Response to Reviewers

We thank both reviewers for their thoughtful and constructive feedback, which has substantially improved this manuscript. Our responses are interwoven as text in blue italics in the reviewer comments below.

Reviewer 1.

1.0. This study performs a thought experiment to explore the CO_2 removal effect via ocean alkalinity enhancement (OAE) by the hypothetical quicklime addition in the Amazon River watershed. The calculation results suggest that the total carbon uptake in the Amazon River Plume is ~ 0.07-0.1 $MtCO_2$/month. A Monte Carlo simulation is made to assess the detectability of alkalinity perturbation, which shows that the detectability depends on the perturbation strength, the sample sizes and background alkalinity variability. This paper also discusses other potential issues related with the OAE deployment, including secondary mineral precipitation, ecological consequence, and heat release during quicklime dissolution. In summary, the authors argue that the proposed thought experiment could serve as a great starting point for investigating further the feasibility of using OAE for CO_2 removal.

I find this study interesting, and the argument is well organized and convincing. I do have, however, several concerns that need to be addressed first, which I summarize in the following.

We thank the reviewer for the compliment and gladly address all the comments below.

1.1. Carbonate system calculation for excess CO_2 uptake estimate. The author applies a subtle method to estimate the CO_2 uptake via the quicklime addition. One fundamental assumption is the constant DIC before any significant air-sea equilibrium occurs (Line 123). It is supported by that the air-sea equilibration takes weeks in the study region while CaO dissolution happens on hour-scales. Correct me if I am wrong, but I think this assumption needs more justification. The CO_2 uptake estimate is based on the whole Amazon River plume region. Although CaO dissolves fast, the timescale for spreading of alkalinity perturbation along the plume may be comparable to that required for the air-sea equilibration. It is reasonable to expect a DIC increase from the river gateway to the oceanic part. With an increase of DIC, the pCO_2 in the distal plume seawater will increase, which will reduce the CO_2 uptake in this region. According to Figure 5, the plume at near-oceanic salinity level contributes to the majority of CO_2 uptake due to the large area. Thus, I suggest the authors discuss or test the sensitivity of CO_2 uptake estimate to the CO_2 exchange between ocean and atmosphere along the plume route.

We thank the reviewer for raising this point, which prompted us to clarify the assumption further in the text.

The reviewer is correct about the implication of this assumption. We assume that the pCO_2 deficit inferred from the mixing model + OAE deployment is "static" in the Figure 3 map and use the resulting static surface seawater pCO_2 field to calculate the fluxes across the entire plume (Figure 5 and Table 2). In reality, exchange with the atmosphere along the path of Lagrangian parcels in the plume means that the pCO_2 deficit will slowly be diminished as *the DIC increases. Thus, the true pCO_2 map and the integrated flux calculated from the pCO_2 deficit map will differ from our calculations.*

However, we argue that this error is unlikely to strongly bias our results or change our overall conclusions, as the time elapsed between the river discharge at the mouth and mixing with ocean water to relatively high salinity (SSS > 15) is short. Comparing Figure 5 in Coles et al. (2013; copied below) to maps of SSS (e.g., Figure 1 from the manuscript), it is clear that a Lagrangian parcel discharged at the mouth of the Amazon spends little time (< approximately 2 weeks) in the fresh part of the plume (SSS < 30). The implication is that mixing of fresh river discharge with ocean water happens quickly relative to air-sea CO_2 exchange. Trying to add more precision to these statements would likely require analysis of a realistic circulation-biogeochemical model, which could comprehensively capture the transport, air-sea exchange, and other chemical transformations. We leave such analysis for future work. We have added this explanation to the text.

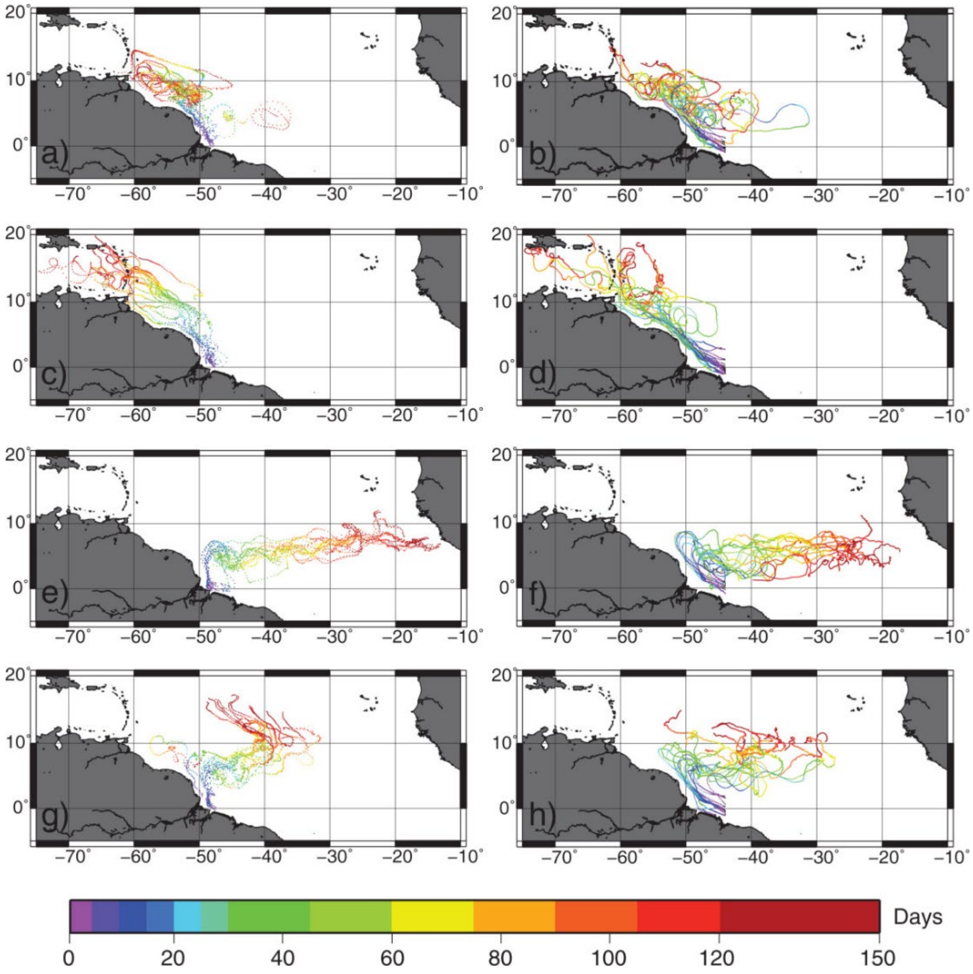
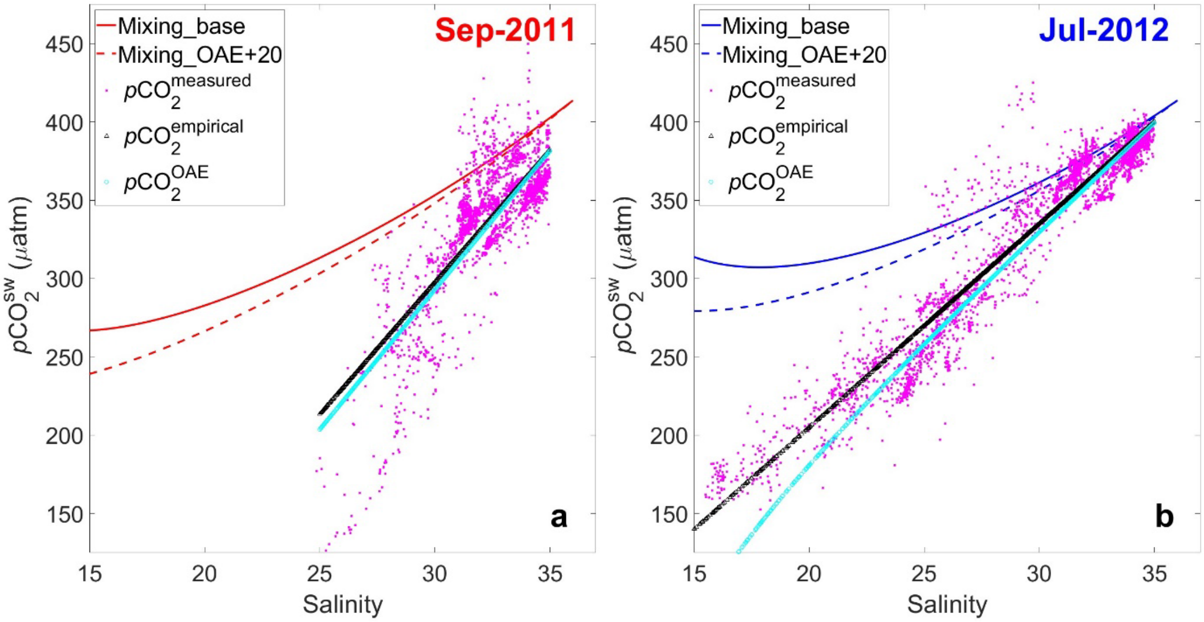


***Figure 5** from Coles et al. (2013). Time in days since a Lagrangian particle entered the river mouth (in days). Panels on the left are made from a general circulation model; on the right shows observational surface drifters that entered the river mouth.*

1.2. The pCO_2 baseline derived from the mixing model is essential for the reliability of CO_2 uptake estimate. However, the robustness of pCO_2 baseline lacks discussion in the paper. I suggest plotting a figure (may be put in the extended figures) to compare the pCO_2-baseline with the pCO_2-empirical, which will make the performance of a simple mixing model more accessible to the reader.

Agreed. We added the figure at the reviewer's suggestion in the supplementary material (i.e., Figure S3).



***Added Figure S3**. Surface pCO_2 in the Amazon River plume at 15 < salinity < 35 and river-ocean mixing curve before and after the TA perturbation at the mouth for (a) September 2011 and (b) July 2012. TA perturbation strength is 20 μmol kg^{-1}. The TA and DIC for the baseline mixing curves (solid red and blue lines) are calculated from the river and ocean endmember values, from which $pCO_2^{mix\_base}$ at each salinity stamp is calculated using the CO2SYS program. The dashed lines show the OAE-perturbed mixing curve at ΔTA = 20 μmol kg^{-1}. Black triangle markers show the empirical pCO_2 ($pCO_2^{empirical}$) at the plume surface computed from satellite-derived salinity and measured pCO_2 ($pCO_2^{measured}$; magenta dots) versus salinity regression, and open cyan circles represent the OAE-perturbed plume pCO_2 (pCO_2^{OAE}) at ΔTA = 20 μmol kg^{-1}. Salinity as low as 15 was observed in the July 2012 survey, while no salinity under 25 was recorded during the September 2011 cruise.*

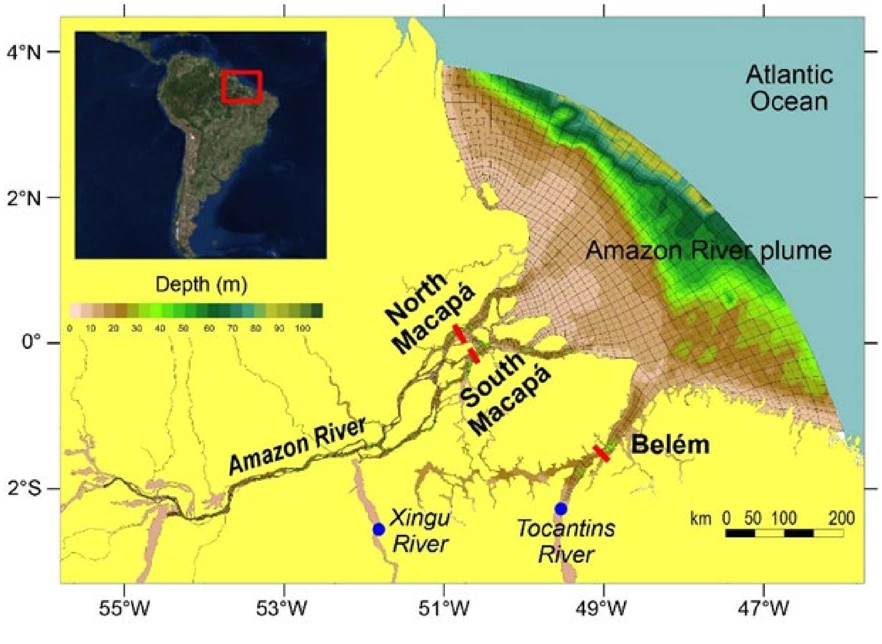
1.3. As the authors said, the detectability experiment results depend on the background variability. There are six available alkalinity measurements for each gateway near the Amazon River mouth, which could be potentially applied to constrain the natural alkalinity variation. However, only data from North Macapá is used in this paper, which is "for a concise demonstration" according to Line 97. I did not get the meaning of concise demonstration here. So please elaborate the data choice here. Also, more discussions on the background variability from other regions (in addition to North Macapá) might also be helpful.

Thank you for bringing this to our attention. To provide more details on the "gateway" definition and why North Macapá alone was chosen to represent the river mouth, we edited the paragraph below at the end of Section 2.1:

"... Briefly, the Amazon River mouth region receives freshwater runoff from three channels: the north and south channels near Macapá, and the channel of the Tocantins River near Belém (Figure S2 copied below). Sampling was conducted at the lower reaches of the three channels near the mouth (or "gateways") in each month. Six TA and DIC samples were collected at three cross-channel locations of each gateway (left bank, center, and right bank) from both surface and 50% depth (5–10 m). For a concise demonstration on the detectability of the alkalinity addition in the river, we chose to target one gateway (North Macapá) as the perturbation site and consider how many samples would be needed to observe the TA perturbation relative to that gateway's background variability. However, to quantify the potential CDR induced by a TA perturbation just above detectability, we assumed the entire river mouth would be perturbed equally as in North Macapá. Because the outflow through both Macapá gateways comprise > 80% of total discharge (Ward et al., 2015; Mu et al., in revision) and their chemical properties are almost identical seasonally (Mu et al., in revision), North Macapá is representative of the mouth's chemical composition. In an actual OAE field trial, perturbing one gateway will perturb the mouth region by an amount proportional to the percentage discharge there (relative to the combined discharge), and the natural variability in the unperturbed gateways will affect the background variability at the mouth. There are key unknowns in seasonal TA contributions from other gateways to the mouth which prevents us from combining all the gateways. Therefore, the mean and standard deviation of the six TA values at North Macapá, respectively, were then used as the river TA endmember and its natural background variability (Table 1)."

We also added one sentence at the beginning of Section 2.4:

"To assess the TA detectability, we evaluate perturbations in one river gateway (North Macapá)."



Added Figure S2. *Map of the Amazon River lower reach. Geochemical surveys (in particular, river TA and DIC measurements) were conducted at the outer gateways (North Macapá, South Macapá, and Belém)* *during September 2011 and July 2012 River Ocean Continuum of the Amazon (ROCA) project. This figure is reproduced from Ward et al. (2015) and Mu et al. (in revision).*

1.4. The theoretical saturation state for aragonite after the alkalinity perturbation is quite important to assess the performance of OAE, since secondary mineral precipitation will increase the oceanic pCO_2 and reduce the CO_2 uptake. The authors need to explain more about the calculation method (for instance, the Ca and CO_3^{2-} concentration, aragonite dissolution equilibrium constant for the calculation) for results in Table 3, rather than simply give the reference (Line 249). This is particularly important when salinity is low, because a lot of omega calculation is focused on seawater (with a high salinity). At low salinity (close to river), the equation to calculate omega might not hold.

At the reviewer's suggestion, we added more descriptions for the omega aragonite calculations in the Table 3 caption:

*"**Table 3.** Theoretical aragonite saturation state (Ω_A) at the surface of the Amazon River-ocean continuum, calculated from the river-ocean mixing model (see Section 2.1 and Figure 2) for different TA perturbation strengths (ΔTA) at various salinities in September 2011 using constant water temperature of 29 °C, according to the equation $\Omega_A = [Ca^{2+}][CO_3^{2-}] / K_{sp}^{A(*)}$. $[Ca^{2+}]$ is calculated by adding the additional $[Ca^{2+}]$ due to TA perturbation (i.e., ΔTA/2) to the unperturbed $[Ca^{2+}]$; the latter term is comprised of relative contributions from both the river and ocean $[Ca^{2+}]$ endmembers at a specific salinity. $[Ca^{2+}]$ of 0.15 mmol kg^{-1} is used as the river endmember approximating results from Drake et al. (2021), and the global ocean average $[Ca^{2+}]$ of 10.28 mmol kg^{-1} is used as the ocean endmember. $[CO_3^{2-}]$ is derived from theoretical TA and DIC in the river-ocean endmember mixing model; the temperature- and salinity- dependent stoichiometric solubility product for aragonite, $K_{sp}^{A(*)}$, is calculated from Mucci (1983). The following equations in Mucci (1983) are involved in the determination of $K_{sp}^{A(*)}$ for each salinity: $\log K_{sp}^{A(*)} - \log K_{sp}^{A(0)} = (b_0 + b_1 SSTK + b_2/SSTK)\, S^{0.5} + c_0 S + d_0 S^{1.5}$ and $\log K_{sp}^{A(0)} = -171.945 - 0.077993 SSTK + 2903.293/SSTK + 71.595 \log SSTK$; SSTK is the sea surface temperature in Kelvin (i.e., SSTK = 302.15 K); b, c, and d are constants reported in Mucci (1983)."*

Because K_{sp} is temperature and salinity dependent, we calculated the K_{sp} at a constant temperature 29°C and at each representative salinity value, from which the Ω_A can be accurately calculated.

Below are my minor comments:

1a. Two time periods, Sep-2011 and July-2012, show distinct TA background (Figure 4a), empirical pCO_2 values (Figure 1), and responses to alkalinity perturbation (Figure 4 and 5). These are good and I suggest the author adds more description and explanation of the differences between these two time periods, which will offer more insights into the seasonal dynamics of the carbonate system and how this will affect the OAE effects.

Though the difference in carbonate chemistry at the river mouth is evident between July 2012 and September 2011, we have no definitive knowledge of what might have caused the observed heterogeneity (could be a combination of seasonal variations in river hydrology, community production, drainage basin composition, etc.). Each survey happened in a single day at 6 different locations/depths in the North Macapá gateway. The analysis suggests the need for dedicated pre- and post-alkalinity deployment surveys to characterize the *background mean and variability, a point we call attention to in the revised manuscript. We note at the end of Section 3.2.:*

"In an actual field OAE trial, each season (and gateway) may have different background variability that would require measurement and characterization in advance of any perturbation to design a clear strategy for sampling."

1b. Line 78 TA is tracked by the addition of extra Ca^{2+}, instead of using the carbonate species in Equation 1. Thus, I suggest changing the TA equation to the one that relies on the charge imbalance between major cations and anions.

We thank the reviewer for this suggestion, and have revised the TA expression using its charge balance definition:

"$TA = [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + \cdots - [Cl^-] - 2[SO_4^{2-}] - [Br^-] - \cdots$"

We also noted in the revised manuscript:

"We adopt the explicitly conservative form of TA here (Wolf-Gladrow et al., 2007) so that the addition of our hypothetical calcium-based alkalinity feedstock can be fully tracked by the increase in calcium ion concentration."

1c. Line 81 & 85 Ocean endmembers are not given explicitly in this manuscript, including the oceanic alkalinity and salinity.

The ocean endmember from Mu et al. (2021) has been added in the Methods section, i.e., $S = 36$, $TA = 2{,}369\ \mu mol\ kg^{-1}$, and $DIC = 2{,}025\ \mu mol\ kg^{-1}$.

1d. Line 94 The authors state "measurements were made in both the river and throughout the Amazon River plume". What kinds of measurements are made? In the later part of the same paragraph, the authors explain the TA and DIC measurement strategy for the Amazon River mouth. However, the measurements for the Amazon River plume are not explained clearly.

We revised the corresponding paragraph and added details for the plume survey. We noted at the end of Section 2.1.:

"...During the river plume/ocean expeditions, surface seawater pCO_2, temperature, salinity, and chlorophyll fluorescence were continuously measured shipboard across the Amazon-influenced regions; An oceanic station was specifically sampled for TA and DIC during each cruise as the ocean carbonate endmember (Mu et al., 2021)..."

1e. Line 115 The way to parameterize α (solubility of CO_2 in seawater) is not clearly explained.

Thank you for your keen eye. We added the following description to the CO_2 solubility and included the reference:

"... α is the solubility of CO_2 in seawater (a function of water temperature and salinity; calculated from equations in Weiss, 1974)..."

Citation: https://doi.org/10.5194/egusphere-2022-1505-RC1

Reviewer 2.

2.0. This review is for the preprint manuscript submitted to Biogeosciences entitled "Considerations for hypothetical carbon dioxide removal via alkalinity addition in the Amazon River watershed" by Mu, Palter, and Wang. The authors conduct a series of calculations to investigate the potential for alkalinity enhancement to enhance the CO2 flux in the Amazon River and its plume. Mixing relationships are recalculated using several values of an enhanced-alkalinity river end member, mixed conservatively into the open-ocean end member using salinity. The plume's potential for CO2 uptake is calculated using satellite-derived salinity retrievals for the months of interest. Considerations for real-world deployment and MRV are posed.

Overall, this was an interesting manuscript and provides the kind of scale analyses that the community will need to move forward on OAE deployments and their MRV. However, I do have some comments and questions about the calculations that could be addressed before full publication. In particular, I have concerns about the pCO2-Salinity relationships, their variability in space and time, and the applicability to the entire plume. Some considerations of additional carbonate system variables (e.g., pH, DIC) should also be considered for MRV and sensitivity. I hope my comments are helpful and constructive.

We thank the reviewer for his constructive review and we are happy to respond to every reviewer comment below.

Specific comments line-by-line below:

2.1. Line 7: I am curious why the authors choose to limit themselves so early to quicklime addition. Most (if not all) of the calculations are insensitive to the style of OAE; it could even be accomplished through electrochemical alkalinity production. The authors could keep the discussion of quicklime below, but reframe the article to be about general OAE rather than a specific method. Then, give the example of quicklime later on.

We agree that there is merit in generalizing the choice for alkalinity feedstock early in the manuscript before narrowing into a specific example. However, by choosing quicklime as our example relatively early, we can show the specific stoichiometry for the reaction, and also support the key assumption of relatively rapid and complete dissolution. In the revised manuscript, we added the following paragraph to the beginning of Section 2.3:

"The core of this sensitivity analysis is to manipulate the concentrations of TA at the river mouth by the addition of a hypothetical alkalinity feedstock. There are several feedstocks that could be considered for this purpose, each with a distinct set of considerations (Hartmann et al., 2013; Renforth and Henderson 2017). Magnesium or silicate-rich rocks such as olivine and other basalts (Hartmann et al., 2013), carbonate minerals (e.g., Rau, 2011; Renforth et al., 2022), mineral derivatives found in some industrial waste products, or even electrochemical production of alkalinity (Tyka et al., 2022; He and Tyka, 2023) are all candidates (NASEM, 2021). The stoichiometry of the reaction, dissolution rate, risk of secondary precipitation, and contamination with metals are all specific to the particular alkalinity source chosen. Quicklime (CaO) has been identified as being promising, due to its high solubility in sea water and rapid dissolution rates (Kheshgi, 1995; Bach et al., 2022). Quicklime is made by heating limestone (primarily $CaCO_3$), an abundant rock at the Earth's surface. The heating of each molecule of $CaCO_3$ releases one molecule of quicklime and one molecule of CO2 (Kheshgi, 1995). Therefore, carbon capture

and storage of the released CO_2 would be necessary for OAE to be effective from the application of quicklime (Paquay and Zeebe, 2013; Renforth et al., 2013; NASEM, 2021; Moras et al., 2022). Hereafter, we assume that the alkalinity feedstock for the hypothetical OAE deployment is quicklime, which simplifies the discussion of stoichiometry, precludes contamination from metals and other industrial contaminants, justifies our assumption of rapid dissolution, and informs our discussion of potential unintended consequences."

2.2. Line 12: It might be useful to mention the interesting conclusion here that most of the CO2 uptake happens at high salinity, because of the tradeoff between alkalinity enhancement and plume area during mixing with the open ocean.

This comment and comment 2.19 prompted us to look more closely at how much flux we might miss by excluding the very freshest plume area (SSS<15). Although this area is only < 15% of the total plume area, its lower buffer capacity also means pCO_2 is more sensitive to TA addition there, and therefore still could contribute a considerable amount to CDR. We have added more detail to this explanation in response to comment 2.19, and also mentioned this caveat throughout the paper.

For example, we added in the abstract:

"Adding 20 μmol kg^{-1} of alkalinity at the river mouth could elevate the total carbon uptake in the Amazon River plume ($15 < S < 35$) by at least 0.07−0.1 $MtCO_2$ $month^{-1}$, and a major portion of the uptake would occur in the saltiest region ($S > 32$) due to its large size, comprising approximately 80% of the $S > 15$ plume area. However, the lowest salinity region ($S < 15$) has a greater drop in surface ocean partial pressure of CO_2 (pCO_2^{sw}) due to its low buffer capacity, potentially allowing for observational detectability of pCO_2^{sw} reduction in this region. Reduced outgassing in this part of the plume, while more uncertain, may also be important for total additional CO_2 uptake."

2.3. Line 29: The Bach et al., 2019 reference seems out of place here. I suggest Renforth and Henderson, 2017 as it surveys a number of different OAE approaches including liminal ones (in rivers/along coasts). The Bach reference has to do with ecological impacts following OAE deployment in the ocean.

This suggestion is well taken, we have fixed the reference in this paragraph.

2.4. Line 51: Throughout the article, please check for consistency when referring to calcification (often shorthand for biological calcification) and secondary chemical precipitation. Again, the Bach paper refers to biological calcification feedbacks, whereas the Hartmann (and Moras) references investigate abiotic precipitation.

We made sure to be consistent with the terms; the reference is fixed.

2.5. Line 56a: I am wondering about this "thin layer" of surface salinity and what it means for total CO2 uptake by the plume. Does the total inventory of CO2 flux (in either mmol m-2 d-1 or in total Mt mo-1) depend on the assumption that salinity is constant in the mixed layer, and that the entire mixed layer is taking up CO2? I have seen these "thin layers" in the field and they can be quite thin!

The CO_2 flux density ($mmol/m^2/d$) and cumulative CO_2 flux ($MtCO_2$/month) both deal with the very surface ocean layer (in immediate contact with the atmosphere). When the surface layer is allowed sufficient time to fully equilibrate with the atmosphere (i.e., all the added TA *is 100% consumed to remove CO_2) - an underlying assumption in this manuscript - both flux density and cumulative flux should be unchanged and regardless of how water below surface may vary or how deep the layer goes.*

For the purpose of this manuscript, we assumed 100% equilibration efficiency and the air-sea equilibration still occurred at levels where pCO_2 changes were too dilute to measure (especially at higher salinities). How plume layer depth could affect the air-sea CO_2 exchange should require additional tools, such as a circulation model, to be fully understood.

2.6. Line 56b: I am not sure what you mean by "low-carbonate plume." Can you clarify?

Sure, we should add that the "low-carbonate" is relative to the open ocean, because the Amazon River generally has much lower DIC and TA levels (e.g., ~300-400 µmol/kg in Sep-2011 and July-2012) compared to the open ocean (> 2,000 µmol/kg), and therefore, the river plume with salinity < 35 has carbonate concentrations lower than the ocean endmember as a result of river-ocean mixing. We added a remark at where "carbonate-poor river waters" was first mentioned.

2.7. Line 67: Don't sell yourselves short -- this is not just a "thought experiment" but maybe a "sensitivity analysis"?

Thank you, we will take the compliment and make this change!

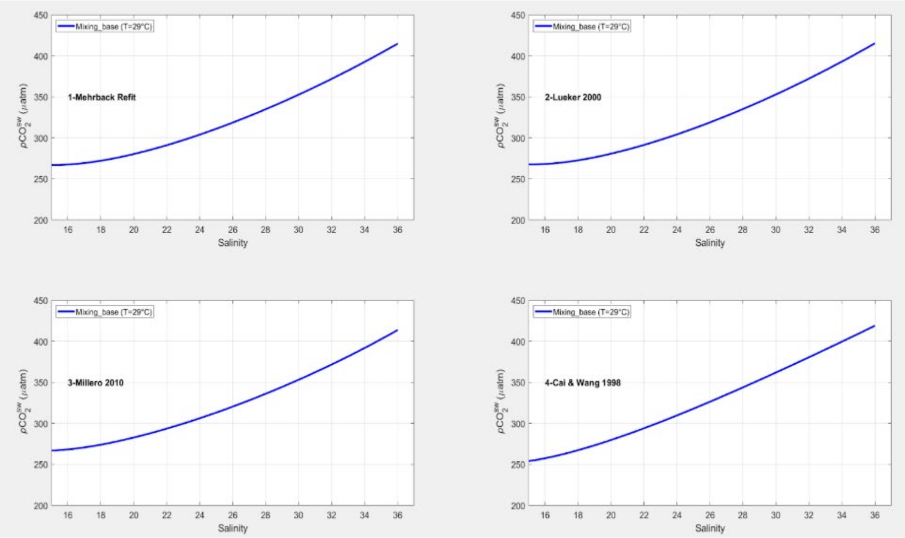
2.8. Line 85: Is the river end member actually zero? Or some small nonzero number? Also, is the calcium concentration in the river zero, or is it a small but nonzero number? This will matter for mixing saturation state values. If you are specifically targeting quicklime, it may also be useful to be explicit about the dissolution of quicklime and its impact on [Ca] (maybe negligible but potentially important at low salinity).

The river endmember has 0 salinity at the mouth, as measured by underway thermosalinograph during an ANACONDAS cruise (Mu et al., 2021). Calcium ion in the river is a small but nonzero number; we adopted [Ca^{2+}] measured by Drake et al. (2021; reference added in the revised manuscript) as the river [Ca^{2+}] endmember and added description on the omega saturation state calculation (Please see our response to Comment 1.4 for details). Regarding the concern of quicklime's impact on [Ca^{2+}], we noted in the caption of Table 3:

"... [Ca^{2+}] is calculated by adding the additional [Ca^{2+}] due to TA perturbation (i.e., ΔTA/2) to the unperturbed [Ca^{2+}]; the latter term is comprised of relative contributions from both the river and ocean [Ca^{2+}] endmembers for a specific salinity. [Ca^{2+}] of 0.15 mmol kg^{-1} is used as the river endmember approximating results from Drake et al. (2021), and the global ocean average [Ca^{2+}] of 10.28 mmol kg^{-1} is used as the ocean endmember. "

2.9. Line 92-93: I am not sure that these equilibrium constants are appropriate for low-salinity waters. As stated in the header material for CO2SYS, the Mehrbach Refit is valid for salinities between 20-40. I would try the Cai and Wang constants; try out a couple that are valid for low salinity and see how much that impacts your calculations. It might be quite a bit in the low-salinity range, given the large sensitivity of pKa2 to salinity.

Indeed, different choices of K1 and K2 will affect the baseline pCO_2 calculated from TA and DIC. We tried several different pairs of dissociation constants (namely, Cai and Wang 1998, Lueker et al. 2000, and Millero 2010) in CO2SYS and compared the pCO_2 results with the original (i.e., Mehrback refit by Dickson and Millero). We found negligible differences in the baseline pCO_2 (S > 15) calculated using any pairs of constants except when the Cai and Wang constants were used. See the difference in the September-2011 baseline mixing curve (solid blue line) below, especially at lower salinities.



It is unknown what might cause the Cai and Wang constants to stand out among all the choices. We eventually decide to use the Millero (2010) constants for the calculations because their eligible salinity range of 1-50 suffices our needs (to cover S > 15) and using them yields similar results as with a number of other pairs of constants.

2.10. Line 98: The discussion of gateways confused me. What is a gateway? What does it mean to "use one single gateway" with the mean and standard deviations of the TA values?

Reviewer 1 shared this concern at Comment 1.3., and we have clarified what a gateway is and justified using one representative gateway for OAE in the manuscript:

"Briefly, the Amazon River mouth region receives freshwater runoff from three channels: the north and south channels near Macapá, and the channel of the Tocantins River near Belém (Figure S2). Sampling was conducted at the lower reaches of the three channels near the mouth (or "gateways") in each month. Six TA and DIC samples were collected at three cross-channel locations of each gateway (left bank, center, and right bank) from both surface and 50% depth (5–10 m). For a concise demonstration on the detectability of the alkalinity addition in the river, we chose to target one gateway (North Macapá) as the perturbation site and consider how many samples would be needed to observe the TA perturbation relative to that gateway's background variability. However, to quantify the potential CDR induced by a TA perturbation just above detectability, we assumed the entire river mouth would be perturbed equally as in North Macapá. Because the outflow through both Macapá gateways comprise > 80% of total discharge (Ward et al., 2015; Mu et al., in revision) and their chemical properties are almost identical seasonally (Mu et al., in revision), North Macapá is representative of the mouth's chemical composition. In an actual

OAE field trial, perturbing one gateway will perturb the mouth region by an amount proportional to the percentage discharge (relative to the combined discharge), and the natural variability in the unperturbed gateways will affect the background variability at the mouth. There are key unknowns in seasonal TA contributions from other gateways to the mouth which prevents us from combining all the gateways. Therefore, the mean and standard deviation of the six TA values at North Macapá, respectively, were then used as the river TA endmember and its natural background variability (Table 1)"

2.11. Line 102: You mention calcification here, but also abiotic CaCO3 precipitation could be important.

We have added "abiotic dissolution/precipitation of calcium carbonate" as a TA/DIC controlling process.

2.12. Line 107-108: I assume that the ships have underway CTD systems as well as pCO2. How well does the satellite SSS correspond with the underway salinity in the ANACONDAS transects? Given that the Mu et al (2021) calibration is only valid for salinity 15-35 how valid is it to apply this calibration to lower salinities? See for example Fig. 6B in Mu et al., 2021...it appears that a lot of lower salinity data falls off the mixing trend, and does not even appear to match with the end member composition of the river. I am thus skeptical of extrapolating this mixing trend back to salinities below 15.

To address the first question: Yes, the ships had underway salinity measurements which we compared with satellite SSS in Mu et al. (2021). Unfortunately, the spatial and temporal resolution of the satellite SSS (8-day average, 0.04°lon x 0.04°lat) is not amenable to comparisons over the time and space scales of the ANACONDAS transects (crossing through the many strong gradients of the plume over ~30 days).

With respect to the second question: It is true that the pCO_2 vs SSS relationship in Mu et al. (2021) does not apply for SSS < 15, which is the reason why SSS < 15 is excluded in most of our calculations of OAE-induced pCO_2 and C uptake additionality (Figure 3 and 5). It is worth pointing out that the mixing curves are independent of the pCO_2 vs SSS relationship, meaning that the mixing curve is valid across the full salinity range (i.e., 0 < SSS < 36). But because empirical pCO_2 cannot be calculated below SSS = 15, there is no "empirical baseline" pCO_2 to complete the estimate of the post-OAE seawater pCO_2 decrease in this salinity range.

Prompted by this question, however, we did a back-of-the-envelope calculation and realized the low salinity part of the plume (SSS<15) cannot be ignored as it could contribute an equal (or higher) amount of additional OAE-induced CO_2 uptake by the 15 < SSS < 35 plume, despite being only <15% the size of the 15 < SSS < 35 portion. This is mostly due to the low buffer capacity in the fresher plume causing high pCO_2 sensitivity to TA changes. We added descriptions on this calculation and updated relevant conclusions throughout the manuscript. Please also see our response to Comment 2.19 for more details.

2.13. Line 125: One other important assumption in these calculations is that the alkalinity is homogeneously added to the river. If the addition is patchy, that adds another layer of variability that must be accounted for. Worth mentioning either here, or below.

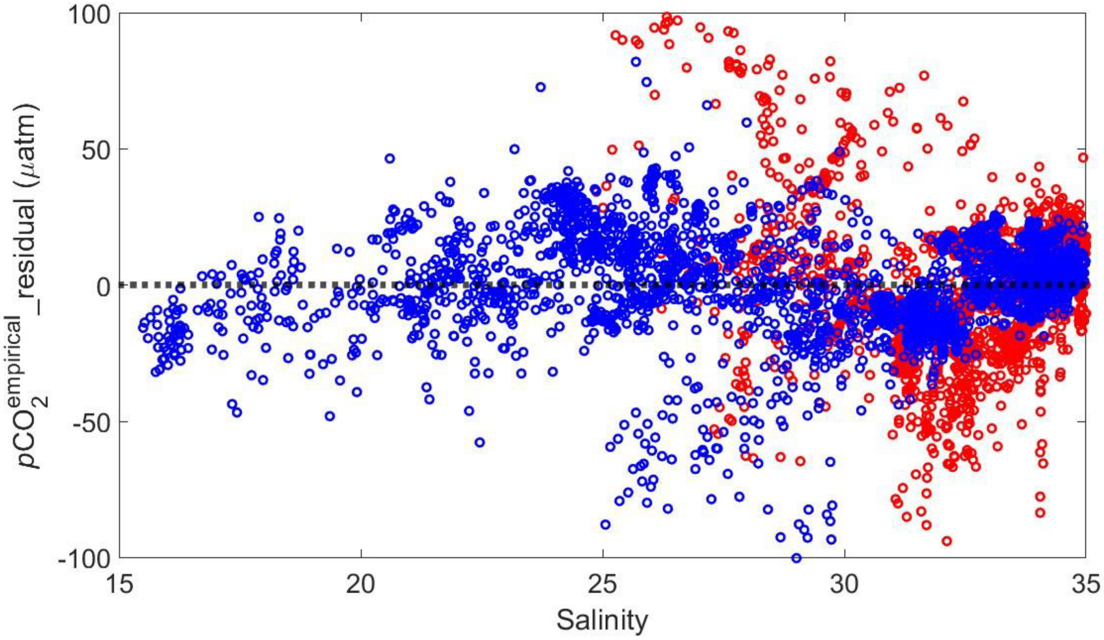
We added this statement in this paragraph:

"… Another underlying assumption is that CaO is homogeneously mixed across the river mouth gateway, eliminating potential uncertainty / variability due to patchiness of the TA addition … "

2.14. Line 150: Thinking out loud here, but is there a "sweet spot" at intermediate salinities where the variance is reduced compared to the river end member, giving a better chance of seeing a smaller perturbation?

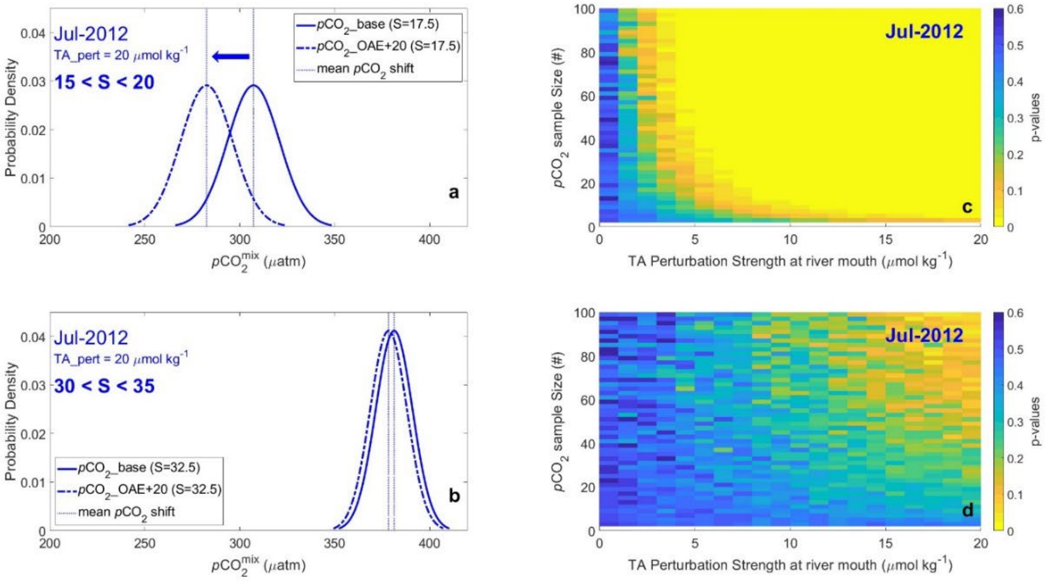
Great suggestion! This suggestion prompted us to investigate the natural pCO_2 variability in the plume via the difference between measured pCO_2 and empirical pCO_2 (the latter is predicted from measured pCO_2 VS salinity relationship).

Figure S7 below depicts this difference / residual in plume water pCO2. Specifically, this residual is the difference between the $pCO_2^{measured}$ versus SSS regression and the measured pCO_2 at a given salinity. Because empirical pCO_2 is directly calculated from the pCO_2 VS SSS regression, this residual also reflects the error on $pCO_2^{empirical}$. We could use the RMS error (RMSE) of this residual for $15 < S < 20$ from the July survey to explore the detectability, because it appears the RMSE is small enough in this part of the plume that could offer the best opportunity for the detectability "sweet spot" for the TA enhancement. In contrast, the RMSE is extremely large for $25 < SSS < 30$, and the pCO_2 perturbation very small above SSS = 30, neither of which are ideal conditions for achieving the detectability goal.



Added Figure S7. *The residual of empirical pCO_2 relative to the measured pCO_2 at the same salinity across the salinity spectrum of $15 < SSS < 35$ for September 2011 (red circle) and July 2012 (blue circle). Note that $pCO_2^{empirical}$_residual = $pCO_2^{empirical} - pCO_2^{measured}$ at $15 < SSS < 35$. $pCO_2^{empirical}$ is calculated from cruise-specific $pCO_2^{measured}$ versus SSS regression at a satellite-derived salinity (Mu et al., 2021).*

We calculated the RMSE for pCO_2 residual at $15 < S < 20$ for July and used it as the background pCO_2 variability. We also used S = 17.5 to represent the $15 < S < 20$ range and thereby simplify the calculation of perturbed TA. Finally, we investigated the minimum *detectability of pCO$_2$ in 15 < S < 20 plume water due to OAE in the river. The resultant "Figure 4-alike" plot (but using pCO$_2$ as the proxy instead) is shown below (Figure S8c).*



Added Figure S8. *Detectability of OAE-induced pCO$_2$ variation at different salinity ranges of the plume water. (**a**). The theoretical shift of plume pCO$_2$ (μatm) distributions at 15 < SSS < 20, as a result of a TA perturbation of 20 μmol kg^{-1} at the river mouth. Black lines indicate the baseline pCO$_2$ calculated from the river and ocean carbonate endmembers at SSS = 17.5 (following the mixing curve shown in Figure S3b). The standard deviation of the baseline pCO$_2$ distribution is calculated from the root-mean-square error of pCO$_2$ residual values for 15 < SSS < 20, described in Figure S7. The mean of the pCO$_2$ in the perturbation scenarios (dash-dot lines) are calculated from perturbed TA and DIC values that follow the dash-dot line in Figure S3b. (**a**). Similar to (a) but for the salinity range of 30 < SSS < 35. (**c**)(**d**). The p-value plots from t-tests simulated between baseline and perturbed pCO$_2$ in the plume, induced by TA perturbation scenarios at various sample sizes and perturbation strengths for 15 < SSS < 20 and 30 < SSS < 35, respectively, in July 2012. Areas in yellow (p < 0.1) indicate conditions where an analyst would conclude that the TA perturbation was detected through pCO$_2$ relative to its baseline condition with 90% certainty.*

The detectability of OAE-induced pCO_2 variations in the 15 < S < 20 part of the plume appears to be very promising, as even an 8 µmol kg^{-1} of TA perturbation can potentially be detected with under 10 measurements. In contrast, pCO_2 detectability in the 30 < S < 35 plume water is obviously less promising (figure S8d, lower panel), because the OAE-induced TA and pCO_2 changes are very small due to heavy diluting at high salinities. We have added this content in several places of the manuscript.

2.15. Line 174: Still not sure I understand what the gateway is referring to.

We addressed this in response to the Comment 1.3 and 2.10 above.

2.16. Line 181: State the variance of these measurements, as you do with the July measurements.

Fixed!

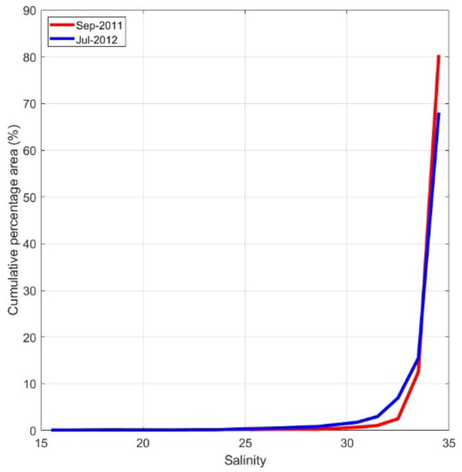
2.17. Line 183: I thought the samples are each from their own "gateway"? So, wouldn't this variance actually be inter-gateway variance, not variance at each gateway?

At the suggestions from both reviewers, we included more details on the gateway definition and sampling procedures at the river mouth (please see our responses to Comment 1.3. and 2.10.). In reality, three channels of river outflow converge at the lower reach of the Amazon and form the "mouth" region. But we decided to simplify the calculations involving the mouth for the following reasons: (1) There are key unknowns in seasonal TA contributions from other gateways to the mouth, preventing us from combining all the gateways in calculation. (2) Outflow through both Macapa stations contribute >80% of the total outflow when combined and have similar chemical conditions. Therefore, we treat the TA and DIC measurements at N. Macapa as if they are representative of the entire river mouth region (i.e., ignoring the carbonate contribution from the other two gateways).

If this was a real OAE implementation in the field, however, carbonate species at the mouth would be calculated by adding discharge-weighted concentrations from each gateway, and the variability / error / variance would also be discharge-weighted involving all three gateways.

2.18. Line 193: It might be nice to see a plot of plume area as a function of salinity, maybe as part of Figure 5, for each month.

The suggested figure is added below (and as a supplemental).



***Added Figure S4**. Cumulative percentage area (%) of the Amazon River plume across salinity bands within 15 < SSS < 35 for September 2011 (red) and July 2012 (blue). Note that the freshest part of the plume (SSS < 15) is excluded from the total area to compute the percentages. This figure is reproduced from Mu et al. (2021).*

2.19. Line 193 cont'd: Given the breakdown in the empirical relationship for SSS<15, I am wondering if you could somehow state how much this relationship matters at these low salinities, especially because most of the CO2 flux does indeed fall in the 15<S<35 range.

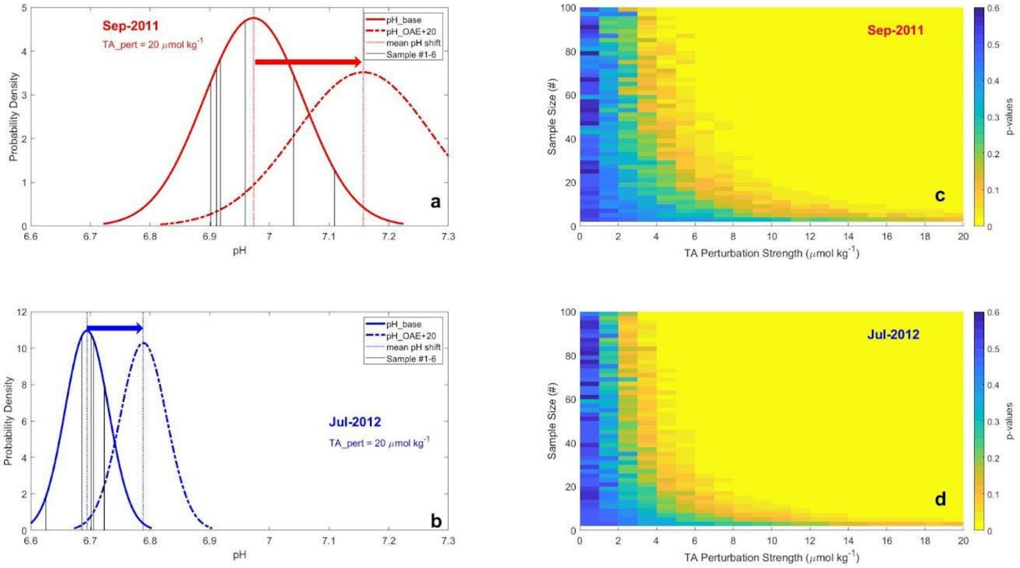
This comment really inspired us to explore this interesting part of the plume to the point we added a new sub-section around it to make our story more complete. Thank you!

Please see Section 4.1 in the manuscript on the CDR potential for the S < 15 part of the river plume.

2.20. Line 200: Obviously, TA detection is great because you're measuring the thing you added. But TA sensors aren't really commercialized yet and their precision/accuracy will likely be lower than laboratory measurements. You could do similar sensitivity calculations for pH and pCO2, which have commercial sensor options...given the large pH change you mention below, it may actually be much more sensitive to the perturbation than alkalinity, and give you a chance to see a clearer OAE signal in the river.

The point is well taken that pH or pCO_2 in the plume could be proxies for detecting minimum OAE signals due to their sensor readiness. We discussed the eligibility of pCO_2 in detail at Comment 2.14, and conducted a similar detectability test for pH presented below.

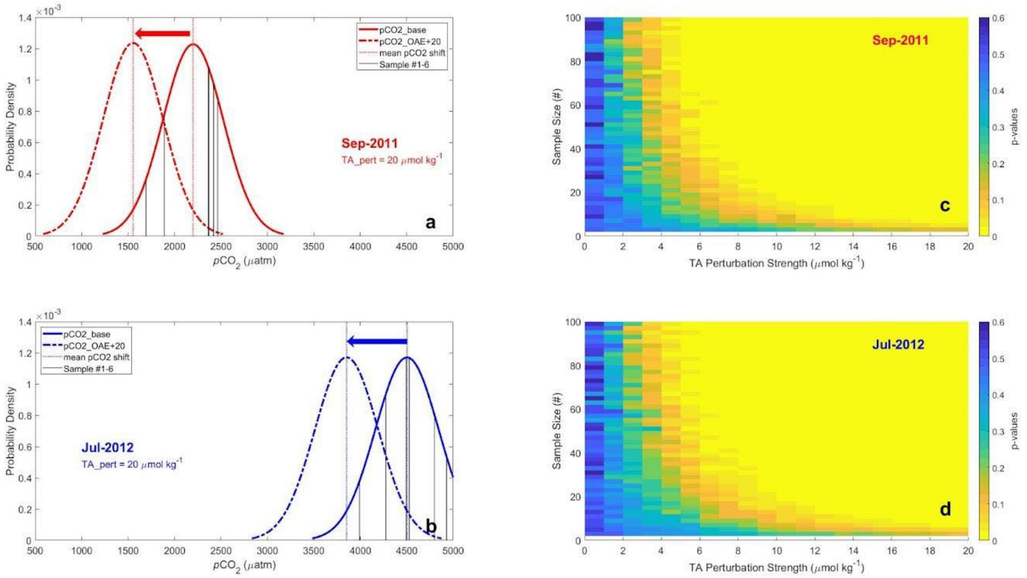
Following the sensitivity analysis with respect to TA, we also produced the p-value plots for pH (Figure S5, shown below). The main take-home message from the pH sensitivity analysis is that it is likely to detect a minimum pH change with weaker TA perturbation strength and fewer samples than those required by detecting a TA change. We added this finding in the manuscript.



Added Figure S5. *Detectability of OAE-induced pH variation relative to its background variability. (**a**)(**b**). The theoretical shift of pH (μmol kg^{-1}) means and distributions for September 2011 and July 2012 due to the addition of 20 μmol kg^{-1} of TA at the Amazon River mouth. Black lines indicate baseline pH calculated by baseline TA and DIC at the river mouth. The mean and standard deviations of pH in the perturbation scenarios (dash-dot lines) are calculated from perturbed TA and DIC values. (**c**)(**d**). The p-value plots from t-tests simulated between baseline and perturbed pH induced by TA perturbation scenarios at various sample sizes and TA perturbation strengths for September 2011 and July 2012. Areas in yellow ($p < 0.1$) indicate conditions where an analyst would conclude that the TA perturbation was detected relative to the baseline condition with 90% certainty.*

2.21. Line 213-215: Why not try to do the same calculation as Fig. 4 for pCO2?

In response to Comment 2.14, we've now explored the detectability of pCO_2 in the plume, and in response to 2.20, we showed the detectability of pH in the river. We have also added a similar plot for pCO_2 in the river to the Supplement (Figure S6, shown below). Making these plots does align with the reviewer's expectations that pH and pCO_2 could provide readily detectable proxies for the TA addition. The fact that commercial autonomous sensors are available to make these measurements would seem to give them an advantage in a detectability study. On the other hand, we retain the focus of detectability in the river on the TA, since this is the target of the hypothetical CDR deployment. The pCO_2 response to the TA addition in the plume is an excellent illustration of the surmountable challenge of detecting the relevant ocean response for CDR.



Added Figure S6. *Detectability of OAE-induced pCO$_2$ variation relative to its background variability. (**a**)(**b**). The theoretical shift of pCO$_2$ (µatm) means and distributions for September 2011 and July 2012 due to the addition of 20 µmol kg^{-1} of TA at the Amazon River mouth. Black lines indicate the baseline pCO$_2$ calculated by baseline TA and DIC at the river mouth. The mean and standard deviations of pCO$_2$ in the perturbation scenarios (dash-dot lines) are calculated from perturbed TA and DIC values. (**c**)(**d**). The p-value plots from t-tests simulated between baseline and perturbed pCO$_2$ induced by TA perturbation scenarios at various sample sizes and TA perturbation strengths for September 2011 and July 2012. Areas in yellow ($p < 0.1$) indicate conditions where an analyst would conclude that the TA perturbation was detected relative to the baseline condition with 90% certainty.*

One advantage of investigating pCO_2 in the space of minimum OAE detectability is that pCO_2 can be reliably measured in the river plume with good accuracy. We further explored pCO_2 detectability at the part of the plume of a selected salinity range. Please see our response to Comment 2.14 for specific details.

2.22. Line 221: You could also use limestone to make ikaite, which is soluble at ocean surface conditions: https://doi.org/10.1016/j.joule.2022.11.001. In general, this section is good, but it feels limiting to the paper to just focus on quicklime.

Suggested reference added in Section 2.3 of the manuscript. We addressed the general concern regarding alternative feedstocks specifically in our response to Comment 2.1.

2.23. Line 240: This is a very large pH signal! I'd be very interested to see a similar calculation as Fig. 4, for pH.

Yes, this is indeed a massive immediate change in pH upon adding 100 μmol kg^{-1} of alkalinity. The main reason is that river TA is so low that such level of TA perturbation changes TA by as much as > 30%.

We added minimum detectability p-value plots for pH in the supplemental material and descriptions in the Discussion. Please see our response to Comment 2.20 for details.

2.24. Line 271-275: The longer TA is left unequilibrated, the more time it has to be removed from the system as CaCO3, as well.

Table 3 shows that when TA perturbation strength ranges between 1 and 100 μmol kg-1, and resultant Ω_A is always below 5, an upper Ω_A limit for not causing $CaCO_3$ precipitation that we adopted from Moras et al. (2022). And at ΔTA = 20 μmol kg-1, the likelihood that runoff $CaCO_3$ occurs should be further lower than that at greater perturbation. Therefore, for the purpose of this study, we assume runaway $CaCO_3$ is negligible.

2.25. Line 282: Please consider also citing Subhas et al., 2022, that showed some minor but largely negligible effects of OAE in shipboard incubations over a large range of alkalinity perturbations. They also showed no measurable changes in biological CaCO3 precipitation over the incubation period.

Subhas, A. V., Marx, L., Reynolds, S., Flohr, A., Mawji, E. W., Brown, P. J., & Cael, B. B. (2022). Microbial ecosystem responses to alkalinity enhancement in the North Atlantic Subtropical Gyre. Frontiers in Climate, 4, 784997. doi: 10.3389/fclim.2022.784997

We thank the reviewer for suggesting this critical evidence that further supports our hypothesis - OAE causes no detectable changes to the biological CO_2 drawdown. We have added this reference at the end of this paragraph:

"... Another microcosm incubation study reveals the alkalinity enhancement inducing minor but largely negligible short-term effects on primary productivity and no measurable changes in biological $CaCO_3$ precipitation, even at TA perturbation levels of +2000 μmol kg-1 (Subhas et al., 2022)..."

2.26. Line 292: You haven't proposed anymore, you have done it! Consider rewording to " We conducted a sensitivity analysis of alkalinity enhancement..."

Thank you! We gladly replaced “thought experiment” with “sensitivity analysis” throughout the manuscript.

Citation: https://doi.org/10.5194/egusphere-2022-1505-RC2