<table>
<thead>
<tr>
<th>Deliverable 5.3</th>
<th>Report on parameterizing seasonal response patterns in primary- and net community production to ocean alkalinization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>GEOMAR</td>
</tr>
<tr>
<td>Related Work Package</td>
<td>WP 5</td>
</tr>
<tr>
<td>Related Task</td>
<td>Task 5.2</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Jan Taucher, Markus Schartau</td>
</tr>
<tr>
<td>Prieto Dissemination Level</td>
<td>Public</td>
</tr>
<tr>
<td>Due Submission Date</td>
<td>30.11.2021</td>
</tr>
<tr>
<td>Actual Submission</td>
<td>30.11.2021</td>
</tr>
<tr>
<td>Project Number</td>
<td>869357</td>
</tr>
<tr>
<td>Start Date of Project</td>
<td>01. July 2020</td>
</tr>
<tr>
<td>Duration</td>
<td>60 months</td>
</tr>
</tbody>
</table>

**Abstract:**
We applied a 1-D plankton ecosystem–biogeochemical model to assess the impacts of ocean alkalinity enhancement (OAE) on seasonal changes in biogeochemistry and plankton dynamics. Depending on deployment scenarios, OAE should theoretically have variable effects on pH and seawater pCO2, which might in turn affect (a) plankton growth conditions and (b) the efficiency of carbon dioxide removal (CDR). Thus, a major focus of our work is how different magnitudes and temporal frequencies of OAE might affect seasonal response patterns of net primary productivity (NPP), ecosystem functioning and biogeochemical cycling. With our study we aimed at identifying a parameterization of how magnitude and frequency of OAE affect net growth rates, so that these effects could be employed for Earth System Modell applications. So far, we...
learned that a meaningful response parameterization has to resolve positive and negative anomalies that covary with temporal shifts. As to the intricacy of these response patterns, the derivation of such parameterization is work in progress. However, our study readily provides valuable insights to how OAE can alter plankton dynamics and biogeochemistry. Our modeling study first focuses at a local site where time series data are available (European Station for Time series in the Ocean Canary Islands ESTOC), including measurements of pH, concentrations of total alkalinity, dissolved inorganic carbon (DIC), chlorophyll-a and dissolved inorganic nitrogen (DIN). These observational data were made available by Andres Cianca (personal communication, PLOCAN, Spain), Melchor Gonzalez and Magdalena Santana Casiano (personal communication, Universidad de Las Palmas de Gran Canaria). The choice of this location was underpinned by the fact that the first OAE mesocosm experiment of WP5 was conducted on the Canary Island Gran Canaria, which will facilitate synthesizing our modeling approach with experimental findings at a later stage of the project.

For our simulations at the ESTOC site in the Subtropical North Atlantic we found distinct, non-linear responses of NPP to different temporal modes of OAE. In particular, phytoplankton bloom patterns displayed pronounced temporal phase shifts and changes in their amplitude. Notably, our simulations suggest that OAE can have variable stimulating and impeding effects on NPP, depending on the magnitude and frequency of alkalinity addition. Furthermore, we find that increasing alkalinity can lead to a shift in phytoplankton community composition (towards coccolithophores), which even persists after OAE has stopped. The extent and exact timing of enhanced coccolithophore growth remains uncertain, as it depends on the small background calcification by coccolithophores of the calibrated reference model run, as well as on interannual variability of deep mixing events. But the general trend is a robust finding. In terms of CDR, we found that a decrease in efficiency with increasing magnitude of alkalinity addition, as well as substantial differences related to the timing (season) of addition. Altogether, our results suggest that annual OAE during the right season (i.e. physical and biological conditions), could be a reasonable compromise in terms of logistical feasibility, efficiency of CDR and side-effects on marine biota.

With respect to transferability to global models, the complex, non-linear responses of biological processes to OAE identified in our simulations do not allow for simple parameterizations that can easily be adapted. Dedicated future work is required to transfer the observed responses at small spatio-temporal scales to the coarser resolution of global models. In particular, we will further refine the reference model solution and then extend the period of simulation from five years to several decades, based on repeated hydrographic forcing and prescribed trends (scenarios) in atmospheric carbon dioxide concentration.
## Document History

<table>
<thead>
<tr>
<th>Date</th>
<th>Version</th>
<th>Description</th>
<th>Name/Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.11.2021</td>
<td>1.0</td>
<td>First submitted version.</td>
<td>Jan Taucher &amp; Markus Schartau,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>GEOMAR</td>
</tr>
<tr>
<td>03.06.2022</td>
<td>2.0</td>
<td>Revised version based on experts’ reviews, reviewed and evaluated by Judith</td>
<td>Jan Taucher &amp; Markus Schartau,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Meyer and David Keller.</td>
<td>GEOMAR</td>
</tr>
</tbody>
</table>

### Disclaimer:
This document reflects only the author’s view and the European Commission and their executive agency are not responsible for any use that may be made of the information it contains.
List of figures

Figure 1  Equilibrated and non-equilibrated states of the carbonate system in response to different degrees of alkalinity enhancement

Figure 2  Simulation results and observational data at the ESTOC site (29°N, 15°W): vertical turbulent diffusivity and mixed layer depths, annual cycle of nitrate in the mixed layer

Figure 3  Interannual variability and seasonal cycle of chlorophyll-a at the ESTOC site in the model simulations and observational data

Figure 4  Vertical changes in alkalinity and DIC in response to seasonal alkalinity enhancement

Figure 5  Temporal modes of alkalinity enhancement and their effects on total alkalinity

Figure 6  Development of carbon dioxide removal (CDR) under different temporals modes of alkalinity addition and influence of the OAE addition on CDR efficiency

Figure 7  Speciation of dissolved inorganic carbon (relative) and pH (absolute) under different magnitudes and temporals mode of alkalinity addition

Figure 8  Seasonal pattern of NPP and relative differences [%] to control simulation

Figure 9  Influence of the temporal mode of OAE addition on the temporal variability of NPP

Figure 10  Coccolithophore-to-phytoplankton ratio in NPP under extreme OAE and its dependence on the temporal mode of OAE addition

Figure 11  Changes in pH and changes in relative growth rate (RGR) of phytoplankton, including coccolithophores.

Figure 12  CO2 concentration of the reference solution and for annual additions of alkalinity in summer and winter

Figure 13  Amplitude of alkalinity changes in the surface layer in the all-at-once deployment; changes in pH and dissolved CO2 and CDR efficiency

Figure 14  OAE “all-at-once” impact on total NPP and the time-scale of NPP recovery after alkalinity addition

Figure 15  OAE “all-at-once” impact on NPP of “generic” phytoplankton and coccolithophores
List of tables

Table 1  Scenarios for OAE: different temporal frequencies and magnitudes
1. Introduction
1.1 Context
OceanNETs is a European Union project funded by the Commission’s Horizon 2020 program under the topic of Negative emissions and land-use based mitigation assessment (LC-CLA-02-2019), coordinated by GEOMAR Helmholtz Center for Ocean Research Kiel (GEOMAR), Germany. OceanNETs responds to the societal need to rapidly provide a scientifically rigorous and comprehensive assessment of negative emission technologies (NETs). The project focuses on analyzing and quantifying the environmental, social, and political feasibility and impacts of ocean-based NETs. OceanNETs will close fundamental knowledge gaps on specific ocean-based NETs and provide more in-depth investigations of NETs that have already been suggested to have a high CDR potential, levels of sustainability, or potential co-benefits. It will identify to what extent, and how, ocean-based NETs can play a role in keeping climate change within the limits set by the Paris Agreement.

1.2 Purpose and scope of the deliverable
One of the major aims of WP5 is the assessment of ecological and biogeochemical impacts of ocean alkalinization approaches on natural pelagic ecosystems, particularly regarding ecological risks and side effects. These may theoretically arise due to expected changes in seawater carbonate chemistry in response to ocean alkalinization. Amongst others, one such critical change in seawater carbonate chemistry is associated with a shift in the relative proportions of the availability of carbon dioxide and bicarbonate for algal growth. Task 5.2 applies modeling to extend experimental results to open ocean conditions, particularly by simulating seasonal changes in biogeochemistry and plankton dynamics in response to alkalinity perturbation and different deployment rates. With this deliverable D5.3 we inform about our modeling approach and report about our first findings. According to our model design we resolve variations in the carbon-to-nitrogen (C:N) ratio and nitrogen-to-phosphorus (N:P) of inorganic and organic matter, as well as photo-acclimation effects (variable chlorophyll-to-carbon ratio) that remain either crudely parameterized or even unresolved in the global biogeochemical model applications. In particular, carbon assimilation rates are distinguished from uptake rates of dissolved inorganic nitrogen and phosphorus. The original idea was to come up with a parameterization based on response patterns of our simulation results that can then be applied to global model applications. With the parameterization we aimed at emulating responses in algal growth that cannot be explicitly resolved in the 3D-global model applications in WP4. Also, for the deliverable we wanted to account for some more expedient scenarios and evaluate simulation results where the timing, frequency and intensity of alkalinity perturbation have been varied at a local ocean site.

1.3 Relation to other deliverables
The scope of the modeling work in WP5 in OceanNETs is to (a) complement the experimental mesocosm work conducted in this WP and (b) improved process understanding on small spatio-temporal scales and on a detailed physiological ecological level. In contrast to the global modeling work in WP4, our work focuses on response patterns that are not resolved in global models (physiological / biotic detail, time scales, spatial (vertical scales), in order to provide parameterizations of these processes for coarser,
global models. This also includes simulations of the mesocosm experiments conducted in WP5 to improve and calibrate the biogeochemical models (Task 5.5). However, since the mesocosm campaigns were delayed due to the Covid pandemic, we first set up a model environment that allowed us to assess seasonal ecosystem responses to ocean alkalinity enhancement. This work is complementary to the experimental mesocosm work in terms of OAE levels and different temporal modes of deployment (see section 2.3, “Methodology - OAE scenarios”).

1.4 Limitations of this work

The modelling work presented here does not consider constraints derived in other work packages, e.g., socio-economic constraints. This is because this deliverable was scheduled early in the project, but also since its objective is solely to understand and better quantify fundamental biogeochemical processes. That is the objective is to help fill a fundamental knowledge gap in our understanding of how ocean biogeochemistry may respond to ocean alkalinity enhancement.

2. Description of modeling experiments

2.1 General background and approach

Different biomes, e.g. Arctic/Antarctic high latitude systems, temperate ecosystems and, tropical/subtropical ocean ecosystems can be expected to display different sensitivities to OAE. A major potential bottleneck in the application of ocean alkalinization is considered to be the dispersion of added alkalinity (in the form of mineral powder or in aqueous solution) at the site of deployment. Depending on the degree of vertical and lateral mixing, added alkalinity might generate substantial out-of-equilibrium conditions of the carbonate system (pH, $pCO_2$) that potentially affect plankton communities on local and short-term scales. In this regard, subtropical open-ocean ecosystems can be considered the most vulnerable, as these regions display a strong thermal stratification of the water column with a relatively low degree of vertical mixing (compared to higher latitude waters). Therefore, we chose to prioritize our first modeling work for such subtropical ocean ecosystems. Another reason for starting off with a subtropical location is the general availability of observational data for one particular site, namely the “European Station for Time Series in the Ocean” (ESTOC), which is operated since 1994 (Neuer et al., 2007).

ESTOC is located about 100 km North of the Canary Islands (29°N, 15°W) at the Eastern boundary of the North Atlantic subtropical gyre and characterized by mostly oligotrophic waters. Data on environmental conditions (physical and biogeochemical) could be collected from various data sources (PLOCAN, PANGAEA, World Ocean Atlas) in order to allow for a calibration of our 1-D ecosystem model. Additional data (climatological means) were provided by Andres Cianca (personal communication, PLOCAN, Spain), and from Melchor Gonzalez and Magdalena Santana Casiano (personal communication, Universidad de Las Palmas de Gran Canaria).

We used the OPPLA model (OPtimality-based PLAnkton ecosystem model; developed by Markus Pahlow at GEOMAR, see e.g. Pahlow et al. (2020; 2013) for simulating biotic and biogeochemical responses to ocean alkalinization. This model has been applied, calibrated and analysed in several studies, including global applications (Chien et al., 2020; Pahlow et al., 2020) and simulations of mesocosm experiments (Krishna et al., 2019). The optimality-
based approach accounts for an exceptionally high level of physiological detail. The main model features variations in growth conditions due to intracellular resource allocation of carbon, nitrogen, and phosphorus, which have been evaluated against a variety of independent laboratory experimental data and field measurements, e.g., at the location of the Bermuda Atlantic Time-series Study (Fernández-Castro et al., 2016). Overall, OPPLA applies first order principles (optimal resource allocation) that are relevant when considering responses to changing environmental conditions. Such detail remains unresolved by most Earth System Models, but specific simulation effects to OAE could possibly be emulated in global models by some meaningful parameterization, e.g., changes in relative growth rates of the phytoplankton, which is one our objectives. For our modeling study we implemented a dependency between the maximum potential carbon assimilation rate and pH, expressed in terms of the proton (H+) concentration in seawater (Paul and Bach, 2020). The relationship derived by Paul and Bach (2020) has been applied and fitted to independent data of different experiments that cover a broad range of different phytoplankton taxa, primarily to explain differences in the responses of phytoplankton to changes in seawater carbonate chemistry under ocean acidification. Robust parameter estimates, because of a large number of available data, were obtained for calcifying algae as well as for diatoms. We adopted these parameter values, thereby accounting for the difference between estimates of the low-calcifying and non-calcifying phytoplankton.

This way we have introduced slightly different sensitivities in growth rates for calcifying and non-calcifying phytoplankton to variations in pH (ambient H+ concentration). Any OAE is expected to increase pH conditions to a range where the carbon assimilation rates become sensitive and where calcifying and non-calcifying algae are affected differently and thus diverge. Ultimately, the robustness and usefulness of the simulated response to changes in H+ concentration depends, most of all, on our model’s ability to reproduce the observed seasonal cycle of pH in combination with nutrient and light colimitation of growth i.e. carbon fixation and the utilization of inorganic nitrogen.

The physical environmental data for our simulations are based on the FOCI (Flexible Ocean and Climate Infrastructure) model, operated at GEOMAR. FOCI results of temperature, salinity, shortwave radiation, wind speed and eddy diffusivities for the local ESTOC site were made available by Chia–Te Chien (personal communication), covering a thirty years period, from 1990 though 2020. When comparing wind speed observations collected nearby ESTOC with the simulated wind speed, similar statistical means and variances are found. We could not infer any considerable bias in the atmospheric forcing, including shortwave radiation, temperature and salinity. However, eddy diffusivities (for momentum) appeared to be too high, occasionally exceeding values beyond 5 m² s⁻¹. We found out that if such high diffusivities were applied to any moderate surface concentration of inorganic nutrients or organic biomass, then this mass would become homogeneously mixed through a 200 m water column within less than two hours. Since the time scale of vertical mixing (e.g., of alkalinity added to the surface) is relevant for our model simulations we decided to cut-off eddy diffusion coefficients at a maximum value of 0.1 m² s⁻¹. Still, for some years we have deeper than typically observed mixing events that introduce some bias with respect to interannual variability in nutrients reaching the surface layers, and as a consequence, contributes to overestimation of late-winter phytoplankton blooms and chlorophyll-a concentration.
2.2 How will OAE alter carbonate chemistry and environmental conditions for phytoplankton?

The temporal frequency of ocean alkalinization is a crucial factor in the context of potential ecological risks and side effects. An increase in alkalinity enhances the capacity of seawater to take up CO$_2$ from the atmosphere, thereby eventually leading to higher concentrations of dissolved inorganic carbon (DIC) and a relatively slight increase in pH. Such conditions may theoretically favor photosynthesis by phytoplankton (due to higher availability of bicarbonate, HCO$_3^-$, a substrate for photosynthesis) and favor calcifying organisms (due to higher pH and saturation state of calcium carbonate). These conditions occur once the $p$CO$_2$ of seawater after alkalinity enhancement is in equilibrium with the atmosphere (see Fig. 1, green area). However, reaching such an equilibrium takes some time, depending on the velocity of air-sea gas exchange, which in turn is controlled by a variety of environmental factors (Jones et al., 2014). Previous studies have shown that it can take weeks to months, until a $p$CO$_2$ equilibrium between atmosphere and ocean is reached.

<table>
<thead>
<tr>
<th>Alkalinity [µmol kg$^{-1}$]</th>
<th>DIC [µmol kg$^{-1}$]</th>
<th>pH</th>
<th>$p$CO$_2$ [µatm]</th>
<th>DIC [µmol kg$^{-1}$]</th>
<th>pH</th>
<th>$p$CO$_2$ [µatm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>2090.8</td>
<td>8.04</td>
<td>413</td>
<td>2135.9</td>
<td>8.06</td>
<td>400.2</td>
</tr>
<tr>
<td>2700</td>
<td>2334.1</td>
<td>8.09</td>
<td>413</td>
<td>2135.9</td>
<td>8.44</td>
<td>149.8</td>
</tr>
<tr>
<td>3000</td>
<td>2574.9</td>
<td>8.12</td>
<td>413</td>
<td>2135.9</td>
<td>8.69</td>
<td>71.9</td>
</tr>
<tr>
<td>3300</td>
<td>2813.2</td>
<td>8.16</td>
<td>413</td>
<td>2135.9</td>
<td>8.91</td>
<td>36.9</td>
</tr>
<tr>
<td>3600</td>
<td>3049.4</td>
<td>8.19</td>
<td>413</td>
<td>2135.9</td>
<td>9.10</td>
<td>18.8</td>
</tr>
<tr>
<td>3900</td>
<td>3283.4</td>
<td>8.22</td>
<td>413</td>
<td>2135.9</td>
<td>9.31</td>
<td>9.0</td>
</tr>
<tr>
<td>4200</td>
<td>3515.6</td>
<td>8.24</td>
<td>413</td>
<td>2135.9</td>
<td>9.52</td>
<td>3.9</td>
</tr>
<tr>
<td>4500</td>
<td>3745.9</td>
<td>8.27</td>
<td>413</td>
<td>2135.9</td>
<td>9.76</td>
<td>1.5</td>
</tr>
<tr>
<td>4800</td>
<td>3974.6</td>
<td>8.29</td>
<td>413</td>
<td>2135.9</td>
<td>10.00</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fig. 1: Example calculations for the difference between equilibrated (green) and non-equilibrated (red) states of the carbonate system in response to different degrees of alkalinity enhancement. Lower panel: Visualization of pH (left) and $p$CO$_2$ (right) for different degrees of alkalinity enhancement under equilibrated (green) and non-equilibrated (red) conditions.
Accordingly, alkalinity enhancement can be expected to temporarily result in non-equilibrated pCO$_2$ conditions, which are accompanied by a strong increase in pH and a sharp decline in pCO$_2$ over a short period (see red area in Fig. 1). Such conditions may exceed thresholds beyond which photosynthesis by phytoplankton becomes inhibited due to CO$_2$ limitation and/or pH effects. For instance, previous studies have found that pCO$_2$ conditions <100–150 µatm had negative impacts on productivity of phytoplankton communities (Rost et al., 2003; Taucher et al., 2015). As can be seen in Fig. 1, such conditions can already be reached at alkalinity enhancement of ~ 500 µmol kg$^{-1}$ under non-equilibrated conditions. Consequently, the interplay between (a) the magnitude of alkalinity enhancement and (b) the time-scale of CO$_2$ equilibration between ocean and atmosphere determine whether ecological risks and side effects (due to transient changes in carbonate chemistry) can theoretically be expected.

2.3 Methodology - OAE scenarios

Following these considerations, one major focus of our 1-D model experiments was to test how different temporal modes of alkalinity deployment may affect short- to medium-term responses of carbonate chemistry and assess associated implications for net primary production (NPP) and ecosystem state in the subtropical oligotrophic ocean. Such temporal factors of alkalinity enhancement have so far not been considered in global simulation studies, because the applied models are not capable of resolving the required small temporal and spatial scales, and therefore introduce a constant and steady increase in alkalinity over time (González and Ilyina, 2016; Keller et al., 2014; Köhler et al., 2013).

To test the effect of the temporal mode of alkalinity enhancement, we simulated the addition of a given amount of alkalinity over a wide range of temporal frequencies, ranging from continuous (daily) addition (considered analogous to the approach in the aforementioned global studies), over weekly, monthly, seasonal, and annual addition, and also including a scenario, in which the entire amount of alkalinity is deployed at once. Note that we add pure alkalinity in our simulations due to the current uncertainties about possible applications of OAE, particularly with respect to the mineral used. For instance, addition of olivine would also add silicate and trace metals, which both could potentially modify the responses of marine biota. Within the scope of these simulations, OAE was carried out over a period of three years in the different temporal modes. To reach target alkalinity required for different levels of CDR (see Table 1 and explanations below), these various OAE deployment scenarios would actually need to continue until the end of the century. In terms of logistical effort and cost-efficiency, this poses a massive challenge based on the current infrastructure. In theory, it would also be possible to add the entire alkalinity for a given target level (here of a three year period) in one single deployment. We call this “all-at-once” OAE here.

The total amount of alkalinity enhancement was chosen according to previous modeling studies and describes the global average change in surface ocean alkalinity between present-day conditions and end-of-the-century. Idealized modeling studies suggest that OAE could increase surface seawater alkalinity by about 100 to >2,000 µmol kg$^{-1}$ by the year
2100 (Bach et al., 2019) although the upper estimates are based on extreme, likely unrealistic, application scales (González and Ilyina, 2016; Ilyina et al., 2013; Keller et al., 2014; Köhler et al., 2013; Lenton et al., 2018). However, given the short period of OAE we first look at (i.e. immediate responses to initiation of OAE), we expect to find responses in the extreme scenario that would likely occur with moderate OAE as well, but after some prolonged period e.g. of several decades, which will be tested once we have prepared the forcing for some extended model runs. It should be kept in mind that a real implementation of OAE will likely occur in specific regions and/or in a spatially non-uniform way. Thus, even at moderate global OAE, local alkalinity changes would be much higher. According to these considerations, we separated the possible range of OAE into three scenarios, “moderate”, “high”, and “extreme”. As explained in the following, these OAE levels reflect different deployment scenarios and also mirror the range of OAE treatments of the mesocosm experiment in Gran Canaria in fall 2021 (part of WP5), which ranged between alkalinity increases of 300 to 2,400 μmol kg$^{-1}$.

- **“Moderate” OAE**: This scenario is based on considerations regarding the current technological infrastructure (e.g. mining capacities, transport capacity of cargo ships) following Keller et al. (2014) and Lenton et al. (2018), resulting in a maximum increase in total alkalinity (TA) by 100-200 μmol kg$^{-1}$ by the year 2100.

- **“High” OAE**: This scenario is based on the required amount of carbon dioxide removal (CDR) to maintain atmospheric CO$_2$ concentrations following a RCP4.5 pathway, but under emissions following a RCP8.5 scenario (sensu Gonzalez and Ilyina, 2016). This results in a surface ocean alkalinity increase of 700-1000 μmol kg$^{-1}$ by the year 2100.

- **“Extreme” OAE**: This scenario accounts for more realistic deployment options. Note that numbers for both “moderate” and “high” scenarios (and the global modeling studies that these numbers are based on) assume a globally uniform application of alkalinity enhancement. In reality OAE may be applied only in certain regions or in a spatially non-uniform way. The “extreme” OAE scenario accounts for this, thereby following the study of Ilyina et al. (2013), in which they simulated application of OAE in certain oceanic regions, e.g. in the North Atlantic and North Pacific. Local alkalinity changes in their study reached 1000-4000 μmol kg$^{-1}$. Furthermore, preliminary data from the mesocosm experiment in Gran Canaria in fall 2021 indicate that alkalinity enhancement may be feasible up to levels of 1,800-2,100 μmol kg$^{-1}$. Thus, we used 2,000 μmol kg$^{-1}$ for the “extreme” scenario, and focus some parts of the results analysis and interpretation on this possible upper boundary of OAE application. Thereby we can assess whether such an optimistic (and economically efficient) OAE implementation would have any ecological side effects or not. In addition, the “extreme” scenario may reveal effects within the three years simulated that otherwise occur only after some prolonged period of “moderate” OAE.
According to the described scenarios we prescribed and tested different temporal frequencies of alkalinity enhancement, shown in Table 1. Note that alkalinity is added only to the uppermost box in our simulations, thus assuming alkalinity deployment to the surface ocean. In our simulations, we let the model spin up for 2 years, then simulate a period of alkalinity enhancement of 3 years (according to the scenarios in Table 1) and then follow the system after perturbation for another 2 years, until a new equilibrium is reached.

Table 1: Scenarios for temporal frequency of alkalinity enhancement: Number of alkalinity deployments for different scenarios of temporal frequency, assuming a period of 80 years (year 2020 to 2100). Average increase in seawater alkalinity concentration in the mixed layer [mmol m\(^{-3}\)] for different scenarios of alkalinity enhancement (moderate, high, and extreme; see text for explanations), broken down into theoretically expected changes for the different temporal modes of deployment (i.e. change in alkalinity after each deployment). Note that the different scenarios also mirror the range of OAE treatments of the mesocosm experiment in Gran Canaria in fall 2021 (part of WP5), which ranged between alkalinity increases of 300 to 2,400 µmol kg\(^{-1}\).

<table>
<thead>
<tr>
<th># of deployments during 80 years</th>
<th>moderate</th>
<th>high</th>
<th>extreme</th>
</tr>
</thead>
<tbody>
<tr>
<td>(assuming OAE from 2020 to 2100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>daily (continuous)</td>
<td>29200</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>weekly</td>
<td>4160</td>
<td>0.05</td>
<td>0.19</td>
</tr>
<tr>
<td>monthly</td>
<td>960</td>
<td>0.21</td>
<td>0.83</td>
</tr>
<tr>
<td>seasonal (4x)</td>
<td>320</td>
<td>0.63</td>
<td>2.50</td>
</tr>
<tr>
<td>annual</td>
<td>80</td>
<td>2.50</td>
<td>10.00</td>
</tr>
<tr>
<td>all at once</td>
<td>1</td>
<td>200.00</td>
<td>800.00</td>
</tr>
</tbody>
</table>

2.4 Results for present-day conditions (reference baseline)

The reference model solution was determined by visual comparisons between observational data and their simulated counterparts. Note that such manual adjustments or parameter values (model constants) are common practice in biogeochemical modeling. A more rigorous scheme for parameter optimization has not been employed, mainly due to time constraints, as this will not be straightforward to achieve, given the limited availability of observational data for the ESTOC site. Doing so will require special considerations for how a cost function (metric for data-model comparison) should be designed in order to be useful. These considerations are planned for the near future during the duration of the OceanNETs project. Definitely, once the data from the WP5 mesocosm campaigns are available for model calibration, we will address problems of parameter identification, including parameter screening, recovery of possible collinearities as well as deriving uncertainties with respect to parameter estimates.

The introduced eddy diffusivities show generally good performance in reproducing the physical boundary conditions (see Fig. 2A), if compared with mixed layer depths derived by Yumrektelepe et al (2020). As outlined before, for some years the mixed layer depths can exceed those derived from observational data, which is here the case for the year 1996. Unfortunately, we do not have similar observational data available for comparison of the
years 2016 through 2020. However, during years when the mixed layer depth reaches beyond 150 m, the observed chlorophyll-α concentrations can become as high as 1 mg m$^{-3}$, which was the case in the year 1999. In our simulations deep mixing events (down to approximately 200 m) occur in the years 2017 and 2019.

The annual cycle of the biogeochemical quantities in the reference solution is well resolved (Figs. 2B, 2C and 2D). Most importantly, the absolute values and the seasonal variation in pH are in accordance with the observations (Fig. 2B). The simulated seasonal variation in alkalinity is slightly less pronounced than in the climatological data (Fig. 2B). A possible reason for this is the presence of strong interannual variations in calcification, which we cannot evaluate based on the data available. We stress that calcification reduces alkalinity whereas the uptake of nitrate introduces an increase in alkalinity. We can only speculate whether the lowered alkalinity during September in the climatological data is associated with calcification, reoccurring either frequently every year or being specific for some years. Finding a credible trade-off between the utilization and remineralization of nitrate and phosphate, calcification and alkalinity is extremely difficult, but the level of alkalinity reached by our reference model solution is satisfactory for providing a meaningful basis for simulations of OAE.

Fig. 2: Comparison between simulation results and observational data at the ESTOC site in the subtropical North Atlantic (29°N, 15°W). (A) simulated vertical turbulent diffusivity and comparison to observational data of mixed layer depths (white line; derived from Argo-floats temperature measurements, see Yumrukete et al., 2020), (B) pH and alkalinity in the surface 20m. (C) annual cycle of nitrate in the mixed layer to 200m depth (note contours are on a log scale), and (D) average values in the surface 20 m.
The simulated nitrate concentrations are marginally higher, compared to the climatological data (Figs. 2C and 2D). As can be seen from Fig. 2D, the interannual variability in surface nitrate concentration is considerable (e.g. $\Delta \text{NO}_3 \approx 1$ mmol m$^{-3}$ in February), while the vertical gradient can be well reproduced. Along with, and because of the year to year differences in nitrate concentration, the interannual variability of the chlorophyll–a concentration is particularly pronounced. In order to get an impression of the range in interannual variations in chlorophyll–a, we compare our results with previous findings of monthly observational data depicted in Neuer et al. (2007), see Figs. (3A and 3B). Clearly, we find higher chlorophyll–a concentrations during years of deep mixing. According to our simulation results, this is the case for the years 2017 and 2019 (with concentrations slightly above 1 mg m$^{-3}$). Similar conditions (maximum concentrations around 1 mg m$^{-3}$) we find for the year 1999 in data of Neuer et al. (2007).

Fig. 3: Interannual variability and seasonal cycle of chlorophyll a at the ESTOC site in the model simulations and observational data. Interannual variability in phytoplankton blooms (given as chlorophyll a) in the simulations (A) and observational data (B), showing the figure from the previous study by Neuer et al. (2007). (C) Simulated and observed annual cycle of chlorophyll in the mixed layer to 200m depth (note contours are on a log scale), and (D) average values in the surface 20m.

Typical observed high chlorophyll–a concentrations range between 0.6 and 0.7 mg m$^{-3}$ (Vega-Moreno et al., 2011). The OPPLA model applied here is known for its tendency to overestimate chlorophyll synthesis rates, especially under conditions of photo-acclimation,
see Pahlow et al. (2020; 2013). Overall, main features of the seasonal cycle at ESTOC, particularly the phytoplankton bloom peak in late winter, as well as the shift in the depth range of chlorophyll-α (near-surface during the winter bloom and deep maximum at ~100 m depth during summer) are captured by the model (Fig 3C and D). In the end it should be noted that chlorophyll-α is hardly suited as a proxy for biomass or for net primary production. Based on our comparison between data and model results with respect to the extent and seasonality of the development of the deep chlorophyll-α maximum, we conclude that our reference model solution is a reasonable, although imperfect, representation of the phytoplankton growth conditions found in the subtropical North Atlantic. A model intercomparison within OceanNETs at or nearby the ESTOC site might elucidate some of the modeling difficulties addresses here.

2.5 Results of alkalinity enhancement simulations

**Physico-chemical conditions**

The physical features at the ESTOC site are typical for subtropical open ocean conditions, with a relatively stable thermal stratification that separates the upper 100-200 m from deeper waters below. Periods of deeper mixing occur regularly due to winter storms and eddies. Our simulations show that these physical properties are an important factor in distributing the enhanced alkalinity across the water column (Fig. 4).

![Fig. 4: Vertical changes in alkalinity (top) and DIC (bottom) in response to seasonal alkalinity enhancement, exemplary for the “extreme” scenario. Note the profound effect of winter mixing in vertically distributing alkalinity, thereby dampening the short-term alkalinity peaks in the surface layer.](image-url)
Fig. 5: Effects of different temporal modes of alkalinity enhancement (here visualized by the example of the “extreme” scenario) for the amplitude of alkalinity concentrations in the surface layer. Note the distinct difference between alkalinity addition during winter or summer due to seasonal differences in vertical mixing.
These results demonstrate that physical mixing determines the temporal and spatial scales, for which (potentially unfavorable) non-equilibrated conditions of the carbonate system may occur. Accordingly, the simulation of different temporal modes of alkalinity enhancement shows a distinct pattern, in which a decrease in the temporal frequency leads to an increase in maximum alkalinity changes in the surface ocean (Fig. 5). Future model simulations should therefore also focus on different spatial and temporal scales of OAE, including lateral dispersion. Note that our simulations focus on the development at a single site of OAE deployment, i.e. where short-term effects may be pronounced (i.e. following the “extreme” scenario), even though larger-scale OAE levels are at the lower end due to lateral dispersion. Thus, the goal of this modeling exercise is specifically to assess the upper limits, i.e. ecological threshold of OAE. This is also the reason why we focus on the upper end of OAE scenarios.

Oceanic carbon uptake under different OAE scenarios

Addition of alkalinity to the surface ocean results in a swift increase in oceanic carbon uptake, as expected from changes in seawater carbonate chemistry due to OAE (Fig. 6A). The efficiency of carbon dioxide removal (CDR), given as the relative increase in DIC per increase in alkalinity scales with the total amount of added alkalinity, as well as its temporal frequency (Fig. 6B). Notably, we find a profound difference between OAE during summer or winter for the annual addition, with higher efficiencies for summer conditions. The variability in CDR between summer and winter OAE is even higher than the variability among the magnitude of alkalinity additions. Surprisingly, CDR efficiency for the “annual, summer” addition was consistently higher than those for more continuous (i.e. higher temporal frequency) additions.

Fig. 6: (A) Development of carbon dioxide removal under different temporals mode of alkalinity addition (here under the extreme OAE scenario), calculated as the depth-integrated difference in the DIC inventory (relative to the control simulation). (B) Influence of the temporal mode of OAE addition on CDR efficiency (calculated as DIC/ALK change in %), including differences between summer and winter.
Responses in primary productivity to OAE

The different magnitudes and temporal modes of OAE have very variable effects on carbonate chemistry (Fig. 7), which introduces, in turn, important physiological constraints on phytoplankton growth. Generally, there is a clear shift from dissolved CO$_2$ and bicarbonate (HCO$_3$) towards carbonate (CO$_3$) due to the increase in alkalinity and the corresponding increase in pH, which drives the shifts in carbonate chemistry. Eventually, it is this shift that introduces variations in carbon assimilation rates of the phytoplankton, assuming that the relationship of Paul and Bach (2020) is credible and representative.

The response of net primary production to these changes depends on the magnitude and temporal mode of OAE due to the seasonal cycle of phytoplankton growth. Under ambient conditions, simulated net primary production displays a distinct seasonal pattern at the ESTOC site (Fig. 8A). The largest portion of NPP is driven by non-calcifying phytoplankton, although the contribution of coccolithophores slightly increases towards the end of the simulation, likely due to the gradual enhancement of the growth conditions of the calcifiers. The temporal mode of OAE has a profound impact on the seasonal cycle of NPP, leading to phase shifts and changes in the amplitude that reach up to ~15% change due to OAE (Fig. 8B). Notably, on annual average (last 3 years of the simulation), NPP under different OAE scenarios is consistently higher than in control simulation (Fig. 8C). For annual OAE, differences between summer or winter addition were substantial, with larger positive effects on NPP for winter conditions. The reason is likely the larger alkalinity perturbation during summer (because of lower vertical mixing and thus slower distribution of alkalinity across the water column; see Fig. 5), which leads to stronger physiological effects on phytoplankton than during winter conditions (during which the alkalinity perturbation is diluted much faster). However, as Fig. 8B shows, the period of higher NPP after winter addition also shows some time lag, indicating complex, non-linear responses throughout the seasonal cycle.
Fig. 7: Changes in speciation of dissolved inorganic carbon (relative) and pH (absolute) under different magnitudes and temporals mode of alkalinity addition. Note that bicarbonate ($\text{HCO}_3^-$) reaches net positive changes only towards the end of the simulation, thus illustrating the long timescale of equilibration with the atmosphere.
The seasonal response patterns to OAE display a higher temporal variability of NPP with increasing OAE, as well as larger NPP variability for winter addition than during summer (for annual OAE) (Fig. 9A). This response is linked to distinct phase shifts and changes in NPP amplitude in response to summer vs. winter addition (Fig. 9B). This result is somewhat surprising, as the alkalinity perturbation during summer is larger and theoretically has stronger physiological effects. A possible explanation for this result is that
during summer, the alkalinity perturbation does not reach the layer of highest NPP (deep chlorophyll maximum), while during winter, the alkalinity perturbation directly affects near-surface NPP.

The changes in total NPP are also accompanied by shifts in phytoplankton community composition. For the reference solution we considered low calcification rates (approximately 0.5 % of NPP), which is similar to assumptions typically imposed in the earth system model applications. In response to OAE, the relative contributions of coccolithophores and other phytoplankton to NPP change over the course of the simulation, with a sharp increase in coccolithophores (Fig. 10A). Interestingly, the shift occurs most strongly during the last two years of the simulation, after OAE has stopped. Thus, enhanced growth conditions of the calcifiers can become expressed even after years of OAE, in response to other additional factors like grazing and winter mixing conditions (entrainment of nutrients to the upper layers). The shift towards coccolithophores scales with OAE magnitude, and also displays a strong difference between summer and winter addition (for the annual OAE case), with winter addition benefitting coccolithophores more strongly (Fig. 10B). The most likely explanation for these results is that the OAE-driven shifts in carbonate chemistry, particularly the increase in pH (i.e. decrease in H⁺ concentration) and carbonate (CO₃) have positive physiological effects on coccolithophore growth.

Fig. 9: (A) Influence of the temporal mode of OAE addition on the temporal variability of NPP (calculated as the standard deviation) relative to the control simulation (relative difference in %), including differences between summer and winter. (B) Differences in NPP temporal phase shifts and magnitudes between summer and winter addition (annual), shown as the relative difference [%] to the control simulation.
Physiological responses to pH and CO₂ and the role of alkalinity intrusion to depth

Relative changes in pH of the extreme event approach 1.2 %, with a gradual decline during years of no alkalinity addition (Fig. 11). The pH changes at the end of 2020 differ only by the amount of alkalinity added and hardly by the frequency of addition. Equilibrated pH at the end of the simulation period remains insensitive to the timing and frequency of alkalination (Fig. 11A). While changes in pH are mainly sensitive to the magnitude of perturbation any superimposed variations due to primary production remain negligible. Clearly, the response patterns in algal growth reveal an enhanced signal, being more sensitive to the frequency of alkalination events (Fig. 11B). The anomalies, induced by the alkalination, show a delay in bloom development, indicated by negative anomalies at times of the blooms in the reference solution. The negative are followed by positive anomalies, but we do not find a clear relationship that determines the switching from negative to positive anomalies, which complicates the entire picture and is one reason for why we could not come up with a meaningful parameterization of the responses on RGR, yet. We will therefore consider various (diagnostic) models, possibly artificial intelligence (AI) approaches.

So far, we realized that after the years of alkalination the response patterns of the different scenarios converge again, being only sensitive to the amount of alkalinity added. The convergence behaviour in RGR after the years of alkalination becomes clear when looking at the CO₂ concentrations (Fig. 12). This example shows similar CO₂ concentrations in the second year after alkalination stopped, although the annual alkalination differs with respect to the timing, summer versus winter addition. Since the CO₂ concentrations in the years 2019 and 2020 are similar we find similar responses in RGR, provided that the imposed RGR sensitivity of RGR to CO₂ is realistic.

Fig. 10: (A) ratio of coccolithophore/phytoplankton in NPP under extreme OAE and (B) its dependence on the temporal mode of OAE addition, including differences between summer and winter.
Fig. 11: (A) Changes in pH, relative to the reference solution, for the different scenarios (alkalinity added), (B) changes in relative growth rate (RGR) of phytoplankton, including coccolithophores.

Fig. 12: (A) CO₂ concentration of the reference solution and for annual additions of alkalinity in summer (B) and winter (C).
Responses to “all-at-once” addition of alkalinity

Above sections describe responses to OAE over an extended period of time (3 years of alkalinity addition in the model simulations here). As described above, it would also be possible to add the entire alkalinity for a given CDR target level in one single deployment (“all-at-once” OAE) to maximize cost-efficiency. This results in substantial changes in alkalinity concentrations in the surface ocean, reaching up to 5-fold higher concentrations than under present conditions (Fig. 13A).

![Graphs showing changes in alkalinity, pH, and CDR efficiency under different OAE scenarios.](image)

**Fig. 13:** (A) Amplitude of alkalinity changes in the surface layer in the all-at-once deployment (here for the extreme OAE scenario). Note the distinct difference between alkalinity addition during winter or summer due to seasonal differences in vertical mixing. (B) Changes in pH and dissolved CO$_2$ and (C) CDR efficiency (calculated as DIC/ALK change in %) under different “all-at-once” OAE scenarios.
Over the simulation period, CDR efficiency for “all-at-once” alkalinity addition increases over time, but at lower rates for higher OAE magnitudes (Fig. 13B). Addition during winter results in considerably higher CDR efficiency than addition during summer, thus showing the opposite winter/summer difference than annual OAE (Fig. 6B). NPP is substantially affected by “all-at-once” alkalinity addition, displaying an almost 100% decrease for the high and extreme scenarios (Fig. 14A). Over the simulation period, NPP does recover, displaying distinct seasonal patterns under the different magnitudes and the timing (winter/summer) of alkalinity addition. The recovery period (defined as the time until NPP reaches a net positive difference compared to the control simulation) is prolonged at larger OAE magnitude, but displays a large difference depending on summer or winter addition (i.e. a reversal of the OAE vs. NPP recovery relationship; Fig. 14B). Furthermore, NPP in the high and extreme OAE scenario increases sharply towards the end of our simulations. This “overshoot” NPP reaches 2- to 3-fold higher levels compared to the control simulation.

The responses in NPP are also linked to underlying changes in community composition after alkalinity addition. While under moderate “all-at-once” OAE, phytoplankton remain dominant, a major regime shift occurs under high and extreme “all-at-once” OAE (Fig. 15). Here, coccolithophores almost completely replace other phytoplankton. However, it should be noted that under extreme OAE conditions, absolute values of coccolithophore NPP are much reduced compared to high OAE. Whether these patterns remain needs to be explored in future simulations, in which a multi-decadal period after “all-at-once” OAE will be monitored.

![Fig. 14](image-url): “all-at-once” OAE impact on (A) total NPP and (B) the time-scale of NPP recovery after alkalinity addition, including differences between summer and winter.
3. Conclusion and outlook

Our model experiments revealed that the sensitivity of phytoplankton productivity to OAE displays a non-linear behavior, which also varies with the magnitude and temporal frequency of alkalinity addition. Frequency of alkalination events hardly affect the overall increase in DIC as well as how alkalinity becomes vertically distributed. In contrast to this, the seasonal cycling of phytoplankton growth and subsequent response in grazing are significantly altered. This is well expressed in variability patterns, in biomass as well as nutrient concentrations within the upper 140 m. It is because of this complex behaviour, in combination with the presence of strong interannual variability, why it is more intricate than originally expected to derive a parameterization that can emulate the responses seen in our simulations for applications in WP4. The derivation of such parameterization of higher level physiological effects on NPP in response to various OAE scenarios remains a central objective in our research approach. However, some further elaboration and consolidation of our simulation results are necessary before we can fully concentrate on such task.

The recent experimental findings of WP5 (mesocosm study in Gran Canaria in 2021) clearly point towards an important model modification, a process that could not be resolved in our model simulations presented here. This process involves the precipitation of calcite at particulate matter that is exported, which in the end can drastically reduce alkalinity at the upper ocean layers and thus counteracts the desired alkalinity enhancement effect on CO₂ uptake from the atmosphere. We plan to introduce a particulate matter pool that a) can act as a kernel for extracellular precipitation of calcite and b) can sink through the water column and can become dissolved again below the CaCO₃ saturation horizon. This is expected to introduce a considerable vertical redistribution of the alkalinity added to the surface and we yet cannot make inference about how this affects phytoplankton growth.
and how the associated responses are on the long term. Furthermore, due this effect of rapid precipitation and export it is suggested by the experimental groups in WP5 to add alkalinity in form of readily CO₂ equilibrated sea water, meaning that CDR already occurs before deployment in the ocean (e.g. in special chemical reactors). In order to assess such a scenario, we will implement a (perturbation) flux of dissolved inorganic carbon (DIC) to be added to the alkalinity flux in our model. The interesting scientific question to address is then how such CO₂ equilibrated OAE relates to our former approach.

In a next step we will conduct extended (multi-decadal) model simulations in order to compare long-term effects of OAE on NPP. We plan to prepare to two types of scenarios, CO₂ non-equilibrated OAE and CO₂ equilibrated OAE. For each type we would consider different frequencies (weekly, seasonal, annual winter, spring, summer, autumn) and only two different magnitudes of OAE (moderate and high). All OAE scenarios already presented here would then be applied to two model configurations, with and without chemical precipitation, and for CO₂ non-equilibrated OAE and CO₂ equilibrated OAE respectively. This will provide a comprehensive assessment of OAE impacts on primary production, carbonate chemistry, and OAE efficiency.

In this way we can better relate the recent WP5 experimental findings to more realistic environmental conditions than those found in the mesocosms, which is also crucial with respect to global modeling work in WP4, as well as to socio-economic implications (e.g. governance, legal aspects, carbon accounting, social acceptance).
4. References


