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## On the emission-path dependency of the efficiency of ocean alkalinity enhancement

To cite this article: Jörg Schwinger *et al* 2024 *Environ. Res. Lett.* **19** 074067

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## LETTER

## On the emission-path dependency of the efficiency of ocean alkalinity enhancement

## OPEN ACCESS

## RECEIVED

21 February 2024

## REVISED

11 June 2024

## ACCEPTED FOR PUBLICATION

20 June 2024

## PUBLISHED

5 July 2024

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Jörg Schwinger<sup>1,\*</sup> , Timothée Bourgeois<sup>1</sup> and Wilfried Rickels<sup>2,3</sup><sup>1</sup> NORCE Climate & Environment, Bjerknes Centre for Climate Research, Bergen, Norway<sup>2</sup> Kiel Institute for the World Economy, Kiel, Germany<sup>3</sup> Department of Economics, Kiel University, Kiel, Germany

\* Author to whom any correspondence should be addressed.

E-mail: [jörg.schwinger0@gmail.com](mailto:jörg.schwinger0@gmail.com)**Keywords:** carbon dioxide removal, ocean alkalinity enhancement, efficiency of CDR, path dependencySupplementary material for this article is available [online](#)**Abstract**

Ocean alkalinity enhancement (OAE) deliberately modifies the chemistry of the surface ocean to enhance the uptake of atmospheric CO<sub>2</sub>. The chemical efficiency of OAE (the amount of CO<sub>2</sub> sequestered per unit of alkalinity added) depends, among other factors, on the background state of the surface ocean, which will significantly change until the end of this century and beyond. Here, we investigate the consequences of such changes for the long-term efficiency of OAE. We show, using idealized and scenario simulations with an Earth system model, that under doubling (quadrupling) of pre-industrial atmospheric CO<sub>2</sub> concentrations, the simulated mean efficiency of OAE increases by about 18% (29%) from 0.76 to 0.90 (0.98). We find that only half of this effect can be explained by changes in the sensitivity of CO<sub>2</sub> sequestration to alkalinity addition itself. The remainder is due to the larger portion of anthropogenic emissions taken up by a high-alkalinity ocean. Importantly, both effects are reversed if atmospheric CO<sub>2</sub> concentrations were to decline due to large-scale deployment of land-based (or alternative ocean-based) carbon dioxide removal (CDR) methods. By considering an overshoot pathway that relies on large amounts of land-based CDR, we demonstrate that OAE efficiency indeed shows a strong decline after atmospheric CO<sub>2</sub> concentrations have peaked. Our results suggest that the assumption of a constant, present-day chemical efficiency of OAE in integrated assessment modeling and carbon credit assignments could lead to economically inefficient OAE implementation pathways.

**1. Introduction**

Ocean alkalinity enhancement (OAE) has been proposed as a carbon dioxide removal (CDR) technique that would increase the oceans' capacity to store carbon, thereby taking up CO<sub>2</sub> from the atmosphere (Kheshgi 1995; see Renforth and Henderson 2017 for a review). In contrast to many other gases, CO<sub>2</sub> does not only dissolve in seawater, but it also acts as a weak acid that reacts with water to form free protons (H<sup>+</sup>) as well as bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. Since atmospheric CO<sub>2</sub> equilibrates solely with the dissolved aqueous CO<sub>2</sub>, and not with bicarbonate or carbonate, the ocean holds much more carbon than predicted by the solubility of CO<sub>2</sub>. The partitioning of the oceanic pool of dissolved inorganic carbon (DIC) into its constituents (dissolved

CO<sub>2</sub>, bicarbonate, and carbonate) is governed by the total alkalinity (TA) and the pH of seawater, where TA is defined as the capacity of seawater to neutralize an acid (see, for example, Dickson and Goyet 1994, Wolf-Gladrow *et al* 2007). An increase in TA shifts the equilibrium of the seawater CO<sub>2</sub> system towards more bicarbonate and carbonate ions, decreases the concentration of dissolved CO<sub>2</sub>, and consequently leads to an uptake of CO<sub>2</sub> from the atmosphere. Due to the oceans' large size, small relative changes in TA could sequester a large proportion of anthropogenic carbon, such that OAE is seen as a CDR technique with high theoretical potential (Kheshgi 1995, Harvey 2008, Ilyina *et al* 2013, Köhler *et al* 2013).

The chemical efficiency ( $\eta$ ) of OAE has been defined as the carbon sequestration per mole of TA added,  $\eta = \Delta\text{DIC}/\Delta\text{TA}$  (Renforth and Henderson

2017) and is a key indicator for assessing OAE as a mitigation option (Oschlies *et al* 2017), since it affects the economic efficiency (cost per ton of CO<sub>2</sub> sequestered) and also monitoring-reporting-verification (MRV) requirements and carbon credit assignment. Many previous modeling studies have investigated large-scale OAE and its efficiency in long-term IPCC emission scenarios up to 2100 and beyond (Harvey 2008, Ilyina *et al* 2013, Köhler *et al* 2013, González and Ilyina 2016, Hauck *et al* 2016, Lenton *et al* 2018, Köhler 2020). However, despite the seemingly simple definition of  $\eta$ , there are important differences between studies in how the efficiency of OAE is defined and calculated, making estimates of  $\eta$  difficult to compare. It is well known that  $\eta$  depends on the chemical state of the surface ocean (e.g. Middelburg *et al* 2020, Hinrichs *et al* 2023), which is projected to change due to the anthropogenic CO<sub>2</sub> disturbance during the course of this century and beyond. Yet, the consequences of this dependency for long-term deployment scenarios of OAE have never been systematically explored. Many of the studies cited above, have investigated OAE under scenarios of very high future emissions, biasing available estimates of overall OAE efficiency towards high CO<sub>2</sub> futures. However, if OAE is deployed to achieve the Paris-Agreement temperature targets, strong CO<sub>2</sub> emission reductions are required, and plausible long-term emission pathways will show declining and net-negative CO<sub>2</sub> emissions. A recent study by Jürchott *et al* (2023) showed that the efficiency of artificial upwelling critically depends on the assumed emission pathway.

The goal of this study is to provide a sound definition of different efficiency measures, and to systematically explore the effects of the long-term background scenario on the simulated efficiency of OAE. We use idealized Earth system model (ESM) simulations, to attribute changes in  $\eta$  to the invasion of anthropogenic CO<sub>2</sub> into the surface ocean and to climate change. We then use ESM simulations of the SSP5-3.4 pathway of the Coupled Model Intercomparison Project Phase 6 (CMIP6; Eyring *et al* 2016) ScenarioMIP (O'Neill *et al* 2016) to show that our finding from the idealized simulations are indeed relevant for more realistic scenarios.

## 2. Methods

### 2.1. Efficiency of OAE

The (chemical) efficiency of OAE is defined as  $\eta = \Delta \text{DIC} / \Delta \text{TA}$ . In a laboratory this efficiency could be measured by adding TA to a seawater sample and waiting until a new equilibrium with the CO<sub>2</sub> in ambient air has been established. Alternatively, since we know the governing equations and reaction rate constants of the sea-water CO<sub>2</sub> system, we can express this efficiency following Tyka *et al* (2022) as

$$\eta_T = \frac{\partial \text{DIC}}{\partial \text{TA}} = \frac{\partial p\text{CO}_2}{\partial \text{TA}} \bigg/ \frac{\partial p\text{CO}_2}{\partial \text{DIC}} \approx \frac{1}{3 - 2\text{DIC}/\text{TA}}, \quad (1)$$

where, for the right-hand side approximation, we have assumed  $\text{DIC} \approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  and  $\text{TA} \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ . We use the subscript *T* (for ‘theoretical’) to indicate that this is not the efficiency that can be expected in real-world deployment of OAE, because equation (1) assumes that a water parcel attains full equilibrium with the atmosphere. However, if alkalinity is added to the ocean surface, some part of it is mixed downward before an equilibrium with the atmosphere can be reached. A considerable part of CO<sub>2</sub> sequestration might therefore occur with a time lag of years to decades and outside the areas where TA has been added (e.g. He and Tyka 2023). Some of the added TA might be lost on even longer timescales if transported into the deep ocean. Therefore, if we estimate the efficiency of OAE using model simulations, deviations from the theoretical efficiency must be expected.

Furthermore, the efficiency of large-scale CDR interventions is influenced by Earth system feedbacks such as a reduced CO<sub>2</sub> uptake by natural sinks due to the decreased atmospheric CO<sub>2</sub> content (Keller *et al* 2014, 2018a). Such carbon-cycle feedback effects are not specific to a certain CDR method, and they depend on the scale of CDR (small-scale deployment will not significantly modify carbon-cycle feedbacks). Here, we distinguish the Earth system efficiency ( $\eta_{\text{ES}}$ ) and the capture efficiency ( $\eta_{\text{C}}$ ), the former including the effect of carbon-cycle feedbacks. These efficiencies can be derived from model simulations by

$$\eta_i = (F_{\text{OAE}} - F) / \Delta \text{TA}, \text{ with } i = \text{C or ES}. \quad (2)$$

Here,  $F_{\text{OAE}}$  and  $F$  are the globally integrated CO<sub>2</sub> fluxes in a simulation with and without OAE, respectively. Whether the efficiency resulting from equation (2) is the Earth system efficiency  $\eta_{\text{ES}}$  or the capture efficiency  $\eta_{\text{C}}$  depends on the simulation design. If atmospheric CO<sub>2</sub> is prescribed (as in our idealized model simulations, see section 2.2), there are no carbon-cycle feedbacks that could act via changes in atmospheric CO<sub>2</sub> concentration and the carbon uptake by OAE is the only process that alters the carbon fluxes. Therefore, if equation (2) is applied to a pair of concentration-driven simulations, it results in the capture efficiency  $\eta_{\text{C}}$ . If simulations are driven by CO<sub>2</sub> emission (as our SSP5-3.4 scenario, see section 2.3), atmospheric CO<sub>2</sub> concentration will be lower in the simulation with large-scale OAE, such that carbon fluxes are not only influenced by the OAE deployment but are decreased by carbon-cycle feedbacks. In this case, application of equation (2) will result in  $\eta_{\text{ES}}$  which is lower than  $\eta_{\text{C}}$ . To derive the capture efficiency  $\eta_{\text{C}}$  from emission-driven simulations, it is

**Table 1.** Idealized simulations with and without OAE deployment used in this study to derive the OAE efficiencies indicated in the last table row. The prescribed rate of increase of atmospheric CO<sub>2</sub> (0.5% or 1% per year) is specified in the simulation names. The subscripts in the simulation names with OAE deployment indicate the rate of TA addition (0.14 or 0.56 Pmol TA per year). All simulations are freely available through the Earth System Grid Federation (ESGF) or the Norwegian Research Data Archive under the DOIs given in parenthesis following the simulation name.

Model configuration for idealized simulations (CO <sub>2</sub> prescribed)			
	Standard	Radiative forcing fixed at pre-industrial level	Standard
No OAE	full-1% (10.22033/ESGF/CMIP6.7802)	no-clim-1% (10.22033/ESGF/CMIP6.13724)	Control (10.22033/ESGF/CMIP6.8217)
	full-0.5% (10.11582/2024.00072)	no-clim-0.5% (10.11582/2024.00069)	
With OAE	full-1%-OAE <sub>0.14</sub> (10.11582/2024.00068)	no-clim-1%-OAE <sub>0.14</sub> (10.11582/2024.00085)	control-OAE <sub>0.14</sub> (10.11582/2024.00074)
	full-1%-OAE <sub>0.56</sub> (10.11582/2024.00073)	no-clim-1%-OAE <sub>0.56</sub> (10.11582/2024.00084)	control-OAE <sub>0.56</sub> (10.11582/2024.00075)
	full-0.5%-OAE <sub>0.56</sub> (10.11582/2024.00070)	no-clim-0.5%-OAE <sub>0.56</sub> (10.11582/2024.00071)	
Derived efficiencies	Transient OAE capture efficiency $\eta_C$	Transient OAE capture efficiency $\eta_C$ without climate change effects	Steady state OAE capture efficiency $\eta_C$

necessary to conduct an additional model simulation (see section 2.3).

## 2.2. Idealized model simulations

Our simulation design (table 1) builds on pairs of idealized simulations with the Norwegian ESM NorESM2-LM (Seland *et al* 2020, Tjiputra *et al* 2020). Each pair consists of a simulation with and without OAE and we derive OAE efficiencies according to equation (2). In simulations with transient CO<sub>2</sub> forcing, the atmospheric CO<sub>2</sub> concentration is prescribed and rises continuously at a rate of 1% (0.5%) per year until quadrupling (doubling). No other forcings than atmospheric CO<sub>2</sub> concentration are varied. In addition to a ‘full’ model configuration, we also run a ‘no-clim’ configuration, where the radiative forcing (i.e. the CO<sub>2</sub> concentration in the radiation code) is kept constant at pre-industrial level. In these pairs of simulations, there is no climate change signal such that we can investigate changes in OAE efficiency due to rising atmospheric CO<sub>2</sub> without the effects of climate change. A pair of pre-industrial control simulations (‘control’, simulations with fixed pre-industrial CO<sub>2</sub> concentration) with and without OAE is used to determine the steady state OAE efficiency.

We have simulated an idealized OAE deployment at two different rates of TA addition, following the protocol of the CDR Model Intercomparison project (CDRMIP; Keller *et al* 2018b). This idealized deployment does not correspond directly to any of the OAE methods that have been proposed, which differ in the feedstock used, the pre-processing of materials, the distribution and delivery of materials to the ocean, and the reaction pathways that increase TA (Renforth and Henderson 2017). We also do not consider equilibrated TA addition, where an alkaline solution is

equilibrated with atmospheric CO<sub>2</sub> before it is added to the ocean (Rau and Caldeira 1999, Hartmann *et al* 2023). Common to all methods is that they eventually would enhance the TA of the ocean, which is the only process that we model, and thereby increase the oceanic carbon pool and decrease the atmospheric CO<sub>2</sub> pool by a corresponding amount. The results presented in this study are not particularly sensitive to the TA addition method, although the difference between  $\eta_T$  and  $\eta_C$  vanishes for perfectly equilibrated TA addition. Some of the proposed methods would also add nutrients (silicate, iron) to the ocean, which can modify the oceanic carbon uptake via alterations of biological activity (e.g. Hauck *et al* 2016). In this study we ignore such additional effects and consider only carbon uptake due to changes in surface ocean TA. In our idealized set-up, alkalinity is added homogeneously to the surface ocean between 70° N and 60° S by increasing the model variable TA at a rate of 0.14 Pmol TA yr<sup>-1</sup> and 0.56 Pmol TA yr<sup>-1</sup>. Note that these rates are not based on considerations of technical or socio-economic feasibility.

## 2.3. Scenario simulations

To investigate the emission-path dependence of OAE efficiency in a plausible emission scenario, we use NorESM2-LM simulations of the SSP5-3.4 scenario (table 2). This is an overshoot pathway that assumes unmitigated high CO<sub>2</sub> emissions until 2040 and aggressive mitigation thereafter, including large-scale deployment of land-based CDR (O’Neill *et al* 2016). In contrast to the idealized simulations, these scenario simulations are run in CO<sub>2</sub> emission-driven mode, such that the atmospheric CO<sub>2</sub> concentration evolves according to emissions into the atmosphere and CO<sub>2</sub> exchanges with the ocean and terrestrial biosphere.



**Table 2.** Scenario simulations with and without OAE deployment used in this study. All simulations are freely available through the Earth System Grid Federation (ESGF) or the Norwegian Research Data Archive under the DOIs given in parenthesis following the simulation name.

Scenario simulations		
No OAE	SSP5-3.4 (10.22033/ESGF/CMIP6.13747)	Standard scenario, CO <sub>2</sub> emission driven, with land-based CDR
	SSP5-3.4-B2 (10.11582/2024.00076)	Scenario with CO <sub>2</sub> prescribed from SPP5-3.4-OAE, needed to determine $\eta_C$
With OAE	SSP5-3.4-OAE (10.11582/2024.00077)	As SSP5-3.4, but with additional OAE. $\eta_{ES}$ can be derived from this simulation and the standard SSP5-3.4 scenario

In addition to the standard SSP5-3.4 scenario, we have performed an OAE simulation, which includes, next to the land-based CDR assumed in SSP5-3.4, OAE deployment similar to the CDRMIP protocol: TA ( $0.135 \text{ Pmol yr}^{-1}$ ) is added to the ocean surface between  $70^\circ \text{ N}$  and  $60^\circ \text{ S}$ , with a linear ramp-up phase between 2025 and 2035. Since these two variants of the SSP5-3.4 scenario are emission driven, and atmospheric CO<sub>2</sub> concentrations and carbon-cycle feedbacks differ, the efficiency calculated from this pair of simulations according to equation (2) is the Earth system efficiency  $\eta_{ES}$ . To determine the capture efficiency  $\eta_C$ , which excludes the effect of carbon-cycle feedbacks, we conduct a third simulation which follows the same atmospheric CO<sub>2</sub> trajectory as the SSP5-3.4-OAE simulation but in CO<sub>2</sub> concentration-driven mode with OAE switched off. This simulation, which we refer to as ‘baseline 2’ (B2, table 2), provides us with the air-sea carbon fluxes at the same atmospheric CO<sub>2</sub> concentration as the OAE scenario, but without the air-sea CO<sub>2</sub> flux caused by OAE. Therefore, we can calculate  $\eta_C = (F_{OAE} - F_{B2})/\Delta TA$ , where  $F_{OAE}$  and  $F_{B2}$  are the globally integrated air-sea carbon fluxes in the SSP5-3.4-OAE simulation and the corresponding B2 simulation.

### 3. Results and discussion

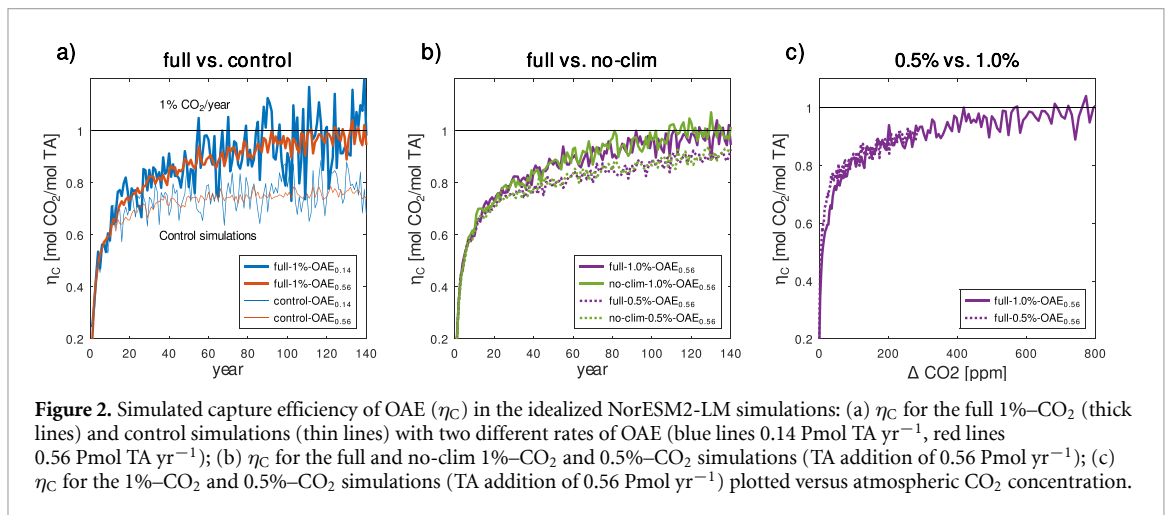
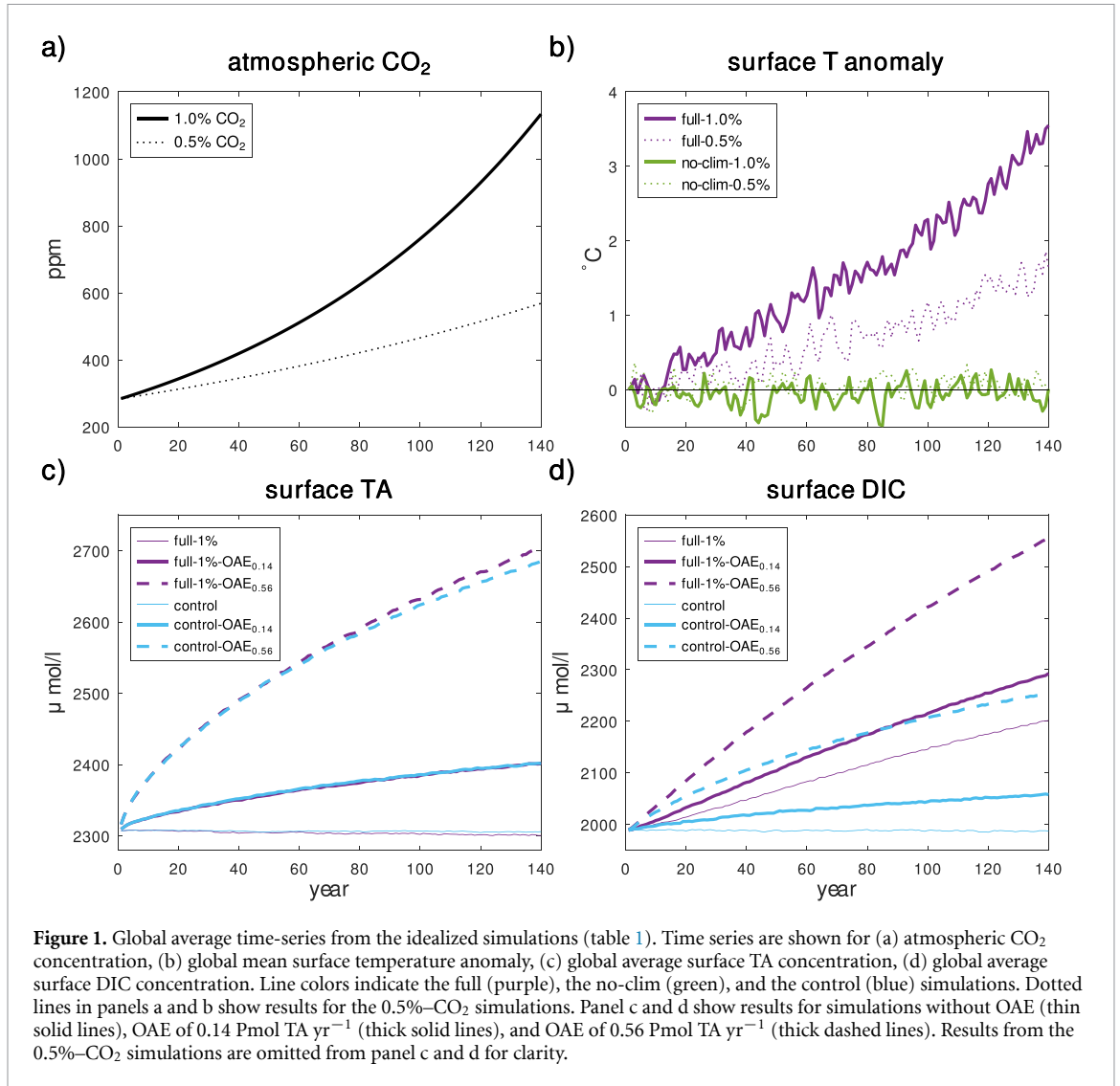
In the idealized full-1% (full-0.5%) simulation, the prescribed atmospheric CO<sub>2</sub> concentration grows from 284 to 1134 ppm (568 ppm), representing a quadrupling (doubling) of atmospheric CO<sub>2</sub> at the end of the simulation (figure 1(a)). The global mean surface temperature in the full-1% (full-0.5%) simulation increases by about  $3.5^\circ \text{ C}$  ( $1.8^\circ \text{ C}$ ), while the modeled temperature remains stable at pre-industrial conditions in the no-clim simulations (figure 1(b)). Surface TA is stable in the pre-industrial control simulation (figure 1(c)) as well as in the no-clim simulation (not shown). However, in the full simulations without OAE, which take into account the impacts of climate change, a slight decrease of surface TA occurs due to increased stratification that reduces the exchange between the surface ocean and deep waters with higher alkalinity, consistent with the study of Chikamoto *et al* (2023).

In the simulations full-1%-OAE, no-clim-1%-OAE, and control-OAE with idealized deployment of OAE, global average surface TA increases by about  $100 \mu\text{mol l}^{-1}$  by the end of the simulation for a rate of  $0.14 \text{ Pmol TA yr}^{-1}$  and by about  $400 \mu\text{mol l}^{-1}$  for the four-fold addition rate (figure 1(c)). The addition of alkalinity is slightly more effective in increasing the surface concentration of TA in the full simulations, due to increased stratification as mentioned above. The global average surface DIC concentration is not only influenced by the addition of TA and subsequent CO<sub>2</sub> uptake, but also by rising atmospheric CO<sub>2</sub> concentrations in the full (figure 1(d)) and no-clim (not shown) simulations.

#### 3.1. Simulated steady state efficiency of OAE

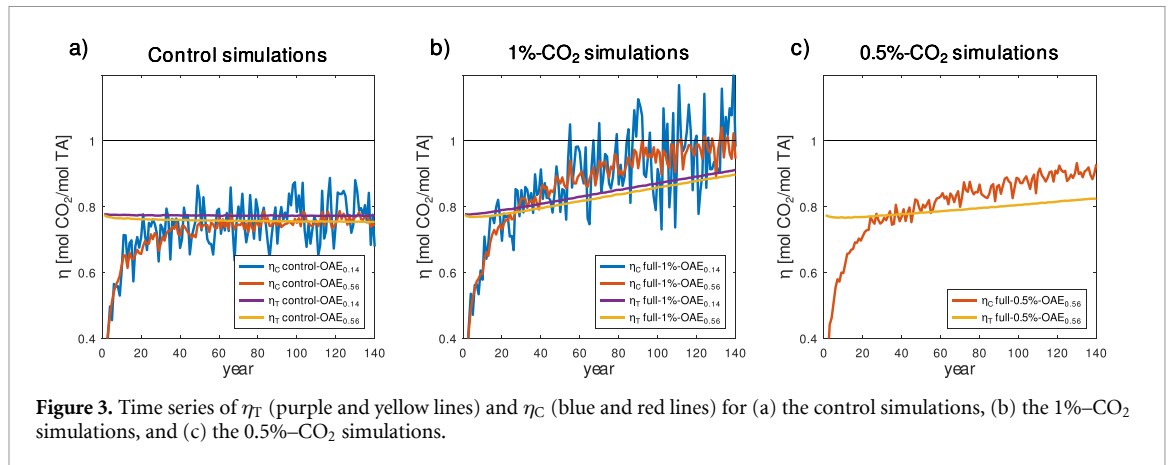
The global average capture efficiency  $\eta_C$  in the control simulations with prescribed constant pre-industrial CO<sub>2</sub> concentration and deployment of OAE is initially as low as 0.2 (figure 2(a)). After about 30–50 years of OAE deployment,  $\eta_C$  reaches a plateau where it slightly increases towards its final value of around 0.76 (average over the last 30 years of the simulation). This behavior can be explained by the timescales of equilibration, consistent with the results of He and Tyka (2023). These authors show that upon addition of TA to the ocean surface, large parts of the excess TA are diluted and mixed downward before equilibration with ambient atmospheric  $p\text{CO}_2$ , and that the time scale to full equilibration is several years to decades depending on location. In our idealized TA addition scheme, we continuously add alkalinity to the surface ocean, such that at any time  $t$ , we see the effects of TA addition at all previous times from  $t_0$  up to  $t$ , where  $t_0$  is the start of the simulation. After 30–50 years, a quasi-steady state is reached because the timespan since  $t_0$  is long enough to cover the majority of equilibration timescales at all locations. After this timespan, we expect  $\eta_C$  to roughly equal  $\eta_T$ , the fully equilibrated theoretical efficiency (see section 3.3).

There is very little difference between the lower and higher rate of TA addition (figure 2(a)), except for the much larger variability of  $\eta_C$  at the lower rate. This is because  $\eta_C$  is calculated from the air-sea CO<sub>2</sub> flux difference between two simulations (with and without OAE, equation (2)), which are not in phase



with respect to modes of internal variability. For the lower rate of TA addition, the internal variability has a larger impact relative to the signal of OAE induced

CO<sub>2</sub> fluxes, but the longer-term averages are very similar (the difference being less than 2.5% when averaged over the last 30 years of the simulations, table 3).



**Figure 3.** Time series of  $\eta_T$  (purple and yellow lines) and  $\eta_C$  (blue and red lines) for (a) the control simulations, (b) the 1%–CO<sub>2</sub> simulations, and (c) the 0.5%–CO<sub>2</sub> simulations.

**Table 3.** Simulated theoretical and capture efficiencies in the 1% and 0.5% simulations. Values are an average over the last 30 years of the simulations.

Simulation	$\eta_T$ (mol DIC/mol TA)	$\eta_C$ (mol DIC/mol TA)
control-OAE <sub>0.14</sub>	0.7723	0.7778
control-OAE <sub>0.56</sub>	0.7544	0.7610
full-1%-OAE <sub>0.14</sub>	0.8968	0.9928
full-1%-OAE <sub>0.56</sub>	0.8833	0.9769
full-0.5%-OAE <sub>0.56</sub>	0.8180	0.9010
no-clim-1%-OAE <sub>0.14</sub>	0.9049	1.0301
no-clim-1%-OAE <sub>0.56</sub>	0.8920	1.0007
no-clim-0.5%-OAE <sub>0.56</sub>	0.8225	0.9034

### 3.2. Simulated efficiency of OAE in idealized transient simulations

In the full-1%-OAE simulations (figure 2(a)),  $\eta_C$  is significantly larger than in the control-OAE simulations and shows an increasing trend also after the first 30–50 simulation years. Towards the end of the simulations (average over the last 30 years) we find  $\eta_C \approx 0.98$  for the full-1%-OAE simulations compared to  $\eta_C \approx 0.76$  for the control-OAE simulations. As seen above for the control-OAE simulations, the carbon uptake of the full-1%-OAE simulations scales almost perfectly with the rate of TA addition, resulting in very similar values of  $\eta_C$  for the two different rates of TA addition with a difference of less than 2.5%.

What are the reasons for the differences in OAE capture efficiencies between the transient and control simulations? As we have seen above (figure 1(c)), a more stratified ocean makes OAE deployment potentially more efficient by retaining more of the added alkalinity close to the ocean surface. On the other hand, a high-alkalinity ocean generally loses more CO<sub>2</sub> when sea-water temperature increases (see supplementary information and figure S1). By comparing the efficiencies in the full and no-clim simulations (figure 2(b) and table 3), we find that the net effect of climate change is a reduction of OAE efficiency, but this effect remains very small. When averaged over the last 30 years of the simulations, climate change reduces the efficiency of OAE by less than 4% for the 1%–CO<sub>2</sub> simulations, and by less

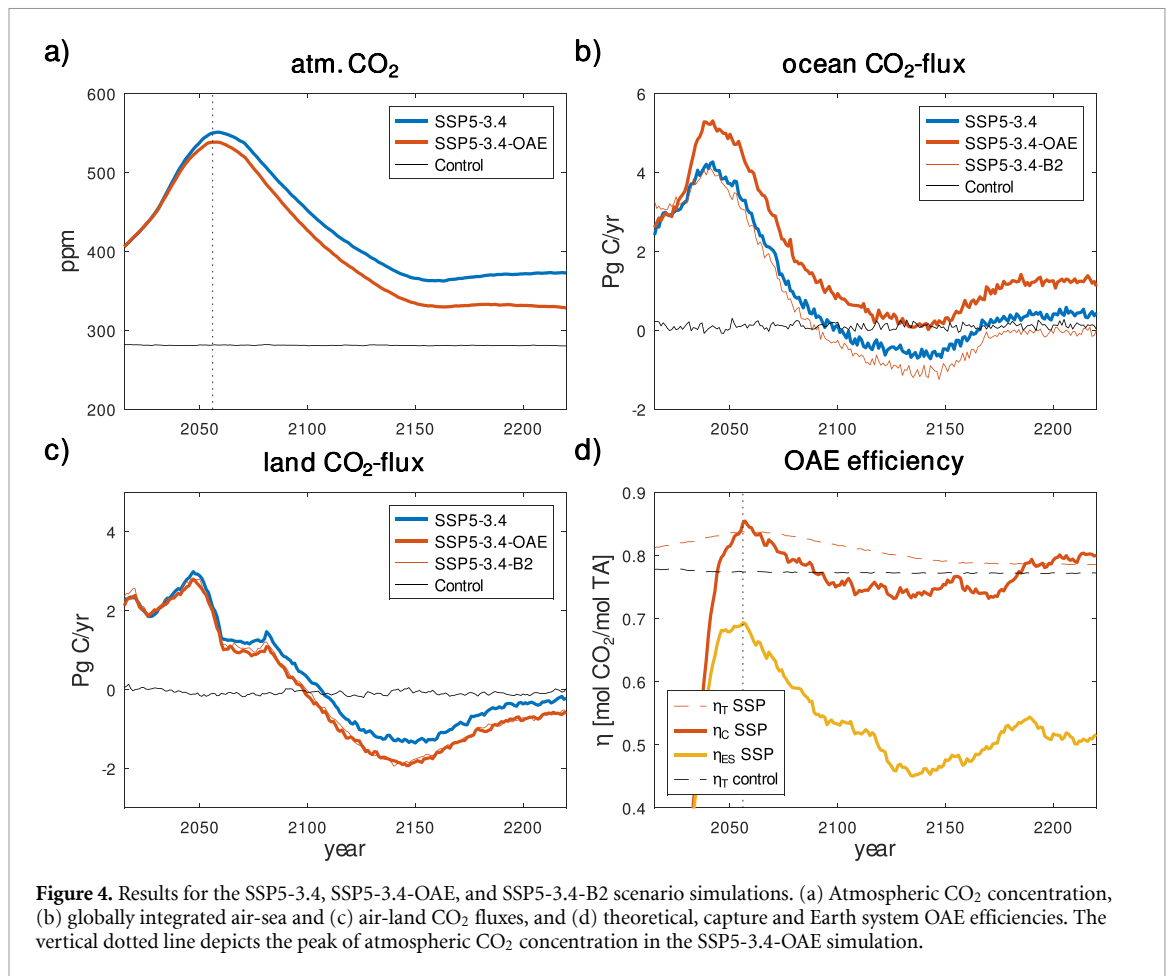
than 1% for the 0.5%–CO<sub>2</sub> simulations. Therefore, climate change effects cannot explain the larger efficiencies in the transient compared to the control simulations. Instead, these differences must be due to chemical effects (changing sensitivities of the CO<sub>2</sub>-system), which we will investigate further in the next section.

### 3.3. Theoretical versus simulated capture efficiency

The theoretical efficiency of OAE ( $\eta_T$ ) is calculated from surface DIC and TA according to equation (1). Figure 3 shows a close agreement between theoretical efficiencies for the low and high rates of TA addition with differences of less than 2.5% (slightly larger for the low rate, table 3) similar to what we have found for  $\eta_C$ . There is little interannual variability for  $\eta_T$  since this quantity is calculated from DIC and TA fields of the same simulation, which strongly covary.

For the control simulations (figure 3(a)), there is also a close agreement between  $\eta_C$  and  $\eta_T$ , after the initial increase of  $\eta_C$ , with values around 0.76 (average over the last 30 years of the simulations). This supports the hypothesis that in our simulations with continuous TA addition,  $\eta_C$  approaches  $\eta_T$  once the simulation covers a long enough time interval that the major equilibration timescales for all regions are represented.

For the full-1%-OAE simulations (figure 3(b)), there is a clear difference between  $\eta_C$  and  $\eta_T$ , which can be explained by the changing sensitivities of the



carbonate chemistry system with increasing DIC concentration. Both,  $\eta_C$  and  $\eta_T$  show an increasing trend over time consistent with a larger carbon sequestration per mol TA at high DIC values (figure S1). However, while  $\eta_T$  increases linearly to values of 0.88–0.90, the increase for  $\eta_C$  is much larger, reaching values of 0.98–0.99 (average over the last 30 years of the full simulations, table 3). This effect can be explained by the fact that the same atmosphere–ocean  $p\text{CO}_2$  disequilibrium leads to a larger air-sea CO<sub>2</sub> flux under high alkalinity as shown in the supplementary and in figure S1. The theoretical efficiency  $\eta_T$  does not account for the CO<sub>2</sub> partial pressure disequilibrium between atmosphere and ocean in the transient simulations. Therefore, the increase in  $\eta_T$  indicates only the increased CO<sub>2</sub> sequestration due to an increased sensitivity to TA addition at high DIC concentrations (figure S1), and we use  $\eta_T$  to estimate the contribution of this effect. The increase from the preindustrial  $\eta_C \approx \eta_T = 0.76$  to  $\eta_T = 0.88$  and  $\eta_C = 0.98$  indicates that the effect of the transient disequilibrium is 43% of the total efficiency increase in the full-1%-OAE simulations.

For the full-0.5%-OAE simulation (figure 3(c)),  $\eta_T$  and  $\eta_C$  increase at a significantly slower rate with values of 0.82 and 0.90, respectively, towards the end of the full-0.5%-OAE simulation. Interestingly, this

indicates that the relative effect of the transient disequilibrium is larger (relative to the change in direct efficiency of TA addition), namely 57% of the total effect. We note that we have used the approximation for  $\eta_T$  made in equation (1) and that numbers given here for the effect of the transient disequilibrium will slightly differ for an exact calculation.

### 3.4. OAE efficiency in an overshoot scenario simulation

Atmospheric CO<sub>2</sub> concentration in our SSP5-3.4-OAE scenario peaks in 2056, three years earlier than in the standard SSP5-3.4 (figure 4(a)). After the peak it declines in both simulations until about 2155. The land-based negative emissions in SSP5-3.4 are ramped back to zero between 2140 and 2170 (Meinshausen *et al* 2020), but in our SSP5-3.4-OAE, the deployment of OAE continues until 2220. Therefore, the atmospheric CO<sub>2</sub> concentration slightly increases again after about 2160 in the standard scenario, because carbon back-flux from the ocean and the terrestrial biosphere (figures 4(b) and (c)) is not countered by negative emissions, an effect that is reduced in SSP5-3.4-OAE. The air-sea CO<sub>2</sub> fluxes in the SSP5-3.4-B2 simulation are always smaller (less ocean CO<sub>2</sub> uptake and increased CO<sub>2</sub> back-flux to the atmosphere) than in the standard scenario,



and considerably smaller than in the SSP5-3.4-OAE simulation, since OAE is switched off in the B2 simulation. The air-land CO<sub>2</sub> fluxes are the same in the SSP5-3.4-OAE and B2 simulations by construction since in both simulations the land ‘sees’ the same CO<sub>2</sub> concentration.

The simulated (capture and Earth system) efficiencies in the SSP5-3.4-OAE scenario reach their maximum one year after the atmospheric CO<sub>2</sub> concentration. After this peak of  $\eta_C = 0.85$  and  $\eta_{ES} = 0.69$ , there is a rapid decline until  $\eta_C$  and  $\eta_{ES}$  reach minimum values of 0.73 and 0.45, respectively. Importantly,  $\eta_C$  remains significantly smaller than  $\eta_T$  during the period with large land-based CDR in this scenario (until 2170). On average, during much of this period, OAE does not act to take up additional CO<sub>2</sub>, but to reduce oceanic outgassing, which occurs after around 2090 in our model (figure 4(b)), in response to land-based CDR. As discussed above and shown in figure S1, a high alkalinity ocean is more prone to losing carbon to the atmosphere, when the partial pressure difference across the air-sea interface becomes negative. The decline of  $\eta_C$  in our SSP5-3.4-OAE scenario demonstrates that this effect is indeed relevant in a plausible future scenario.

#### 4. Conclusions

Model simulations will be needed to assess deployment of OAE and to implement accounting schemes for the CDR that is achieved through OAE. We have shown that the chemical efficiency of OAE (mol of CO<sub>2</sub> removed per mol of TA added) depends critically on the background emission scenario, under which a long-term deployment of OAE is assumed. We have described two main mechanisms that explain an increase of the efficiency of OAE with higher atmospheric CO<sub>2</sub> concentrations. First, more CO<sub>2</sub> is taken up per addition of 1 unit of TA when atmospheric CO<sub>2</sub> increases. Second, a high-alkalinity ocean takes up a larger fraction of anthropogenic emissions. Importantly, both of these effects are reversed under decreasing atmospheric CO<sub>2</sub> as we have shown for a scenario simulation with large scale deployment of both OAE and land-based CDR. The effects of climate change (e.g. warming, stratification, and circulation changes) on the efficiency of OAE are only of secondary importance as we have shown using idealized model simulations where the climate change signal is suppressed.

The continuous and near-global coverage OAE deployment considered in this study is highly idealized. In a hypothetical real-world deployment, OAE would happen much more localized and intermittent (e.g. Bach *et al* 2023, He and Tyka 2023). However,

our main findings are based on well-understood carbon chemistry, and we believe that our results are relatively robust and apply to more realistic deployment scenarios, at least qualitatively. Future work should further investigate the long-term scenario dependence of OAE efficiency in local and regional realistic deployment scenarios.

Given the scenario-dependent chemical efficiency of OAE, any accounting scheme that uses TA addition information as a basis for allocating carbon offset credits should also apply scenario-specific conversion rates to calculate offset credits from the amount of alkaline material added to the ocean. The SSP5-3.4 OAE simulations show that assuming a constant conversion rate of about 0.8 (as suggested by  $\eta_T$  at the start of the SSP5-3.4 OAE scenario) throughout the period to 2100 would not properly incentivize the optimal use of OAE. Scenario-specific conversion rates would instead increase the incentives for OAE deployment when it is most needed around the maximum of atmospheric CO<sub>2</sub> concentrations, while also supporting its phase-down or even phase-out under declining atmospheric CO<sub>2</sub> conditions. The simulations also show that the Earth system OAE efficiency ( $\eta_{ES}$ ) is significantly lower than the OAE capture efficiency ( $\eta_C$ ). Both pieces of information are needed, the former for cost-benefit climate policy considerations and the latter for cost-effectiveness climate policy considerations. Obviously, deciding about optimal climate policies and CDR deployment in a cost-benefit sense requires to consider the Earth system perspective including all feedbacks as reflected in  $\eta_{ES}$ . However, given a climate target and assuming that a corresponding climate policy is in place with instruments like emissions trading implemented, the target is to be achieved cost-efficiently, which requires that different CDR methods can be compared in terms of their cost per amount of carbon captured. Accordingly, in such a cost-effectiveness framework, the capture efficiency  $\eta_C$  would be relevant for determining the amount of carbon offset credits. Note that currently, there is neither an agreed-on method for MRV and carbon offset accounting for OAE, nor is there a framework that would integrate OAE and marine CDR in general into climate policies. In this context, our study highlights the importance of considering variable scenario-dependent long-term efficiencies for OAE and the critical role of model simulations in addressing this issue.

#### Data availability statement

The NorESM2-LM model output used in this study is freely available through the Earth System Grid Federation (ESGF) and the Norwegian Research Data Archive. DOIs for each simulation are given in

tables 1 and 2. NorESM2 including the newly added OAE source code is freely available on github <https://github.com/NorESMhub/NorESM/archive/refs/tags/release-noresm2.0.7.tar.gz>.

All data that support the findings of this study are included within the article (and any supplementary files).

## Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation programme (Project OceanNETs, Grant Agreement No. 869357) and from the European Union's Horizon Europe research and innovation program (Project RESCUE, Grant Agreement No. 101056939). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them. Supercomputing and storage resources for NorESM2 simulations were provided by UNINETT Sigma2 (Projects nn10054k/ns10054k). None of the authors has any competing interest.

## ORCID iD

Jörg Schwinger  <https://orcid.org/0000-0002-7525-6882>

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