Reply to comments on EGUSPHERE-2025-381

RC2: 'Comment on egusphere-2025-381', Anonymous Referee #2, 25th June 2025
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This study investigates the mechanisms that control runaway calcium carbonate ($CaCO_3$) precipitation during ocean alkalinity enhancement (OAE). The researchers use previously published data to construct a process-based model for estimating total alkalinity (TA) losses due to runaway precipitation. The manuscript is well presented and makes significant contributions to our understanding of runaway calcium carbonate precipitation during OAE deployments.

General comments

The manuscript largely builds upon previously published data from Hartmann et al. (2023) and Suitner et al. (2024). This manuscript does build upon the earlier work; however, the authors frequently direct the reader to these articles throughout the manuscript. In several instances I believe it would be beneficial to simply provide the information within this manuscript rather than directing the reader to another article, while in other circumstances I do not feel it necessary to continuously cite these articles. Lines 160-161 direct the reader to the supplementary information of Suitner et al. (2024) while this information if important should be included in this manuscript or its supplementary information. Also, lines 252-259 cite the articles 5 times, in particular line 253 refers the reader to Suitner et al. (2024) for images of the aragonite precipitates which are also depicted in the current manuscript in figure 8.

To my knowledge increases in total alkalinity of 1600 – 2800 µmol/kg above current levels is not realistic in real world settings. The authors state themselves that the standard experimental setup (which used relatively high delta TA values) did not provide enough precipitates. This raises questions about the applicability of such extreme perturbation studies to real-world scenarios.

Understanding such processes are undoubtedly important, however their relevance to actual OAE seems somewhat limited. I would welcome further discussion around this point expanding upon section 4.5.

Additionally, the authors utilise mesocosm and small-scale bottle experiments, while the limitations of such experiments are well understood a short discussion of the limitations of such datasets would be beneficial.

We thank the reviewer for the timely and valuable comments. These insights have greatly contributed to improve this work, particularly regarding particle surface and sinking characteristics, and has helped us to better reflect the model considerations provided. Below, we provide a point-by-point response to each of your comments.

As requested, references to Hartmann et al. (2023) and Suitner et al. (2024) will be reduced, with essential information from these works incorporated directly into this manuscript.

We would like to clarify that no new experiments were conducted for this study, except for a small-scale precipitation setup used to generate sufficient precipitate material for BET surface area measurements. Additionally, sinking velocity measurements using the precipitates from the campaigns in Bergen and Gran Canaria were published in this work.

The main focus of this work was to compile published data to develop an alkalinity loss model, which is controlled by two parameters, the $\Omega_{aragonite}$ and the surface area of abundant particles, represented by precipitates formed during the experiment. The main experiment was conducted in 2022, and at that time, little was known about the full parameter space within which alkalinity is stable. The same applies to the time period or speed of a runaway precipitation process once critical values have been surpassed. To our knowledge, a comprehensive description of such a parameter space for stable

alkalinity enhancement, post-treatment time spans to trigger runaway processes, and rates of TA-loss have never been presented in such detail.
It is probable that if OAE were deployed, the target alkalinity levels in the regional or local water body as a whole would be lower than the high values used in this work. However, we would like to point out that at the release points of alkalinity, in whatever form chosen, TA is likely to be enhanced above the actual target level. For example, when particles are used for alkalinization, it is very likely that carbonate particles precipitate (see Moras et al., 2022, Hartmann et al., 2023). As shown in this work, the amount of added alkalinity and surface area influence the initiation of the runaway processes and the related TA loss rate. In addition, to calibrate the alkalinity loss model based on $\Omega_{aragonite}$ and the abundant surface area from particles, it is necessary to consider extreme cases to achieve accurate calibration results. Specifically, the high alkalinity levels used in this study were useful to understand the shape and continuous evolution of the loss function, as well as identifying which functional terms should be used. To clarify the reasoning behind the chosen level of perturbation, additional information will be provided in the manuscript.
There is indeed considerable debate within the scientific community about the relevance of studies that test very high levels of alkalinity. However, we argue that exploring the full range of possible parameter spaces is necessary for optimal best practice predictions of potential TA loss processes. Waste water management facilities, for example, often release highly alkalized waters regularly, in a range of 4000-6000 µmol kg^{-1}. Therefore, the chosen ΔTA are not unrealistic for the near field space around the injection site. The complementing additional BET- and FlowCam measurements were needed to provide the necessary input to calibrate the empirical rate equation and the sinking velocity.

In contrast to the discussion surrounding omega and precipitation under high alkalinity values I feel the manuscript could discuss the influence of suspended particles further. This factor appears to be much more likely to result in runaway precipitation than the intentional increase in omega aragonite above 20, particularly as researchers and companies look to rivers to transport alkalinity to the ocean.

Following the reviewer's suggestion, we will discuss this further in the new version of the paper by addressing these points. Specifically, we will describe more clearly the importance of surface area as a controlling factor in precipitation events. That is also one of the reasons why we have been conducting the additional BET surface area measurement and the size and shape description of hundreds of precipitated particles. We are aware of the discussion around river alkalinity enhancement. Just recently, we published a work focusing on the TA-loss after river alkalinity enhancement (see Tian et al., 2025, ERL), addressing these points.

Specific comments

Comment 1

Figure 4. This is an extremely busy figure, and I would recommend removing some of the text from within the actual figure and placing it outside. For example, the APP explanation, breaks up the plot to a point where it seems as if there are two distinct plots. A distinct legend would likely be beneficial, and I recommend the authors consider this as well as simplifying/removing some of the text within the plot.

The APP explanation and legend will be placed outside of the diagram space to simplify the visual impression.

It is unclear as to why the triangles for the TA1200 treatment are hollow and smaller in comparison to the other two treatment levels utilise filled triangles.

The triangles will be standardized for consistency. Hollow markers were chosen to enhance readability when overlapping. Thank you very much for pointing out this issue.

The secondary x axis is difficult to interpret as it appears to show start and end deltaTA values for CO2 equilibrated but only start values for the unfiltered and end values for filtered non-co2 equilibrated measurements. Proper axis labelling here would be beneficial or removal of this secondary x axis.

ΔTA 1200 and 1400 in the non-CO_2-equilibrated and ΔTA 4400 in the CO_2-equilibrated approaches are only thematized in this diagram. The purpose of these additional markers was to provide a simple visual orientation to clarify the added alkalinity compared to the baseline. We would like to keep this information, as some readers may find it beneficial for orientation.

Comment 2

Both figures 4 and 5 depict TA on the x axis and time on the y axis, however all other figures in the manuscript appear to utilise the opposite axis labelling. This is confusing. I strongly recommend the authors use consistent labelling of the axis throughout the manuscript.

The diagrams follow the rationale of plotting the variable on the x-axis and the output value on the y-axis. We acknowledge that using time as an output could be misleading. Normally, the depending variable of a functional relationship is plotted on the y-axis. The intention was to depict the induction time (Fig. 4 and Tab. 2) and the APP timespan (Fig. 5) in dependence on the initial TA level, meaning e.g., that induction time = f(TA)). Therefore, we would like to recommend maintaining the current version.

Comment 3

Lines 222 – 224. Suggest that the initiation of APP may be estimated via initial TA or omega aragonite values. However, figure 6 illustrates this to also be dependent on the approach and assumingly particle density. I appreciate this is highlighted in the figure caption but believe this should be explicitly stated in the text.

We will add the information that APP is also a function of surface area into the main text in section 3.4: "[…] these functions could therefore assess the initiation of the APP for specific initial TA or $\Omega_{aragonite}$ levels based on a given starting particle surface area […]".

Comment 4

Line 299: Might help prevent

It will be corrected, thanks a lot for noticing.

Comment 5

Line 390: it is unclear what cf. stands for and no black triangles are present in fig 3c

"cf." is used as an abbreviation for "compare" to refer to a reference or figure throughout the text. In this case, the reference "(cf. Fig. 3)" is ambiguous. The referred black triangles can be found in Fig. 9. "(cf. Fig. 3)" will be changed to "(also see Fig. 3)".

Comment 6

Line 389: description of the line/fits in figure 9 throughout this section are change wording from "graph" to "line/fit" throughout.

Wording will be standardized.

Comment 7

I appreciate section 4.5 and the discussion surrounding the context of this experiment in a real-world setting. However, lines 427 – 429 state "Nevertheless, since these projected APP induction times are also within the suggested residence times of treated water in the upper ocean layers, it is necessary to conduct studies lasting at least for the projected timespans, depending on the local environmental conditions". I question whether a perturbed water parcel would remain in its perturbed state given the physical processes occurring in the surface ocean. Irrespective of its residence time, if the water parcel becomes diluted the omega values which the authors state as a for determining precipitation would be significantly lower rendering any further precipitation highly unlikely.

We thank the reviewer for this comment. We agree that for a single point source in an average open ocean setting, a persistent runaway process might be unlikely. However, so far, it is unclear how and where alkalinity addition would take place in practice. Large-scale arrays could potentially be employed to scale up OAE to an industrial level and it would be possible that inappropriate treatment could result in an initial seeding with small-sized precipitates. Assuming these particles are not dragged down by physical processes, they would lower the precipitation threshold to around $\Omega_{aragonite}$ 5 in the near-field, thereby reducing the overall efficiency. Similar patterns may also apply in coastal regions, bays, and lagoons, as well as in slurries or stock solutions that utilize seawater as a feedstock for alkalinization.
Further discussions on the consequence of particles and surface area removal is provided in the responses to Comment 9 and 10. The goal of this work is to provide a tool for estimating TA loss through a process-based formulation, employing established methods from aquatic geochemistry, and to assess its plausibility. Following the analysis of patterns in this study, which identified $\Omega_{aragonite}$ and surface area as the main drivers of potential carbonate precipitation, the next step to develop a more comprehensive model would involve assessing TA loss in relation to particle abundance, whether from natural background suspension loads or introduced solid phases for alkalinity enhancement. The presented functions are independent of initial conditions and suitable for application to scenarios where manipulated water is mixed with untreated water, enabling their implementation in future model considerations.
Finally, we agree with Referee #2´s comments and suggest that local test sites should be chosen in an open-world setting to further explore and understand related processes and whether the identified functions described in this work are actually applicable.

Comment 8

I question the use of stokes law which as stated by the authors is used for solid spherical particles. Given the SEM images provided by the authors the particles appear to have significant cavities likely increasing the SA/V ratio and thus significantly influencing the sinking velocity. It is also unclear whether measured or calculated sinking velocities are used.

We thank the reviewer for this comment. To calculate and standardize the sinking velocities, the common practice of equivalent spherical diameters (ESD) is used, following the methods described in (Bach et al., 2012), also used for the FlowCam measurements in this work. As stated in the text, such simplification might come with certain difficulties: "However, most particles are not spherical and contain numerous cavities within their structure, which likely contributes to an underestimation of particle densities." (L276-278) [Reworked as a request of Referee #1 to: "However, most particles are non-spherical and contain numerous internal cavities within their structure (see Fig. S1), and their densities are therefore expected to be lower than those of pure aragonite"], but we believe that it allows a practical way to operate within reasonable accuracy. Taking into account the characteristics of every single shape or even just categories of shapes would result in a level of complexity which is out of the scope of this work. Nevertheless, considering the cylindrical or dumbbell shaped particles with rough uneven surfaces with irregular cavities would potentially yield values closer to reality.
The sinking velocity measurements were used to determine the density of the precipitates. The outcome (~2.358 g/cm^3) was then used to calculate the sinking velocities for particles following the ESD practice.

Comment 9

I question the relevance of using 10 m as the upper water layer given mixed layer depths often range from 10 – 100m. Understandably it is important that the perturbed water remains in contact with the overlying atmosphere for CO2 uptake to occur. However, if one is to consider the removal of particles from a system, they must consider it in the context of the MLD. Any particle flux above the MLD at the current point in time is not equivalent to the removal of the particle from the discussed water layer as it is entirely possible that the particle may re-enter the 10 m layer due to various mixing processes.

Thank you very much. We would like to clarify that it was not stated that a mixed layer depth of 10 m was assumed. Indeed, 10 m was used as an estimate for the thickness of an alkalized plume. The mixed layer depth was set to: "[…] mixed layer depth (assumed to be 200m), […]" (Caption Fig. 8, L292). In addition, the sinking/growth model presented in this study, is a first-order model estimate; and detailed sinking and/or fluid dynamics are not in focus of this work. Future model assumptions should be refined if such processes are relevant to determine the efficiency of an OAE application scenario.

Further to this I question if the authors considered two important aspects of particle fluxes 1) attenuation with depth and 2) variable mixed layer depth and reinjection of particles into the surface layer. Understandably the particles described here are abiotic but a comment on the potential attenuation of these particles would be appreciated.

These are important points to address in future work, given the complexity modelers already face when predicting the distribution of alkalinity alone. Future collaboration with modelers is anticipated in order to better constrain the particle fluxes and their distribution within the water column over time. We acknowledge that accurately capturing particle reactivity as growth seeds, along with the depth-dependent evolution of particle size distribution, growth during sinking, and varying saturation

levels, represents a considerable modeling challenge. Given the length and complexity of this work, we would recommend to wait for further adapted sinking and particle redistribution models, which might be coupled with the here presented TA-loss model in the future.
The discussion on this topic can be found from line 440 to 447: "Particles larger than 15 µm are expected to sink within one day under the environmental conditions of the Raunefjorden. If those particles were removed by sinking while they were still growing, it can be estimated that approximately 30- 40% of the available surface area would be removed from the upper 10 m of the water column within one day (also see SI). This would decrease the precipitation rate accordingly as surface area and formation rates are linearly proportional. Potential aggregation would increase the sinking speed and was not considered in this model calculation, but may be relevant in other settings. In general, the abundance and sinking of particles need to be addressed if the stability or loss is to be assessed with a high level of confidence."

Following this, have the authors considered reinjection of the particles via mixing processes? Although unlikely for the fast-sinking fraction I question if this may enable a delayed CO2 uptake or alter the OAE efficiency.

Aragonite particles formed in the water column typically do not dissolve in standard seawater, with the possible exception of specific anoxic conditions. Therefore, the resurfacing of the particles will not lead to a larger CO_2-uptake of seawater, as they would not increase the CO_2-uptake potential. However, if particles sink below the carbonate compensation depth and dissolve, they may contribute to additional "redissolved" CO_2 uptake potential in the water. Since deep water is often supersaturated with respect to CO_2, we assume that the outgassing potential of upwelling deep water might actually decrease. However, the modeling and evaluation of such processes are beyond the scope of this study, and we refer to published and ongoing research by Earth system modelers addressing these specific questions.

Comment 10

I appreciate the authors thoughts surrounding the transport of particles and their subsequent effect on runaway precipitation. However, given the context of this study I believe an estimation of the effect of particle export on OAE efficiency would be beneficial. Especially considering that the sinking velocities and abundance of particles have been calculated. I also again query how the authors differentiate between small particles capable of staying in the upper layer for months and those which sink "while still growing". Could it be more realistic to assume that most particles continue to grow until they aggregate or reach a sinking threshold? And if so, how would this translate to OAE efficiency? Particularly given that the removal of growing or fully grown particles would likely begin to dissolve as they descend the vertical water column and have differing impacts on the alkalinity export.

In the main text, we provide a first-order estimation for a simple scenario to assess whether the sinking process is relevant, and also question ourselves on how to better represent these processes. We reached out to modelers in Canada, the UK, and Germany to explore the most robust way to represent this. The experts estimate that developing a model capable of reproducing the features mentioned by Referee #2 would take years. We consider these points to be relevant and suggest waiting until the processes can be modeled in more detail.
In the presented first-order model, all particles are considered to grow over time. Aggregation is not considered in the calculation: "Potential aggregation would increase the sinking speed and was not considered in this model […]" (L445).

Comment 11

Supplementary figure S1 could benefit from some slight adjustments so that the brightness of each image is similar. S1.B is very dark making it difficult to see any important details such as the branching shown in figure S1 A and B.

We will adjust the brightness of each image in Fig. S1.

Comment 14

Image quality of the supplementary figures S2, S3, S7, S8, S9 and S10 is poor and should be improved prior to publication.

Yes, we agree, and vector graphics have already been provided to the journal.

Comment 15

Figure S8 describes plots as the interplay between omega aragonite and surface area of particles. However, I would argue that it is the omega aragonite controlling the size of the precipitated particles and thus surface area.

As the $\Omega_{aragonite}$ evolution is predominantly driven by the $[CO_3^{2-}]$ concentration, it is mainly dependent on the TA and pH evolution and their effect on the carbonate system. The same accounts for the mass and therefore the surface area of precipitated particles. So, both parameters are related and their evolution roots from the same process.

Comment 16

Figure S10. I appreciate the lengthy explanation by the authors here however they fail to link such particle transformations back to the primary purpose of OAE, namely CDR. It is important to understand how such particle transport mechanisms would act upon the overall efficiency of the OAE deployment not just the particle surface area. To expand, an export of particles due to caco3 precipitation is still a loss of alkalinity and thus a reduction in efficiency. What would be interesting is to understand at what point this reduction in efficiency is beneficial if at all? Is there a point at which such extreme perturbations would be beneficial over smaller or medium sized perturbations. Otherwise, such a discussion may have limited relevance unless connected directly to implications for CDR efficiency.

We agree that an assessment of the effect of particle generation and sinking on the overall efficiency would be of relevance. The first order and 1-D character of the presented sinking model might unfortunately, not be an appropriate approach to realize this in a relevant manner. Since this is only a site calculation exploring whether this process could be relevant, we believe it is appropriate to argue that further studies with more complex models are studies on their own. This study wanted to evaluate whether a process-based model for TA-loss rates can be developed and validated. Further investigation and extension of the sinking/efficiency effects might be a bit out of focus for this work, but could be a topic for the future. Thank you very much for pointing it out.