Ocean liming effects on dissolved organic matter dynamics

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Abstract. Ocean liming has gained attention as a potential solution to mitigate climate change by actively removing carbon dioxide (CO_2) from the atmosphere. The addition of hydrated lime ~~($Ca(OH)_2$)~~ into oceanic surface water leads to an increase in alkalinity, which in turn promotes the uptake and sequestration of atmospheric CO_2.

Despite the potential of this technique, its effects on the marine ecosystem are still far to be understood, and there is currently no information on the potential impacts on the concentration and quality of Dissolved Organic Matter (DOM), that is one of the largest, ~~-~~the most complex and yet the least understood mixture of organic molecules on Earth.

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).

~~The aim of this study is to provide the first experimental evidence about the potential effects of pH peaks, that might be generated by the $Ca(OH)_2$ dissolution in seawater, on DOM dynamics by assessing changes in its concentration and optical properties (absorption and fluorescence).~~

To investigate the effects of liming on DOM pools with different concentrations and quality, seawater was collected from two contrasting environments: the oligotrophic Mediterranean Sea ~~(MedSea)~~, known for its Dissolved Organic Carbon (DOC) concentration comparable to that observed in the oceans, and the eutrophic Baltic Sea ~~(BalSea)~~, characterized by high DOM concentration mostly of terrestrial origin. hydrated lime~~$Ca(OH)_2$~~ was added in both waters, to reach a pH of 9 and 10.

Our findings reveal that the addition of hydrated lime has a noticeable effect on DOM dynamics in both the Mediterranean Sea ~~MedSea~~ and Baltic Sea~~BalSea~~, determining a reduction in DOC concentration and a change in the optical properties (absorption and fluorescence) of DOM. These effects, detectable at pH 9, become significant at pH 10 and are more pronounced in the Mediterranean Sea ~~MedSea~~ than in the Baltic ~~BalSea~~Sea. These potential short-term effects should be considered within the context of the physico-chemical properties of seawater and the seasonal variability.

1 Introduction

Oceans are a natural sink for atmospheric CO_2 having the potential to mitigate its increase and therefore the effects of climate change (Gattuso et al., 2013; Heinze et al., 2015). The massive amount of atmospheric CO_2 absorbed by the oceans in the last decades (~ 30-40% of anthropogenic emissions), is generating dramatic global-scale changes in seawater chemistry, such as a decrease in pH, in carbonate concentration and in the ocean buffering capacity (Chikamoto et al., 2023). Even if the ongoing efforts toward a global reduction of anthropogenic CO_2 emissions should be rapidly intensified, the available projections highlight the need for additional strategies, such as the development of efficient ocean-based Negative Emission Technologies (NETs) (Calvin et al., 2023; Royal Society and Royal Academy of Engineering, 2018). Some NETs are not only capable of removing atmospheric CO_2 and store it as bicarbonate ions into the oceans, but also of increasing the water pH, restoring ocean buffering capacity to the pre-industrial era (Butenschön et al., 2021; Gore et al., 2019). One of these NETs is Ocean Alkalinity Enhancement (OAE) (also called Artificial Ocean Alkalinization, AOA), which relies on the dissolution of alkaline minerals such as hydrated lime (calcium hydroxide, $Ca(OH)_2$) into the oceans) (Kheshgi, 1995). Although the exact amount of hydrated lime to be released, as well as its sparging methods, is still under debate one of the proposals is to discharge highly concentrated slurry (*lime milk*) from large cargo ships, tankers and/or dedicated vessels. ~~(~~Caserini et al., (2021) simulated the pH dynamics within the ~~Modeling studies, simulating the flow dynamics in the~~ wake of a sparging ship ~~, indicate~~releasing ~~that the addition of~~ $Ca(OH)_2$ with an initial particle radius of 45 µm ~~into seawater~~at ~~-~~a rate of 10 kg s^{-1}. The results of their modeling study suggest that in these conditions ~~can cause~~ a temporary, sharp increase in pH of about 1 unit can be observed at the discharge site, and that the effects decrease moving far from the discharge site, becoming lower than ~~becoming lower than~~ 0.2 pH units at a distance of~~,~~ 1400 – 1600 m (0.8-0.9 nautical miles). ~~far from the discharge site (in the hypothesis of a discharge rate of 10 kg s^{-1},~~

The discharge of alkaline minerals may trigger the inorganic precipitation of calcium carbonate ($CaCO_3$), reducing the efficiency of the CO_2 sink and negatively affecting seawater transparency and photosynthetic rates (González and Ilyina, 2016), with possible consequences for the biogeochemical cycles and the functioning of the marine ecosystem (Camatti et al., 2024). The side effects of OAE techniques on the marine environment need to be thoroughly investigated before making any decision on their use. To the best of our knowledge, there is no information on the effects that ocean liming may have on Dissolved Organic Matter (DOM) and its chromophoric fraction (CDOM, i.e. the light-absorbing fraction and FDOM, i.e. its fluorescent fraction). Holding an amount of carbon of 660 billion metric tons and being the most concentrated dissolved component in the oceans (Hansell et al., 2009), every action that could modify seawater chemistry is expected to have an impact on this key component of the carbon cycle. DOM represents the main source of energy for heterotrophic prokaryotes, a change in its concentration and/or quality could therefore have a cascading effect on the functioning of marine ecosystem.

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 order to investigate the impact on DOM pool with different origin and optical properties, seawater was collected from two highly diverse environments; (1) the oligotrophic Mediterranean Sea ~~(MedSea)~~, characterized by Dissolved Organic Carbon (DOC) concentration comparable to those observed in the open oceans, and (2) the eutrophic Baltic Sea ~~(BalSea)~~, characterized by high DOC concentration, mostly of terrestrial origin.

2 Materials and methods

In order to investigate the effects of ocean liming on DOM dynamics, an ultra-pure $Ca(OH)_2$ powder was added to natural seawater and changes in DOC concentration, absorption and fluorescence of CDOM were followed for 24 hours at the laboratories of the Biophysics Institute, CNR (Pisa, Italy). Based on the results by Caserini et al. (2021) ~~Caserini et al., (2021)~~, which suggested a sharp increase of 1 unit of pH at the discharge site of a sparging ship, the experiment was carried out at pH 9. Although unlikely under actual conditions of dilution in the open sea, an additional experiment was carried out at pH 10 because this situation may occur in coastal waters (e.g. coastal lagoons, high primary productivity enhanced by eutrophication) (Hinga, 2002) ~~(Hinga, 2002). Based on the results of Caserini et al. (2021)Caserini et al. (2021)The experiments were carried out at pH 9 and 10, based on the results of , which assumes conservative values of lime milk ($Ca(OH)_2$ 86.5 g/l) discharge rates (≤ 25 kg/s) in the ships' wake.~~ $Ca(OH)_2$ was provided by UNICALCE (Sedrina (BG), Italy) and supplied as powder (Tab. S1). Seawater was collected at Marina di Pisa, Tyrrhenian Sea, Italy (Mediterranean Sea) and in the coastal area surrounding Riga, Latvia (Baltic Sea) (Tab. 1).

	Sampling Date	Salinity	pH	DOC (µM)	a_{254} (m^{-1})	$S_{275-295}$ (nm^{-1})
Mediterranean Sea	Mar-22	38	8.2	66 ± 0.5	1.9	0.024
Baltic Sea	Apr-22	6	8.1	364 ± 3	24.5	0.021

Table 1: Chemical and physical properties of the Mediterranean Sea and Baltic Sea water used for the experiment.

2.1 Experimental setup

In order to investigate the impact of slaked lime on chemical-physical processes affecting DOM dynamics, seawater was sterilized by filtration through a 0.2 µm pore size filter (Polycap AS36 filter capsule, Whatman, UK) using a peristaltic pump (Masterflex™ L/S™, Germany). Salinity was measured by using a HI 9033 portable probe (Hanna Instruments, USA). The experiments were carried out in 2 L acid-washed polycarbonate ®Nalgene bottles as follows:

1. **Mediterranean Sea**
   a. Treatment: filtered surface seawater enriched with $Ca(OH)_2$ powder to reach:
      - pH 9, $[Ca(OH)_2]$ 0.04 g/L
      - pH 10, $[Ca(OH)_2]$ 0.25 g/L
   b. Control: filtered surface seawater (pH = 8.2)
2. **Baltic Sea**
   a. Treatment: filtered surface seawater enriched with $Ca(OH)_2$ powder to reach
      - pH of 9, $[Ca(OH)_2]$ 0.01 g/L
      - pH 10, $[Ca(OH)_2]$ 0.06 g/L
   b. Control: filtered surface seawater (pH = 8.1)

All the experiments were carried out in triplicates and the bottles were stored in the dark and at room temperature (22 ± 1 °C). Immediately after the addition of the $Ca(OH)_2$ powder, the bottles were gently mixed. Before and after powder addition and before each sampling time, pH was measured using an edge HI2002-02 pH-meter (Hanna Instruments, USA). In the treatment at pH 9, the pH slightly decreased by 0.06 (Baltic Sea) and 0.29 (Mediterranean Sea) between 3 and 22 h after the addition (Tab. S2). In the treatment at pH 10, 3 hours after the addition the pH decreased by 0.3 in the Mediterranean Sea and after 22 hours it decreased by 0.45 in the Mediterranean Sea and 0.26 in the Baltic Sea (Tab. S2). Subsamples for DOC (40 mL) and CDOM/FDOM (60 mL) analyses were collected before $Ca(OH)_2$ addition and 5', 30', 3 h and 22 h after $Ca(OH)_2$ addition.

The bottles were gently mixed before subsampling at 5', 30', and 3 h. ~~Since, a~~After 22 hours, carbonate sedimentation was clearly visible at the bottom of the bottles~~, after 22 hours~~, ~~an additional~~one ~~sample~~s of the supernatant ~~was~~ were therefore collected before mixing for both DOC and CDOM/FDOM ~~and~~analyses, and an additional sample ~~was~~ collected after gently ~~mixning~~mixing only for DOC analys~~ies~~es, since CDOM/FDOM would have been ~~be~~ strongly affected by the scattering due to the suspended particles.

Samples for CDOM/FDOM analyses were brought to pH 7.5 ± 1.0 with high purity 2 M HCl, to avoid the effect of pH on DOM absorption and fluorescence and filtered through a PES 0.2 µm pore size syringe filter (Minisart 16534K, Sartorius, Germany), to avoid the scattering due to the presence of carbonate particles in solution.

2.2 DOC

Samples for DOC ~~analysis~~ analyses were acidified at pH 2 with high purity 2 M HCl. DOC measurements were carried out with a TOC-L analyzer (Shimadzu, Japan), by high temperature catalytic oxidation following Santinelli et al. (2015). Samples were sparged for 3 min with CO_2-free ultrahigh purity nitrogen to remove inorganic carbon. 150 µL of the sample were injected into the furnace after a three-fold rinsing with the sample to be analyzed. From 3 to 5 replicate injections were performed until the analytical error was lower than 1%. A four-point calibration curve was measured using a standard solution of potassium hydrogen phthalate in the same concentration range as the samples. The system blank was measured every day at the beginning and the end of the analyses using low-carbon water (2-3 µM C). The instrument performance was verified daily using the DOC Consensus Reference Material (CRM) (Hansell, 2005) (CRM Batch #20/08-20, nominal concentration of 42 ± 1 µM; measured concentration 40 ± 2 µM, ~~n of samples~~76 CRM samples analyzed~~= 76~~).

2.3 CDOM optical properties

2.3.1 Absorption

Absorption spectra were measured between 230 and 700 nm with a UV–Vis spectrophotometer (Mod-7850, Jasco, USA), using a 10 cm quartz cuvette. The absorption spectrum of Milli-Q water was subtracted from each sample spectrum. The absorption coefficient at 254 nm (a_{254}) and the spectral slope between 275 and 295 nm ($S_{275-295}$) were calculated from the absorption spectra using the ASFit tool (Omanović et al., 2019). a_{254} is used to have semi-quantitative information on CDOM, since primary CDOM absorption is caused by conjugated systems having the absorption peak near 254 nm (Del Vecchio and Blough, 2004; Weishaar et al., 2003). $S_{275-295}$ can be related to changes in the average aromaticity and

molecular weight of the molecules in the CDOM pool (Helms et al., 2008). The absorption coefficient at 280 nm and 325 nm (a_{280}, a_{325}) and the spectral slope ratio (Sr, ratio between $S_{275-295}$ and $S_{350-400}$) are also reported for comparison (Tab, S2), being among the most used CDOM indices in the literature.

2.3.2 Fluorescence

Fluorescence excitation-emission matrices (EEMs) were recorded with an Aqualog fluorometer (Horiba-Jobin Yvon, UK), using a 1 cm quartz cuvette. Excitation ranged between 250 and 450 nm at 5 nm increments; emission was recorded between 212 and 619 nm at 3 nm increments. The EEMs were ~~elaborated~~ processed using the TreatEEM software (Omanović et al., 2023). EEMs were corrected for instrumental bias in excitation and emission, and Rayleigh and Raman scatter peaks were removed using the monotone cubic interpolation (shape-preserving). EEMs were normalized to the water Raman signal, dividing the fluorescence by the integrated Raman band of Milli-Q water (λ_{ex} = 350 nm, λ_{em}= 371-428 nm; Lawaetz and Stedmon, 2009) measured on the same day of the analyses. The fluorescence intensity is therefore reported as equivalent to water Raman Units (R.U.).

Parallel factor analysis (PARAFAC) was separately applied to the Mediterranean Sea ~~(number of EEMs: 63)~~ and Baltic Sea ~~(number of EEMs: 50)~~ samples (number of EEMs: 45 for each experiment), using the decomposition routines of the EEMs toolbox for MATLAB software (drEEM) (Murphy et al., 2013). The PARAFAC validated a 3-component model for both the Mediterranean Sea and the Baltic Sea (Fig. S1 and S2). OpenFluor, an online database of environmental fluorescence spectra, was used as a validation tool to characterize the three components (Tab. ~~S2~~ S3 and ~~S3~~S4). OpenFluor compares excitation and emission spectra of the validated components with all the components present in the database and allows comparing the spectra using the Tucker Congruence Coefficient (TCC; Murphy et al. (2014)).

2.4 Statistical analyses

For all parameters, differences were tested using the Kruskal~~l~~–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).

3. Results

3.1 Mediterranean Sea

3.1.1 DOC

In the ~~MedSea~~Mediterranean Sea, ~~DOC concentration was 67 ± 2 µM.~~ ~~t~~Three hours after $Ca(OH)_2$ addition, a 4 µM (6%) DOC decrease was observed in both treatments (Fig. 1, Tab. S2). A further decrease was observed in the supernatant of the unmixed sample 22 h after the addition, with DOC reaching 59.5 ± 0.~~2~~ 1 µM (~~1~~29% decrease) at pH 9 and 56.3 ± 1.7 µM (1~~8~~6% decrease) at pH 10 (Tab. S2). It is noteworthy that such a decline was only observed in the unmixed samples, whereas no significant change was observed in the mixed samples 22 h after the addition (Fig. 1, ~~and~~ Tab. S2)~~).~~

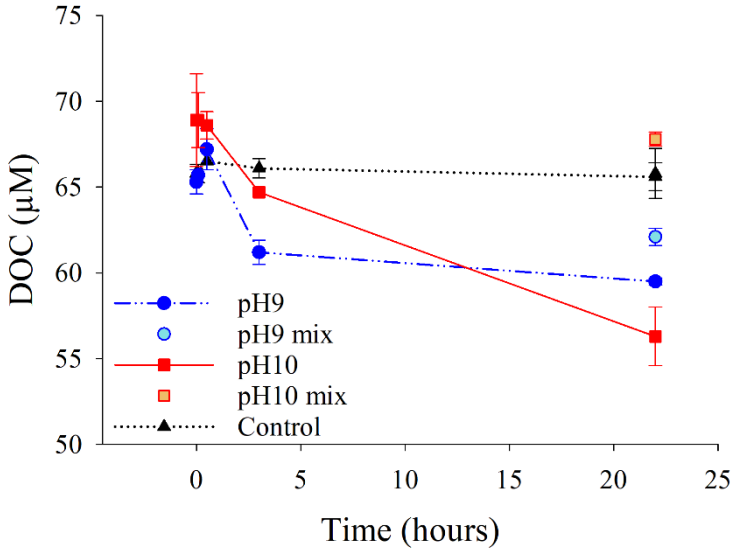

Figure 1: Trend of DOC concentration in the ~~MedSea~~Mediterranean Sea treatments at pH 9 and 10, and in the control. Error bars refer to the standard deviation among the 3 replicates. Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.

3.1.2 CDOM Absorption

A slight decrease in a_{254} was observed 3 hours after $Ca(OH)_2$ addition at both pH (9 and 10). Interestingly, 22 h after the addition, in the supernatant of unmixed bottles, a marked decrease of 0.2 m^{-1} (~~11~~10%) and 0.4 m^{-1}(~~20~~19%) was observed (Fig. 2a, Tab. S2) together with an increase in $S_{275–295}$ from 0.024~~71~~ nm^{-1} to 0.0256 nm^{-1} (~~64~~%) and from 0.0239 to 0.0264 nm^{-1} (10%) at pH 9 and 10, respectively (Fig. 2b, Tab. S2). Mixed samples were not collected for CDOM analyses, since scattering due to the particles would have affected the results.

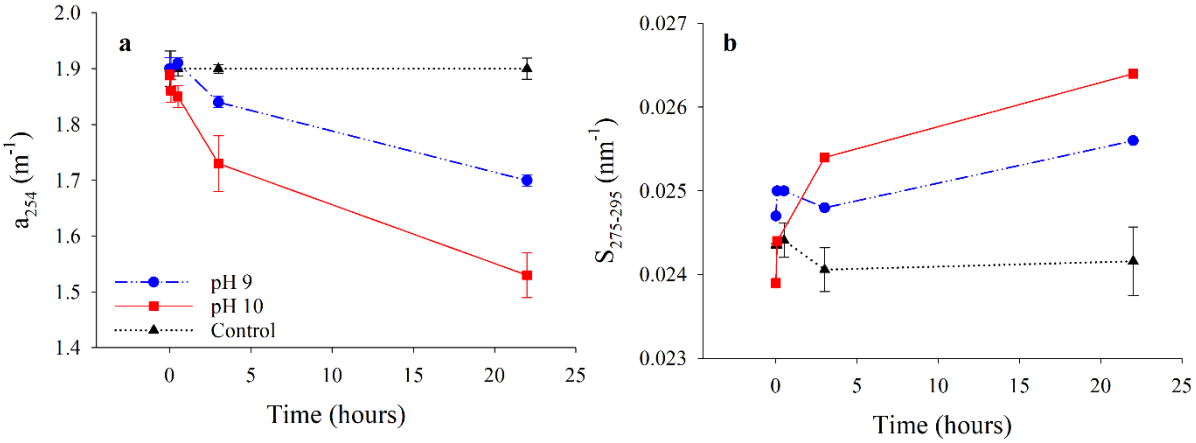

Figure 2: Trend of a_{254} (a) and $S_{275-295}$ (b) in the ~~MedSea~~Mediterranean Sea treatments at pH 9 and 10, and in the control. Error bars refer to the standard deviation among the 3 replicates. Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.

3.1.3 FDOM fluorescence

The PARAFAC validated a ~~3 component~~3-component model for the ~~MedSea~~Mediterranean Sea EEMs (Fig. S1, Tab. ~~S2~~S3). Component 1 ($\lambda_{Ex}/\lambda_{Em}$: 315/409 nm, Fig. S1a) shows spectroscopic characteristics similar to Coble's peak M ($\lambda_{Ex}/\lambda_{Em}$: 312 /[380]420; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as marine humic-like ($C1_{Mh\text{-}Med}$). Component 2 ($\lambda_{Ex}/\lambda_{Em}$: 275/331 nm, Fig. S1b) shows spectroscopic characteristics similar to Coble's peak T ($\lambda_{Ex}/\lambda_{Em}$: 275/340 nm; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as ~~T~~tryptophan~~e~~-like ($C2_{Trp\text{-}Med}$). Component 3 ($\lambda_{Ex}/\lambda_{Em}$: 260/[380]456 nm, Fig. S1c) shows spectroscopic characteristics similar to Coble's peaks C and A ($\lambda_{Ex}/\lambda_{Em}$: 350/451 and 245/451 nm, respectively; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as terrestrial humic-like ($C3_{Th\text{-}Med}$).

$C1_{Mh\text{-}Med}$ did not show significant changes over the incubation time at pH 9 and in the control (Fig. 3a, Tab. S5). At pH 10, a decrease of 0.004 R.U. (20~~19~~%) was observed 22 h after the addition. $C2_{Trp\text{-}Med}$ did not show significant changes during the incubation, neither in the treatments nor in the control (Fig. 3b, Tab. S5). $C3_{Th\text{-}Med}$ showed variations only at pH 10 (Fig. 3c, Tab. S5), with a slight decrease 3 hours after the addition, and a significant decrease of 0.006 R.U. (26%) at the end of the incubation (22 h).

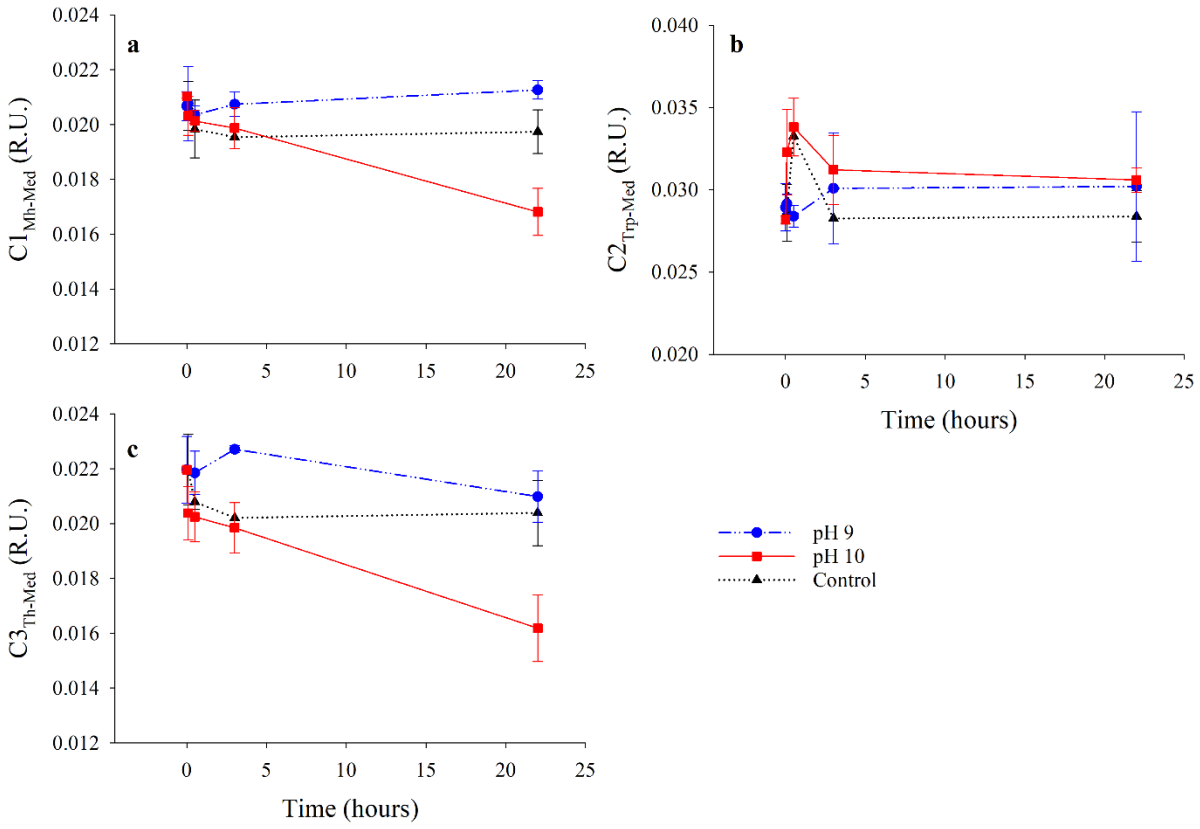

Figure 3: Trend of the fluorescent intensity of C1$_{Mh\text{-}Med}$ (a), C2$_{Trp\text{-}Med}$ (b) and C3$_{Th\text{-}Med}$ (c) in the ~~MedSea~~Mediterranean Sea treatments at pH 9 and 10, and in the control. Error bars refer to the standard deviation among the 3 replicates.

3.2 Baltic Sea ~~(BalSea)~~

3.2.1 DOC

In the Baltic Sea~~, DOC concentration was 362 ± 3 µM. N~~ no significant change was observed 3 hours after $Ca(OH)_2$ addition in both treatments (pH 9 and 10) (Fig. 4, Tab. S2). At the end of the experiment (22 h), DOC decreased by ~~27~~ 23 µM (~~67~~ %) at pH 10, whereas no significant change was observed at pH 9. It is noteworthy that DOC showed significant differences between the mixed and unmixed samples at pH 10, whereas in the mixed samples DOC was similar to the control (Fig. 4, Tab. S2).

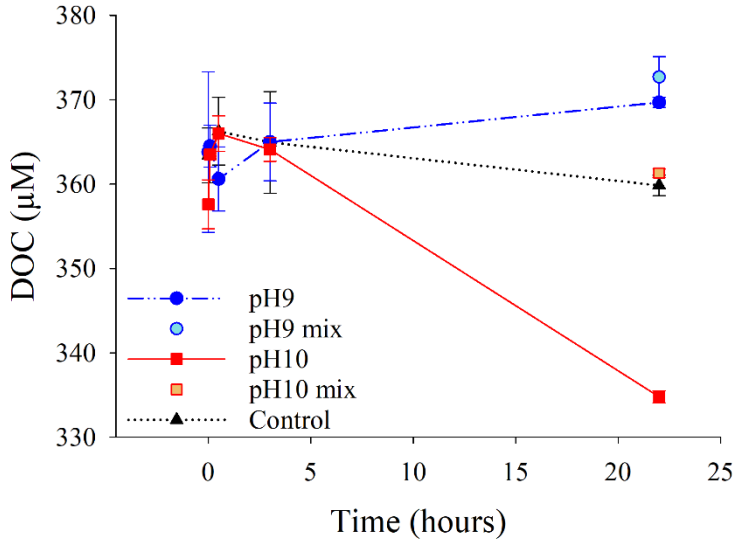

Figure 4: Trend of DOC concentration in the Baltic Sea treatments at pH 9 and 10 and in the control. Error bars refer to the standard deviation among the 3 replicates. Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.

3.2.2 CDOM absorption

Twenty-two hours after the addition of $Ca(OH)_2$, a_{254} decreased by 0.03 m^{-1} (0.~~1~~3%), and 3.~~7~~6 m^{-1} (15%) at pH 9 and pH 10, respectively (Fig. 5a). $S_{275–295}$ increased from 0.0215 nm^{-1} to 0.~~023~~0227 nm^{-1} (6%) at pH 10, whereas no significant change was observed at pH 9 (Fig. 5b). The change in CDOM is therefore visible only at pH 10 (Fig. 5)

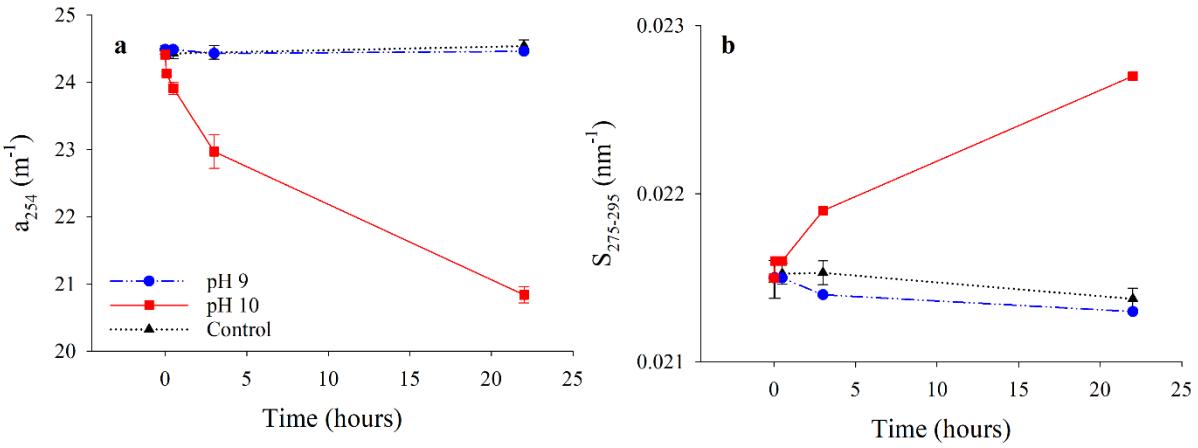

Figure 5: Trend of a_{254} (a) and $S_{275–295}$ (b) in the Baltic Sea treatments at pH 9 and 10, and in the control. Error bars refer to the standard deviation among the 3 replicates. Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.

3.2.3 FDOM fluorescence

The PARAFAC validated a 3-component model for the Baltic Sea EEMs experiment (Fig. S2, Tab. S3). Component 1 ($\lambda_{Ex}/\lambda_{Em}$: 290/400 nm, Fig. S2) shows spectroscopic characteristics similar to Coble's peak M ($\lambda_{Ex}/\lambda_{Em}$: 312 /[380]420; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as marine humic-like ($C1_{Mh\text{-}Bal}$). Component 2 ($\lambda_{Ex}/\lambda_{Em}$: 330/452 nm, Fig. S2) shows spectroscopic characteristics similar to Coble's peak C ($\lambda_{Ex}/\lambda_{Em}$: 350/451; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as Fulvic-like ($C2_{Flv\text{-}Bal}$). Component 3 ($\lambda_{Ex}/\lambda_{Em}$: 280/485 nm, Fig. S2) shows spectroscopic characteristics similar to Coble's peak A ($\lambda_{Ex}/\lambda_{Em}$: 260/[380]460 nm; Coble (1996)). The comparison with similar components in the OpenFluor database (matches with a TCC > 0.95) allowed to characterize it as Terrestrial humic-like ($C3_{Th\text{-}Bal}$).

$C1_{Mh\text{-}Bal}$ did not show significant changes during the incubation neither in the treatments nor in the control (Fig. 6a, Tab. S5). $C2_{Flv\text{-}Bal}$ did not show significant changes during the incubation at pH 9 and in the control, whereas a decrease of 0.03 R.U. (~~9~~10%) was observed at pH 10 ~~between 30 minutes and~~after 22 hours (Fig. 6b, Tab. S5). $C3_{Th\text{-}Bal}$ did not show significant changes during the incubation at pH 9 and in the control, whereas a decrease of 0.~~04~~ 05 R.U. (1~~3~~1%) was observed at pH 10 ~~between 30 minutes and~~after 22 hours (Fig. 6c, Tab. S5).

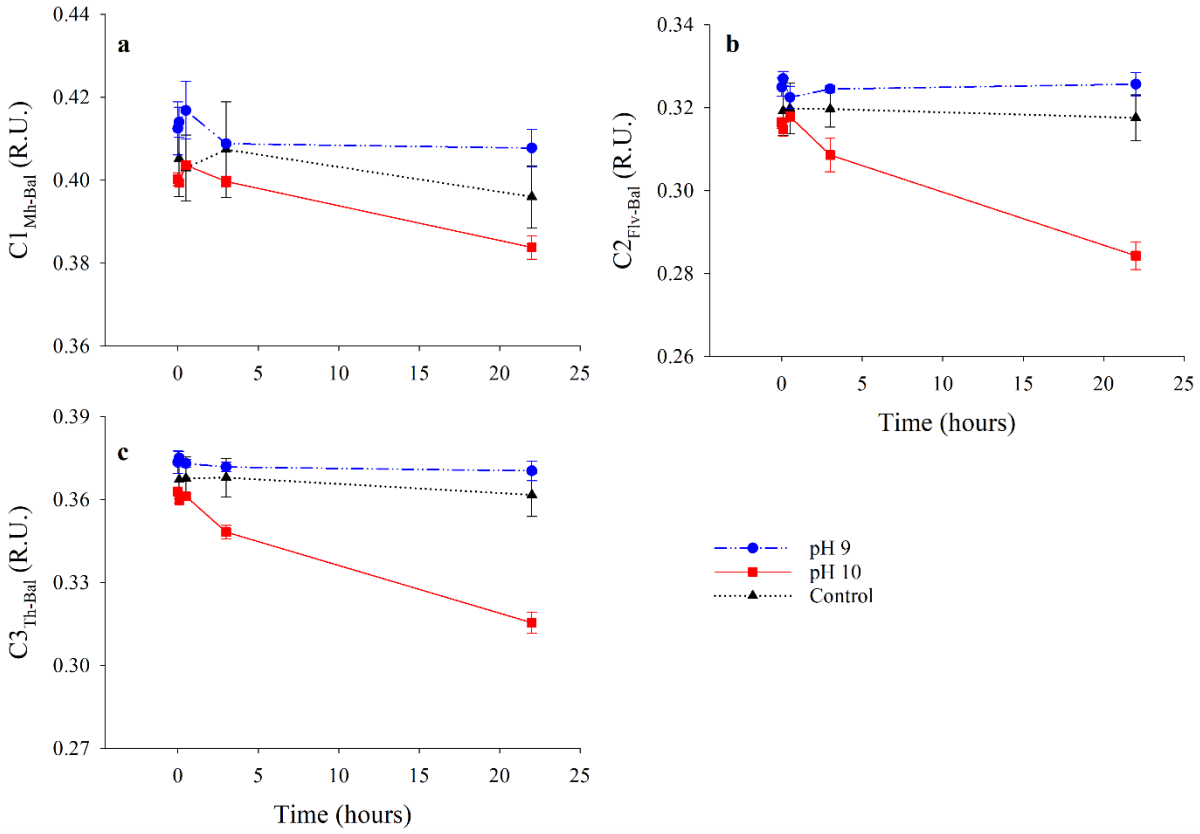

Figure 6: Trend of the fluorescent intensity of $C1_{Mh\text{-}Bal}$ (a), $C2_{Flv\text{-}Bal}$ (b) and $C3_{Th\text{-}Bal}$ (c) in the Baltic Sea treatments at pH 9 and 10, and in the control. Error bars refer to the standard deviation among the 3 replicates. Please, note that for some samples the error bars are smaller than the symbols and therefore not visible.

4 Discussion

Even if OAE using alkaline minerals is considered a promising tool to mitigate climate change through the sequestration and storage of atmospheric CO_2 into the ocean (DOSI, 2022), its impact on the marine ecosystem is still far to be understood. To the best of our knowledge, this is the first study investigating the potential effects of OAE by hydrated lime addition on DOM dynamics, with particular regard to DOC concentration and CDOM optical properties. Given the crucial role that DOM plays in the marine ecosystem, any impact on its dynamics is expected to affect the water quality and ecosystem functioning through a cascading effect on the microbial loop and the microbial food web.

4.1 Liming impact on DOM dynamics

Our data show the potential effects of hydrated lime addition ~~OAE~~ on DOM dynamics determining a decrease in DOC concentration (Fig. 1 and 4) and a change in the optical properties of CDOM (Fig. 2, 3, 5 and 6). The decrease in a_{254}, the increase in $S_{275\text{-}295}$ (Fig. 2 and 5) and the decrease in humic-like fluorescence (Fig. 3 and 6) indicate a change in DOM

quality with a shift towards molecules with lower average molecular weight and aromaticity degree. These effects are already visible at pH 9, but becomes relevant at pH 10. Different hypotheses can explain our results:

1) DOM reacts with $Ca(OH)_2$ and the largest and most aromatic molecules are oxidized to CO_2;

2) the largest and most aromatic molecules adsorb onto primary and secondary carbonate precipitates, that form following the $Ca(OH)_2$ addition, and sink;

3) the largest and most aromatic molecules aggregate forming polymer gels or large colloidal material and sink.

Interestingly, a significant decrease in DOC concentration was observed only in the unmixed samples at the end of the experiment (22 h after the addition, Fig. 1 and 4), DOC oxidation to CO_2 by reaction with $Ca(OH)_2$ (hypothesis 1) can therefore be ruled out as a possible removal mechanism. The other 2 hypotheses remain plausible and are supported by the available literature (Conzonno and Cirelli, 1995; Kaushal et al., 2020; Leenheer and Reddy, 2008; Pace et al., 2012). In lake waters, DOM was observed to adsorb~~s~~ onto carbonate particles and co-precipitate with them; the use of $CaCO_3$ precipitation was indeed suggested as an efficient technique for DOM removal during drinking water treatment processes (Leenheer and Reddy, 2008). The mechanism of DOM co-precipitation and/or physical incorporation into $CaCO_3$ is due to the formation of insoluble calcium. This hypothesis is further supported by the observation of $CaCO_3$ precipitation following the dissolution of hydrated lime, that was enhanced by the occurrence of nucleation surfaces as particles or solid mineral phases in the solution (Moras et al., 2021).
In freshwater ponds, a high affinity of high molecular weight molecules to adsorb onto particles like $CaCO_3$ was observed by Conzonno and Cirelli (1995) together with a preferential removal of high molecular weight humic substances during $CaCO_3$ crystals formation. Since humic acids have important environmental functions in controlling the pH and the bioavailability of dissolved metals (Baalousha et al., 2006), their removal may trigger a cascade effect with possible impacts on water quality. Past studies showed that pH per se can affect DOM dynamics as DOM can undergo a fast transition from dissolved to polymer gels (Chin et al., 1998) or large colloidal material (Pace et al., 2012) when pH switches toward more basic values (pH > 8 for seawater).
Among the ~~three~~ 3 hypotheses mentioned above, the ~~observed~~ decrease in a_{254}, observed in our experiments, supports the hypothesis 2, suggesting that, following the addition of $Ca(OH)_2$, the largest and most aromatic dissolved organic molecules adsorb to primary and secondary mineral particles and sink. This hypothesis is further supported by the high removal of the terrestrial components observed in both the Mediterranean Sea ($C3_{Th\_Med}$, -26%) and the Baltic Sea ($C3_{Th-Bal}$, -13%). This observation agrees with the results of Kaushal et al., (2020) which reported a higher incorporation of the terrestrial humic substances into abiogenically precipitated aragonite, then transferred within coral skeletons, with respect to marine humic substances.

4.2 Different effects on Mediterranean and Baltic waters

The ~~MedSea~~Mediterranean Sea and the ~~BalSea~~Baltic Sea are basins with different biogeochemical characteristics (Tab. 1). Our results show that DOC concentration (Fig. 1 and 4) and a_{254} (Fig. 2 and 5) are 6 and 13 times higher in the ~~BalSea~~Baltic Sea than in the ~~MedSea~~Mediterranean Sea (Tab. 1),– these data are consistent with previous studies

(Hoikkala et al., 2015; Santinelli, 2015; Santinelli et al., 2010). The lower $S_{275-295}$ (Tab. 1) and the different FDOM composition (Fig. S1 and S2) indicate a higher percentage of terrestrial DOM in the ~~BalSea~~Baltic Sea than in the Mediterranean Sea, as previously reported by Deutsch et al. (2012) and Hoikkala et al. (2015). Indeed, in the ~~BalSea~~Baltic Sea, PARAFAC allowed to characterize humic-like and fulvic-like components but not protein-like ones (Fig. S2, Tab. S~~3~~4), differently ~~from~~ in the ~~MedSea~~Mediterranean Sea ~~where~~ the protein-like component was identified (Fig. S1, Tab. S~~3~~2). Protein-like compounds are usually related to in-situ production, whereas fulvic-like substances mostly have a terrestrial origin. The predominance of terrestrial DOM in the ~~BalSea~~Baltic Sea is due to the high freshwater input from the wide catchment area (~ 4 times as large as the sea itself), and the low seawater input from the North Sea. The ~~BalSea~~Baltic Sea is also characterized by a peculiar carbonate system (Kuliński et al., 2017), exhibiting a wider range of total alkalinity (and pH) compared to the oceans. In particular, the Gulf of Riga, where the water for our experiment was collected, is characterized by a higher total alkalinity and a higher pH with respect to the rest of the ~~BalSea~~Baltic Sea (Beldowski et al., 2010; Kuliński et al., 2017).

In our experiments, we observed a different impact of $Ca(OH)_2$ addition in the ~~MedSea~~Mediterranean Sea and ~~BalSea~~Baltic Sea ~~water~~. In the ~~MedSea~~Mediterranean Sea, a DOC decrease of ~~8~~ 6 and 1~~3~~1 µM was recorded at pH 9 and 10, respectively (Tab. S2), indicating a net removal up to ~~16~~18% of the initial DOC (Fig. 1, Tab. S2). In the ~~BalSea~~Baltic Sea, the maximum removal observed was ~~8~~6% at pH 10, whereas no effect was recorded at pH 9 (Fig. 4).

Even if the salinity, being markedly lower in the ~~BalSea~~Baltic Sea than in the ~~MedSea~~Mediterranean Sea, is probably the main driver of the ~~lower precipitation of $CaCO_3$, and consequently of the~~ less pronounced effects on DOM dynamic, it cannot be excluded that the peculiar carbonate system combined with the different concentration and quality of DOM may have influenced the lower removal rates observed in our experiment. The influence of water chemistry is already evident by the 4-times lower amount of Ca(OH)2 needed to reach pH 9 and 10 in the ~~BalSea~~Baltic Sea than in the ~~MedSea~~Mediterranean Sea. Since $CaCO_3$ precipitation can be one of the main mechanisms explaining our results, the lower amount of $Ca(OH)_2$ added in the ~~BalSea~~Baltic Sea can explain the lower decrease of DOC observed in this basin than in the ~~MedSea~~Mediterranean Sea. ~~-~~At pH 10, the overall DOC removed in the Baltic Sea is larger (27 µM) than in the Mediterranean Sea (11 µM), despite the lower Ca(OH)2 added. This suggests a removal of 450 µmol of DOC per gram of Ca(OH)2 added in the Baltic Sea, and 44 µmol of DOC per gram of Ca(OH)2 added in the Mediterranean Sea. This observation can be explained by the predominance of terrestrial DOM in the Baltic Sea which was suggested to be preferentially removed during abiogenic precipitation of aragonite with respect to marine DOM (Kaushal et al., 2020).

It is noteworthy that DOM in the ~~MedSea~~Mediterranean Sea and in the oceans shows a clear seasonal cycle, mostly attributed to the changes in temperature, water stratification and biological activity, affecting DOM concentration, optical properties and stoichiometry (Carlson and Hansell, 2015; Santinelli, 2015; Santinelli et al., 2013). Seasonality strongly affects DOM dynamics also in the ~~BalSea~~Baltic Sea with prevalent allochthonous sources in winter and in-situ production by phytoplankton in spring (Hoikkala et al., 2012; Seidel et al., 2017). Our results, combined with the observed seasonality in DOM dynamics, stress ~~By integrating these observations with the outcomes of our study, it becomes evident~~ that any ~~hypothesis~~ plans for~~of~~ liming-based OAE should ~~not only account for the physico-chemical properties of each basin but~~ also take into consider~~ation the~~ season~~al variability~~.

4.3 Changed DOM dynamics: implication for the marine ecosystems

Our results suggest that $CaCO_3$ precipitation is the main driver for the sequestration of DOM from the water column. The sinking of the largest and most complex fraction of DOM to the deep oceans could lead to different scenarios.

1. If the exported ~~DOC~~ DOM is labile (i.e. it is available to microbial removal on the short temporal scale), its export would determine:

    - A depletion of the energy available for heterotrophic prokaryotes in the surface layer, determining a malfunctioning of the microbial loop that could impact the energy transfer to the higher trophic levels. This process could be further enhanced if the primary production is limited by the reduced water transparency due to carbonate formation.
    - The export of energy to the deepest layer (below the carbon compensation depth, CCD), leading to an increased bacterial production, in response to the labile DOM released due to the $CaCO_3$ dissolution.

2. If the exported ~~DOC~~ DOM is refractory (i.e. it is not available to microbial removal on the short temporal scale), it will contribute to C sequestration in the deep waters.

Our results indicate the preferential removal of the humic-like fractions by $CaCO_3$ precipitation. Humic-like substances are considered to constitute the less labile fraction of DOM (Bachi et al., 2023; Zigah et al., 2017) ~~(Zigah et al. 2017; Bachi et al., 2023)~~, supporting C sequestration in the deep waters (hypothesis 2) and a change in the lability of DOM in the surface waters, with an increase in the percentage of the labile fraction after $CaCO_3$ formation. Even if the lability of DOM is a very complex process, depending on a large number of variables (Dittmar et al., 2021), the change in the lability of DOM could be tested in incubation experiments with natural microbial communities collected in the same area as the water used for the experiment. The water for the experiments was filtered through a 0.2 µm filter and it was therefore considered sterile, in order to investigate the potential removal of DOM by microbes, we could inoculate the natural microbial community adding a 10% of unfiltered water from the same site. In order to avoid artefacts from direct pH impacts on the microbial community, before the inoculum the pH should be brought to natural pH by adding HCl.
It should also be taken into consideration that the adsorption of DOM onto $CaCO_3$ particles, itself might reduce the bioavailability, regardless of the inherent properties of the DOM. This process would increase the carbon sequestration into the deep waters, but it would reduce the energy available for the marine ecosystems. ~~.~~

5. Conclusions

This study reports the first evidence of the potential effects of OAE on DOM dynamics in two contrasting environments: the oligotrophic ~~MedSea~~Mediterranean Sea, known for its low DOC concentration, and the eutrophic Baltic Sea, characterized by high DOM concentration mostly of terrestrial origin. Our findings suggest that ocean alkalinization by $Ca(OH)_2$ sparging may alter DOM dynamics and, consequently, have a potential impact on the entire marine ecosystem. To mitigate these effects, it is crucial to reduce the duration and intensity of pH spikes, ensuring they remain below the safety threshold of pH 9. We stress the need to take into consideration the physico-chemical properties (e.g. salinity, pH,

DOM concentration and quality) of the basin and the season, to efficiently manage ocean liming and mitigate the potential impacts of ocean alkalinization on DOM pool.

Although the experimental conditions used in this study were more severe than actual liming practices, where the release of $Ca(OH)_2$ in the ship's wake undergoes rapid dilution that significantly reduces pH changes, our results provide new insights into the possible impacts due to physico-chemical processes.

It is important to highlight that the experiments in this study were conducted using sterilized seawater, thus excluding the potential interplay of biological processes on DOM dynamics. To gain a more comprehensive understanding of possible OAE impacts, future research should address the influence of biological processes, as well as factors like dilution rates, water mixing, and realistic durations and severities of pH peaks. Scaling up the experimental setup to mesocosms would allow for repeated additions and longer observation periods, enabling a more accurate representation of real-world conditions.

Author contribution

Conceptualization by CS, DB and AA. CS designed and supervised the experiments and SV, RBS, GB, GC, MG carried them out. Funding acquisition by SC and AA. CS prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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