

RC1: '[Comment on egusphere-2024-625](#)', Anonymous Referee #1, [reply](#)

The authors add hydrated lime to filter-sterilized seawater and track the changes in DOC concentration and optical parameters over a 24 hour period. The resulting conclusions provide a preliminary view into how dissolved organic carbon would change immediately following the addition of calcium hydroxide to seawater, work that is relevant for attempts to sequester carbon from the atmosphere. The conclusions from this work are limited, but could be a valid first step towards understanding this portion of the impact of liming on DOC.

We are grateful to the referee for her/his appreciation of our work. We are aware that the conclusions from this work are limited, but we strongly believe that this paper can bring new insights into the impact of ocean liming on DOM dynamics, and we believe that in this moment it is important to stress the need of further studies on this aspect. In the attached file you can find a point by point reply to all the issues raised by the referee.

The abstract discusses 'more pronounced effects', but the manuscript appears to have no statistical tests applied to support the conclusions presented by the authors.

All the differences, discussed in the paper, are supported by Kruskal–Wallis nonparametric test, as reported in the material and methods: *“For all parameters, differences were tested using the Kruskal–Wallis nonparametric test and were considered significant at the threshold of  $p < 0.05$ . All statistical analyses were performed using OriginPro version 9 (OriginLab, USA).”* In the Baltic Sea, no significant change was observed 3 hours after  $\text{Ca}(\text{OH})_2$  addition in both treatments (pH 9 and 10) (Fig. 4). At the end of the experiment (22 h), DOC decreased by 27  $\mu\text{M}$  (7 %) at pH 10, whereas no significant change was observed at pH 9. In contrast, In the MedSea, despite the markedly lower DOC concentration ( $67 \pm 2 \mu\text{M}$ ). Three hours after  $\text{Ca}(\text{OH})_2$  addition, a 4  $\mu\text{M}$  (6%) DOC decrease was observed in both treatments (Fig. 1). A further decrease was observed in the supernatant of the unmixed sample 22 h after the addition, with DOC reaching  $59 \pm 0.2 \mu\text{M}$  (12% decrease) at pH 9 and  $56 \pm 1 \mu\text{M}$  (16% decrease) at pH 10. For these reasons, we wrote in the abstract: *“These effects, detectable at pH 9, become significant at pH 10 and are more pronounced in the Mediterranean than in the Baltic Sea.”*

I am confused a little about how pH was considered as a variable. I recognize that two different conditions were set up (pH = 9 and pH = 10). However, the CDOM/FDOM samples were then brought to neutral pH before analysis. Given that one key parameter under consideration is pH, I don't understand the justification to remove the impact of pH on the CDOM/FDOM measurement.

We thank the referee for this comment, since it highlights a problem, we had to deal with. Absorption and fluorescent measurements are affected by pH, so it makes no sense to compare spectra carried out in different pH conditions, for this reason, after an internal discussion, we decided to work at neutral pH. Changing the pH will not allow us to identify changes in CDOM and FDOM that are strictly dependent on pH, for optical properties of CDOM we will therefore only be able to study the impact of lime addition, not the impact of the consequent pH increase. However, as reported in the introduction: *“The aim of this study is to provide the first experimental evidence about the potential effects of hydrated lime addition on DOM dynamics in the oceans, by assessing changes in its concentration and optical properties (absorption and fluorescence).”* In the revised paper, we will modify the text accordingly.

The authors indicate that pH was measured, but the only pH data are presented for the initial conditions. Did the change in pH over the course of the incubation correspond to any of the changes in DOC/CDOM/FDOM? Given the importance of pH on the solubility of carbon in water this is an important parameter to consider over the time of the incubation.

The pH was indeed measured each time before subsampling as mentioned in the text. We apologize for not having clearly stated that it did not change during the 22h of the experiment. In the revised paper, we will change the text in the methods to clearly state that pH was stable Ca(OH)<sub>2</sub> addition and, in the supplementary material, we can add a summarizing table including pH data.

Abbreviating Mediterranean Sea and Baltic Sea seems unnecessary.

Ok, in the revised text we will avoid them.

Additional comments:

Line 33: ‘These effects...’

Ok, in the revised text we will correct it.

Line 52: ‘sharp increase in pH of about 1 unit, becoming lower than 0.2 units, 1400 – 1600 m far from the discharge site...’ this is somewhat awkward and not clear. Please reword this sentence.

The sentence can be reworked as follows: *“Caserini et al. (2021) simulated the pH dynamics within the wake of a sparging ship releasing Ca(OH)<sub>2</sub> with an initial particle radius of*

*45  $\mu\text{m}$  at a rate of  $10 \text{ kg s}^{-1}$ . The results of their modeling study suggest that in these conditions a temporary, sharp increase in pH of about 1 unit can be observed at the discharge site, and that the effect decreases moving far from the discharge site, becoming lower than 0.2 pH units at a distance of 1400 – 1600 m (0.8-0.9 miles)."*

Line 102: I would alter the order information is presented in this paragraph. The first sentence indicates the bottles were mixed, and then the exception is given. This would be clearer if you start by indicating first that supernatant was collected from each bottle, then the bottles were mixed, and then an additional sample was collected.

*In agreement with this comment, the sentence could be changed as follows: "The bottles were gently mixed before subsampling at 5', 30', 3 h. After 22 hours, carbonate sedimentation was clearly visible at the bottom of the bottles, samples of the supernatant were therefore collected before mixing for both DOC and CDOM/FDOM analyses, an additional sample was collected after gently mixing only for DOC analyses since CDOM/FDOM would be strongly affected by the suspended particles."*

Line 106: the methods section here indicates the particles were removed by filtration, but line 166 indicates no mixed samples were collected. Please clarify.

We apologize for the misunderstanding. Since the particles strongly affect spectroscopic analyses, the mixed samples after 22h were collected only for DOC concentration measurements. Indeed, the results for 22h mixed samples are reported for DOC only (see figure 1 and 4). As reported at the previous point, the text can be changed as follows: *"The bottles were gently mixed before subsampling at 5', 30', 3 h. Since, after 22 hours, carbonate sedimentation was clearly visible at the bottom of the bottles, samples of the supernatant were collected before mixing for both DOC and CDOM/FDOM analyses, and an additional sample was collected after gently mixing only for DOC analyses since CDOM/FDOM would be strongly affected by the suspended particles."*

Line 147: correct to Kruskal Wallis (only one L in Kruskal)

Ok, in the revised text we will correct it.

Line 178: correct to tryptophan

Ok, in the revised text we will correct it.

Line 272: Considering the rather low salinity of the Baltic Sea sample, the statements about the increased terrestrial DOM can be attributed to the fact that the sample was not a truly marine sample. Given the large salinity differences between the two samples, the conclusions about Mediterranean vs. Baltic might be a stretch as they could also be solely due to differences in salinity, as the authors elude to in this paragraph.

We agree with the referee that salinity can be one of the major factors affecting our results. However, given the complexity of the systems it seems difficult that salinity alone can explain the observed results. In the discussion, we highlighted the predominant effect of the salinity as follows: *“Even if the salinity, being markedly lower in the BalSea than in the MedSea, is probably the main driver of the lower precipitation of CaCO<sub>3</sub>, and consequently of the less pronounced effects on DOM dynamic, it cannot be excluded that [...]”* We therefore think that we gave enough emphasis to the predominant role of salinity and we did not elude this aspect in this paragraph.

Line 293: Extrapolating conclusions to the importance of seasons is a bit of a stretch here, two samples collected one month apart do not allow any sort inference about the relevance of season. There are many additional parameters that would be needed before details on OAE would be clear, seasonality is but one.

We thank the referee for this comment, we totally agree with. Indeed, in the conclusions we highlighted all the parameters we need to know before details on OAE can be clear. In agreement with this comment, in the revised text we can integrate the last sentence of this paragraph in the conclusions, pointing out that seasonality should be one factor to take into consideration, in addition to all the others.

Figure 4: are there replicates for all the samples? If yes, please note that the error bars are smaller than the symbol.

Yes, there are 3 replicated for each sample. In the revised version, we can add the sentence: *“ Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.”*, in the caption of figure 4.

Supplemental Table S1 – What is an ‘EU representative product’? Is the product specification the desired set of parameters or the actual set of parameters? What is UniCalce (2021)? It is not in the list of references provided.

We thank the referee for raising this point and we really apologize for the unclear definition. “*EU representative product*” means that the properties of the  $\text{Ca(OH)}_2$  used for the experiments are within the ranges that the EU defined for the  $\text{Ca(OH)}_2$  production. For clarity, in the revised paper, we can replace ‘EU representative product’ by “ $\text{Ca(OH)}_2$  properties” and modify the caption as follows: “*Properties of the high-purity calcium hydroxide used for the experiment. The product was provided by Unicalce (<https://www.unicalce.it/>).*”

Table S2 – tryptophan (no e at the end)

Ok, in the revised text we will correct it.