point that just because the data is not in SOCAT it doesn't mean that there is no data in the region. This is particularly true for global south ocean.

Thank you, we have reorganized the sentences following your suggestion: Continuous surface fugacity of CO_2 (f CO_2) measurements carried out on ships remain the most accurate way to asses CO_2 fluxes and are still too sparse. A notable trend in recent years is the global decline in ship-based CO_2 observations being added to the Surface Ocean CO_2 Atlas (SOCAT) database (Bakker et al., 2016), particularly since 2017 (Friedlingstein et al., 2023), mainly due to reduced fundings (Dong et al., 2024). Despite recent contributions documented in publicly available open-access data, the Brazilian continental margins remain notably under-sampled, with an acute lack of data during specific seasons, such as from August to November (Fig. 1c).

There has been a decline not only in the number of ship-based CO₂ observations uploaded to SOCAT but also in the total amount of data collected across most ocean basins. This is largely due to reduced fundings, as well as changes in merchant shipping practices and shifts in global trade dynamics. We included the reference to Dong et al, (2024) (https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2024GL108502) that analyzed the impact of this issue on the accuracy of the CO2 uptake estimates. While research vessels now contribute more data through continuous measurement systems, access to these datasets is often restricted. Additionally, some national centers maintain datasets (such as those from the Anacondas cruises), but there is no clear indication that data availability in these repositories is increasing.

We acknowledge the reviewer's point that data may exist in these regions outside of SOCAT. To clarify this, we have updated the manuscript to specify 'publicly available open-access data.' However, as far as we know, SOCAT remains the primary international reference for oceanic pCO_2 observations, including in the Global South.

87: Why is the equilibrator system more accurate than membrane systems?

Unlike membrane systems, which rely on gas diffusion through a semi-permeable barrier and can introduce biases due to response time lag and sensitivity to salinity or biofouling, equilibrator systems ensure a more complete gas exchange between water and air within a controlled volume. This allows for near-equilibrium conditions, minimizing uncertainties associated with diffusion limitations. Additionally, equilibrator systems enable regular calibration with reference gases, ensuring greater accuracy. In contrast, most membrane systems do not allow for in situ calibration as easily, making it more difficult to quantify uncertainty or correct for sensor drift (but not impossible, some of them are calibrated with reference gases). Given these advantages, equilibrators remain the preferred method for high-precision pCO_2 measurements in our field.

91-94: The sentence is not completely true in the way it is written. There is the novelty of the sampling in the continuum using a sailboat. So, make sure to write this clearly, because it tends to give the idea that there is no data in these regions you refer to, which is not true. Also, it is very important to have in mind, not only for these lines but for all document, that this dataset is not filling the region data gaps, as it is just a snapshot of the conditions while the boat navigates in these particular areas. You can say that this data contributes to better understanding the area. Please, see the references suggested and provide new references that might be missing in there.

We think there is a misunderstanding here, because in the sentence "Tara missions are unique in that they are continuous for a multi-year duration, with scientists and sailors taking turns on-board", we want to emphasize that it is the way Tara's mission are designed that is unique, and we do not intent to convey any information on data coverage. We therefore rephrased: Tara missions have a unique design, they are continuous for a multiyear duration, with scientists and sailors taking turns on-board.

Nevertheless, we also iterate that despite the references suggested, there is very little data made freely available for this region and this season.

Introduction: You should focus the manuscript only in the Amazonas River Plume and NBC, as you give more attention to this area along the manuscript. Otherwise, you need to explore more and give more overview about the rest of the areas: Vitória-Trindade seamounts, Guanabara Bay, Lagoa dos Patos, and the rest of the Brazilian continental shelf.

We do not think focusing the manuscript only on the Amazon River and River Plume is a good idea as the idea is to publish the whole dataset, that has been acquired and validated in the same way. We therefore agree with the reviewer that the rest of the areas need a more detailed overview in the introduction and added a full paragraph, including some of the references the reviewer kindly suggested.

The Brazilian continental shelf hosts diverse CO_2 flux dynamics influenced by regional oceanographic and biogeochemical processes. The ARP plays a key role in air-sea CO_2 exchange, with strong seasonal variability driven by river discharge, biological productivity, and salinity gradients (eg. Lefévre et al., 2010; Mu et al., 2021; Olivier et al., 2024b). In the North Brazil Current (NBC) region, upwelling and mesoscale eddies contribute to CO_2 flux variability, modulating carbon exchange between the ocean and atmosphere (eg. Monteiro et al., 2022; Olivier et al., 2022). Further south, the Vitória-Trindade Seamount Chain interacts with regional currents (Napolitano et al., 2021), influencing nutrient transport and biological activity that can affect CO_2 fluxes. The Lagoa dos Patos and Guanabara Bay are important estuarine systems where terrestrial carbon inputs, tidal mixing, and anthropogenic influences create spatially and temporally variable CO_2 flux patterns (Cotovicz Jr et al., 2015). Along the broader Brazilian continental shelf, complex interactions between ocean circulation, biological productivity, and local conditions shape regional carbon dynamics, making in situ observations critical for understanding these fluxes.

95-96: Delete: "lesser studied".

We modified the sentence.

107: 14.000 km is a long area, therefore only the dates don't give the real visualisation of the size of each Leg. It would be also very useful if you put the km or range of lat/long of each Leg. See suggestion for figure 1 about the colours.

Thank you for the suggestion. We have now added the latitude ranges of each leg in the table to provide a clearer sense of the spatial coverage. However, since our analysis is not structured by individual legs, we believe that adding this information to Figure 1 would unnecessarily complicate the visualization. Our focus is on the broader regional patterns rather than the segmentation by leg, and we aim to keep the figure as clear and uncluttered as possible.

104: In lines 90-91 you say that the measurements in the South America coast were between August and December 2021. And this line is saying until November 2021. Which one is correct?

Thank you, we modified, it is end of November.

110: Please, correct throughout the document (including figures). The correct name of the city is "Salvador".

Thank you, modified in the text and in the figures.

113: Please, correct throughout the document (including figures). The correct name

of the city is "Buenos Aires", it doesn't have hyphen. *Thank you very much, modified.*

117: Why did you choose this equilibrator system? Would be nice if you could include more details about the equilibrator system instead of just putting the reference, also with a figure/photo in figure 2.

We selected this equilibrator system for several reasons. First, its compact size makes it more suitable for a sailboat compared to the larger GO system. Additionally, our collaboration with the research group in New Hampshire, which has successfully deployed this system in the coastal waters of the Gulf of Maine, provided an opportunity to test its performance in a new and challenging environment.

Regarding the request for a photograph, we believe that the schematic in Figure 2 provides a clearer and more rigorous representation of the system's setup and functioning. A photograph, while useful in some contexts, may introduce visual complexities that do not necessarily enhance the technical understanding of the system. However we included a brief description of the system's physical setup in the text to complement the schematic. The fCO2 system uses a shower spray air-sea equilibrator of 2.5 L as described by Dickson, (2007) and used by Vandemark et al., (2011). Water is sprayed or trickled inside a chamber, creating a large surface area for rapid equilibration with the headspace air. A closed loop of air flows through the equilibrator where the air-water exchanges happen, the equilibrated air is drawn at 100 mL/min through tubing containing a Nafion selectively permeable membrane with a counterflowing stream of dry nitrogen to remove water vapor from the sample gas stream. It is then sent to a non-dispersive infrared CO2 analyzer, a LICOR LI-840A.

119-120: "It is able to capture the fine scale variability of oceanic fCO2 by responding quickly to fCO2 changes in seawater" This seems very vague, please, include reference or rephrase.

The next sentence of the manuscript provides both the reference and the values to justify this statement: The exchange time for the water in the equilibrator is between 30 and 45 seconds, depending on flow rate (Pierrot et al., 2009).

123: How many square meters? Use precise numbers. 2.5 m^2 , modified in the text.

Figure 2: You could include a picture of the equilibrator system. Please, include where SBE 38 is in the scheme.

Thank you, we included the SBE38 in the schematic. Regarding the request for a photograph, see comment above.



Figure 2: Revised version of Figure 2

142: How the equilibrator air was dried? Please, include as much as information you have for this methodology as it can be replicated in future years. Including the sampling rates for STD gases, atmospheric and ocean.

Thank you very much, we added: "the equilibrated air is then dried using a gravity water trap and Nafion tube before being sent to the CO₂ analyzer", to indicate how the air is dried. We added the information regarding the sampling rates of STD gases and atmospheric CO₂:

During the first week, to test the system, a complete set of standards and atmospheric cycle was measured for 15 minutes every hour.

144: I couldn't find the Annex.

The information is in the Annex of Pierrot et al., 2009. To improve clarity, we modified in the text: "It detects the molar fraction of CO2 (xCO2) in dry air by infrared detection, from which fCO2 is computed following Henry's law (Pierrot et al., 2009, detailled in their Annex)".

149: Please, describe how these valves are controlled?

They are electro-valves. We added the information to the manuscript: "Through a system of electro-valves".

151: Why were these two standard gases chosen? There is a reference that suggests that or is something you are suggesting for the first time? As the mission would measure the river-ocean continuum, why didn't you choose a STD gas with a higher concentration to include the values between 0 and the maximum value found in the river, as recommended in SOCAT Cookbook (2018)?

Thank you for this insightful question. The selection of these two standard gases was carefully made to balance multiple objectives. As you correctly pointed out, SOCAT recommends using standard gases that bracket the expected values. However, it is equally important that the standards remain as close as possible to the measured values to minimize calibration uncertainty.

Using a higher standard gas (e.g., 1000 or 2000 μ atm) would have significantly reduced the accuracy of oceanic measurements. We chose 0 and 500 μ atm because they effectively bracket the range of oceanic fCO₂ values in this highly variable environment, encompassing

most of the observed data except for the river. Since this system was designed for longterm deployment in a predominantly oceanic setting, these values were deemed the best compromise.

To address this, we have now clarified in the manuscript the rationale behind our choice and explicitly stated that measurements beyond this range (e.g., in the river) have greater uncertainty due to the lack of higher standard gases.

In the text: "The two 20 L reference gases tanks of 0 ppm and 502.3 ppm are stored on the front deck. These values were chosen because they effectively bracket the range of oceanic fCO₂ values in this highly variable environment, encompassing most of the observed data except in the river. As a result, fCO₂ values above 500 µatm are more uncertain and should be interpreted with caution".

154-155: "It is recommended to measure a complete set of standards every 3 hours."-Include reference. Can you explain more about these changes, in which leg it was made, for example.

Thank you for the comment, we included the reference to Pierrot et al., (2009) and added the date at the time the change was made: the measurement of standards was increased to every 6 hours (on 31/08), then every 12 hours (on 02/09) to save the reference gases

163-164: How regularly the equilibrator was cleaned? There were other methods to avoid mud in the system?

The equilibrator was cleaned at each stopover and each time we exited a major river. We added this information to the manuscript.

The system also has the advantage to be able to work in turbid environment. 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.

168: Why did you proceed with this STD gas if it wasn't in the range reported by the supplier? Also, did you try to measure in a different analyser to see if the problem was the gas or your LICOR?

We appreciate the reviewer's suggestions and acknowledge that further testing of the standard gas would have been ideal. However, due to logistical constraints and limited time in port after receiving the gas in Martinique, additional checks were not feasible. To independently assess the gas, we relied on a comparison with the site in Barbados, which exhibits minimal variability when the wind comes from the sea. This approach provides a reliable calibration reference for the standard gas. The LICOR didn't have any issue with the other standard gas (0) and when back in the laboratory after the Tara mission.

Figure 3: Please, increase the legend font. I suggest a scatter plot to make the comparison clearer and more realistic. Also, a statistical metric to support the relation between the datasets.

Thank you, we increased the fonts. We think the scatter plot suggestion might be for figure 4 instead of 3? We included a scatter plot in the new version of Figure 4.

180: There is an inconsistency between the dates in the figure 3 (18-19/08/2021) and the main text (19-20/08/2021). My concerns about this correction is: i) it used just 7h of measurements, in just one point in the early stage of the campaign. Is this representative? Do you think it is possible to compare to another dataset or increase the calibration curve with the RPB measurements?

Thank you for catching the inconsistency; we have corrected our mistake. We acknowledge that the comparison period is relatively short, but there is no reason to expect that the standard gas values would have drifted over time. Additionally, given the conditions, there is no strong indication that a significant spatial gradient in atmospheric fCO_2 existed between the ship and the land station. Furthermore, we examined the atmospheric fCO_2 values to ensure the robustness of our assessment.

185-189: Which method? Compared the values and decreased one from the other? This is not a reliable calibration method for a long dataset as presented and with all unstable conditions for the gas cylinder. Please, provide a more reliable method that uses a significance range, calibration factor, or something that ensures your data is correctly calibrated and it is possible to replicate your calibration in other parts of the campaign.

Apologies for the confusion; we have replaced 'method' with 'approach' to better reflect our intent. This approach was not used to calibrate the entire dataset but rather to determine the correct value of the standard gas. The rest of the calibration follows standard procedures applied on research vessels. There is no indication that the gas cylinder was unstable or that its properties changed over time, as such stability is generally expected and routinely assumed in similar shipboard measurements.

193: Even though Metzl et al., 2024 provide the synthesis of SNAPO-CO2-v1 dataset, you need to be able to provide a brief explanation of the TA and DIC methodology used in your campaign, especially using these data to validate you fCO2 dataset. You also mentioned 17 samples for the surface, but you present only 13 in figure 4.

Please, be clear in the text how many samples you used.

There were 17 samples collected, but four were either not analyzed correctly (in the Amazon river) or were not collected with simultaneous pCO2. To clear the confusion, we added in the description of Figure 4: The fCO2 system was measuring the standards during stations 36abc and 39, these stations are therefore not represented in (d). We added information on the sampling methodology for DIC and TA: Samples were drawn from the rosette into 0.5 L borosilicate glass bottles, ensuring minimal air contamination, and immediately poisoned with 400 μ L of mercuric chloride (HgCl₂) to prevent biological alteration. TA was measured using open-cell titration with a hydrochloric acid titrant, while DIC was analyzed using acidification followed by CO₂ extraction and detection via infrared or coulometric

methods. Quality control was ensured through calibration with certified reference materials to maintain an accuracy of $\pm 4 \mu$ mol kg⁻¹ (Metzl et al., 2024)

195: Provide which version of CO2SYS you used and the reference.

Thank you, we used CO2SYS v3.1 and included both the version and the reference in the manuscript: The fCO_2 is computed from the near-surface ocean DIC and TA using the CO2SYS v3.1 software (Sharp et al., 2020) to compare with the continuous fCO2 measurements (Fig. 4).

Figure 4: This figure gives a wrong perception of distance between the discrete samples. The figure could be sliced by leg to better visualize. In the current way it is not possible to address the values very easily. I also suggest a table where one column is the fCO2 calculated by the CO2SYS and the other by the equilibrator.

Thank you for your comment. We heavily modified Figure 4 to also integrate the useful suggestions from the other reviewer. We hope this second version, with different ranges of fCO2 values and a scatter plot addresses your request to be able to better compare the fCO2 calculated and measured.



Figure 3: Revised version of Figure 4

205: "the continuous fCO2 compares very well to the one computed from the samples, especially after 26 September" – It is not possible to see this in the figure 4, and no statistical method was applied on the dataset to prove or support this sentence. Again, this is a long area with high variability, a comparison as presented in fig 4 is a weak assumption that your data has the required accuracy, especially for the river areas where you don't have neither discrete samples or the STD gas.

The comparison is explicitly and statistically reported on line 210. We acknowledge that in the river area, the accuracy is lower, partly due to the limitations of the DIC/TA samples collected. Unfortunately, the analysis method used did not allow us to retrieve reliable DIC and TA values, adding further uncertainty in estimating pCO2 in these waters. We have now explicitly stated this in the manuscript (see answer to next comment). While the number of discrete samples remains limited, and the uncertainty from atmospheric xCO2 comparison

should be considered, we have no indication that the data accuracy is lower than what is reported. Additionally, we have modified Figure 4 to enhance the visibility of the comparison.

217: Please, check if your data matches the ones in the suggested references.

Thank you, in answer to this and the comment before, we modified the paragraph accordingly:

Overall, the mean difference remains around 2 μ atm, providing a reasonable estimate of the dataset's uncertainty. In the river, where fCO₂ values fall outside the range of the standard gas used and no discrete samples are available for direct comparison, the uncertainty is likely higher. However, the values obtained align with expected ranges for this part of the river, based on discrete samples collected in April 2017 by Valerio et al. (2022), despite differences in season and year.

226: I strongly recommend you submit to SOCAT 2025 only the data for Amazonas River plume, as you didn't provide a reliable calibration and validation to the other parts of the dataset, especially in the rivers.

We submit the entire dataset, as it follows the same validation and calibration procedures applied to other ship-based fCO_2 observations included in SOCAT. While we acknowledge that uncertainty is higher for the elevated fCO_2 values observed in the estuary and near Macapá and Belém, we explicitly state this in the manuscript. SOCAT includes datasets with varying levels of uncertainty, provided that these uncertainties are well-documented, which is the case here.

Figure 5: Please increase axes and colour bar font. I appreciate the consistency in the maps, however, it is not very easy to see the dataset variation in this. I suggest dividing by the legs. Please, include geopolitical map and include names (especially the ones you use in the text).

Thank you for your suggestion. We increased axes, and changed the projection to increase the focus on the dataset and remove as much white as possible. We added the names of the main cities, and as commented previously we refrain from adding the borders to comply with the ESSD guidelines.



Figure 4: Revised version of Figure 5.

238: 36 is considered salty waters.

Thank-you. We replaced 'saline' by 'salty'.

238: What does "recent ARP" mean in this context?

Thank-you. We rephrased by: The schooner then crosses the salty (36) water of the NBC retroflection, before sampling the river plume that has been recently transported from the Amazon estuary.

248: This can be due to rain in the land, which increases the river discharge, please check this and the references.

We have reviewed rainfall data for the period in question and found no significant rainfall event near the estuary. Instead, we suggest that changes in wind patterns, particularly wind direction, may have played a more substantial role. We have previously discussed this in greater detail in Reverdin et al. 2021.

249: Change "maritime" to "marine". Please revise this in all document. *Thank you, done.*

Figure 6: It gives more the idea of the places however the fCO2 axes need to show with more numbers.

Thank you, we increased the number of ticks for the fCO2 on Figure 6.

267: Please check the suggested references. *Thank you, we included the reference to Napolitano suggested.*

268: The correct name of the city is Rio de Janeiro. *Thank you, modified.*

270: Which is considered low salinities in Santos?

Thank you, we indeed modified low by lower. The salinity is 34.8, which is still quite salty. In the manuscript: It shows strong fCO2 variability, with low values associated to the lower salinities (34.8) close to Santos.

Figure 7: Please include the name of the cities and countries borders.

Thank you very much, we added the name of the main cities. For the borders, we follow the ESSD guidelines.



Figure 5: Revised version of Figure 7.

280: Please provide Lat/Lon of the center of the plume first here, and indicate in the figure 7.

Thank-you. Following your comment, we realize that 'center of the plume' might not be the best wording, and rephrased the sentence as: The minimum observed fCO_2 in the Amazon River plume is of 65 µatm (4.5°N/50.77°W), whereas outside of the plume, in the NBC, fCO_2 is around 420 µatm.

282: "towards the Amazon" what? This seems incomplete.

Thank you for noticing the missing word, we complete with "towards the Amazon estuary".

Table 1 is not very informative as you could include this information in the text. If you follow the suggestion to focus the manuscript only in these areas, it would be interesting to see the difference of the mean fCO2 for these regions which you could include in this table.

We acknowledge that Table 1 may not be particularly informative, and therefore we removed it. Its purpose was to ensure full reproducibility of the figures presented in the manuscript, so we adapted Figure 9 to include the information that was in Table 1. As this is primarily a data paper rather than a scientific analysis, we provide insights into potential uses of the data through the figures, while leaving the scientific interpretation to the users of the data. We do agree that information on fCO2 would be valuable. However, we leave this level of analysis to the data users who may wish to conduct more targeted studies on the subject.



Figure 6: Revised version of Figure 9.

291: "follow well the relationship reported in Lefèvre et al., (2010)". Please provide a statistical metric that supports this, especially because the river region (brown) doesn't look like it fits well.

We completely agree with the reviewer, that is why the sentence states that the data follow well the relationship "From the NBC to the core of the ARP (6°N to 4°N)", so not the river region in brown. That is also why the next sentence is "However, when salinity and fCO_2 increase locally from 4°N to 2°N, they move away from the NL linear relationship". We added the colors in parentheses to make it clearer.

292: What does "NL" mean?

Sorry, we didn't include the definition of the acronym, it stands for Lefèvre et al. (2010) fCO2/SSS relationship. We now explicitly mention it in the manuscript: the fCO₂/SSS measurements follow well the relationship reported in Lefèvre et al., (2010, then NL).

Discussion: Needs to be revised after including the key references and data validation metrics, and study area reduction to Amazonas River plume.

As previously mentioned, we do not agree with limiting the dataset to a specific subset. We have included the necessary validation metrics, which are critical for an ESSD paper, as well as additional references as suggested.

324: Tropical band is from 20°N to 20°S, where the tropics are. Perhaps you mean the equatorial area?

Correct, thank you very much, it has been modified.

332: "changes in biogeochemical and biological properties." You didn't have biological data, so please include a reference for this sentence.

There were biological measurements during the cruise, but they haven't been published yet and we don't comment on them, and thus removed 'biological'.

335: Provide the agreement with salinity. *Thank you, this paragraph has been rephrased.*

343: "Nevertheless, while the large-scale variability of the fCO2 reflects the latitudinal temperature gradient" – include references that support your findings. See suggested references.

Done

345-346: "Other river discharges reach the south Atlantic, such as the one of the Rio de la Plata." – Include references.

I.346-347: "These waters spread on the shelf and generate variability in salinity, suspended sediments and biological activity." – Include references.

Done

352: Update reference. 354: Update reference.

361: Update reference.

If that is ok, we kept the original reference because it refers to the first time these processes where identified, and added more recent ones.

361 – 362: "The source to sink transition is mainly driven by the switch from a respiration dominated system to a photosynthetic one." – Include references. *Done*

362-363: "Several factors impact the suspension of sediments in the water column and the development of phytoplankton, such as the bathymetry, winds and the tides." – include references. Include the rainy season, ITCZ position and, El Niño and La Niña occurrence impact.

We modified by: Several factors impact the suspension of sediments in the water column and the development of phytoplankton, such as the bathymetry, winds, intensity of the outflow (that can be influenced by large-scale climatic modes) and the tides (Gomes et al., 2021).

365: Update reference. *Done*

388: "There are very little previously acquired data in the region that can be used for comparison." - Check references.

Unfortunately, there are little directly relevant data. There are indirect observations, but almost none of fCO₂ during this particular season, and that cover the Amazon estuaryocean continuum. We rewrote this sentence to be more specific. As mentioned, the SOCAT 3-month data map presented still is a rather complete map on what was collected during this season. Thus, actually, although there are some data further north and south that are not in the SOCAT data base (such as from Anacondas cruise), there is no other pCO2 data within 1°S and 6°N in the published literature (except for the river, but as mentioned, this is not the focus of the study, and except near Belem and Para River, but missing most of the Amazon estuary).

393: Delete "if they would exist." Check references first.

We agree and modified the sentence by: it would be more accurate to cross-compare with fCO_2 measurements conducted in the same region at the same time as recommended by SOCAT. In the quality-checking process of SOCAT, the fCO2 measurements need to be conducted in the same region but also at the same time (same year, same month) to be able to qualify as a flag A. Despite the interesting references provided, no fCO2 measurement was conducted in the region in September-October 2021.

408: Delete "which had never been observed before." - Check references first.

Thank you for the references provided, we checked them and we can maintain that this statement is correct for the period. We therefore modified to: "which had never been observed before in this season".

408-409: Change "for the first time a sailboat equipped with a fCO2 system is sampling the river-ocean continuum". Otherwise, this is an overinterpretation, especially because your river-ocean continuum data is not reliable.

Thank you for your comment. We respectfully maintain that our statement is accurate. We originally wrote: "For the first time, a schooner equipped with an fCO_2 equilibrator system measured fCO_2 along the eastern coasts of South America," which remains factually correct, as no other sailboat has been equipped with such a system for this purpose.

We acknowledge the reviewer's concern regarding data reliability in riverine conditions. However, we would like to clarify that the dataset collected in oceanic conditions meets the same reliability standards as other fCO_2 datasets. We agree that data quality is more uncertain in riverine conditions, but this primarily applies to a limited portion of the dataset and does not affect the measurements taken from Belém to Uruguay or from Martinique to the Amazon River.

416: "filling part of the data gap in the coastal regions of the South Atlantic Ocean", this is an over-interpretation, delete or rephrase.

We rephrased by: providing data in the data-poor region of the coastal regions of the South Atlantic Ocean.

420: Delete. The only mention of Guanabara Bay is in the conclusion, and it is not easy to find the data of these regions in your result.

Agreed, we remove the mention to the Guanabara Bay.