

ESSD Manuscript: "Exploring the CO<sub>2</sub> fugacity along the east coast of South America aboard the schooner Tara" - Oliver et al.

Time spent to review: 22h

Reviewer 2 comments:

The manuscript presents CO<sub>2</sub> 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 Additionally, the authors rely on outdated literature, some over 30 years old, which may no longer reflect the current local status and climatology.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.

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., pCO<sub>2</sub>air 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.

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 CO<sub>2</sub> fluxes, ocean pCO<sub>2</sub> and fCO<sub>2</sub> 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](https://doi.org/10.1007/978-3-030-53222-2_2)). pCO<sub>2</sub> data: request to Marinha do Brasil (Brazilian Navy).

In conclusion, while this manuscript has the potential to contribute to understanding CO<sub>2</sub> fluxes in the Tropical and Subtropical South Atlantic, the issues with data quality, limited analysis, and insufficient calibration prevent it from being ready for publication. I recommend a major revision, changing the manuscript focus specifically on the Amazonas River Plume and North Brazil Current. Due to the concerns raised, I do not recommend submitting the whole dataset to SOCAT v.2025, especially without addressing these issues.

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.

54-55: “There are several reasons for this, including the reduced solubility of CO<sub>2</sub> 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.

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

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>) and Lefèvre et al., 2014 (doi: <https://doi.org/10.1002/2013JC009248>).

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 CO<sub>2</sub>. See recommended literature.

63-64: “Opposing this, the Amazon River outgasses nearly as much CO<sub>2</sub> as the rainforest sequesters on an annual basis.” - Include reference. Do you have the numbers?

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).

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

76-78: Are you referring to Argo or BCG-Argo floats? How much of the data gap in the surface ocean  $f\text{CO}_2$  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?

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.

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

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.

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.

95-96: Delete: "lesser studied".

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?

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.

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

113: Please, correct throughout the document (including figures). The correct name of the city is "Buenos Aires", it doesn't have hyphen.

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.

118-119: "Currently, an equilibrator-based fCO<sub>2</sub> system is the most reliable and accurate instrument to measure the in-situ fCO<sub>2</sub> in seawater". Include a reference. Currently, the results of the pCO<sub>2</sub> Compare have not been released yet, is there other reference that has data to prove that?

119-120: "It is able to capture the fine scale variability of oceanic fCO<sub>2</sub> by responding quickly to fCO<sub>2</sub> changes in seawater" This seems very vague, please, include reference or rephrase.

123: How many square meters? Use precise numbers.

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

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.

144: I couldn't find the Annex.

149: Please, describe how these valves are controlled?

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)?

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.

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

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?

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.

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?

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.

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 your fCO<sub>2</sub> 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.

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

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 fCO<sub>2</sub> calculated by the CO2SYS and the other by the equilibrator.

205: “the continuous fCO<sub>2</sub> 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.

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

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.

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).

238: 36 is considered salty waters.

238: What does “recent ARP” mean in this context?

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

249: Change “maritime” to “marine”. Please revise this in all document.

Figure 6: It gives more the idea of the places however the  $f\text{CO}_2$  axes need to show with more numbers.

267: Please check the suggested references.

268: The correct name of the city is Rio de Janeiro.

270: Which is considered low salinities in Santos?

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

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

282: “towards the Amazon” what? This seems incomplete.

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  $f\text{CO}_2$  for these regions which you could include in this table.

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.

292: What does “NL” mean?

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

324: Tropical band is from  $20^\circ\text{N}$  to  $20^\circ\text{S}$ , where the tropics are. Perhaps you mean the equatorial area?



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

335: Provide the agreement with salinity.

343: “Nevertheless, while the large-scale variability of the fCO<sub>2</sub> reflects the latitudinal temperature gradient” – include references that support your findings. See suggested references.

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

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

352: Update reference.

354: Update reference.

361: Update reference.

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

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.

365: Update reference.

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

393: Delete “if they would exist.” Check references first.

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

408-409: Change “for the first time a sailboat equipped with a fCO<sub>2</sub> system is sampling the river-ocean continuum”. Otherwise this is an overinterpretation, especially because your river-ocean continuum data is not reliable.

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

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 results.