Efficiency metrics for ocean alkalinity enhancements under responsive and prescribed atmosphere conditions.

Michael D. Tyka[1]

[1]Google Inc., 601 N 34th St, Seattle, WA 98103, USA

Abstract. Ocean alkalinity enhancement (OAE) and direct ocean capture (DOC) are emerging as promising technologies for enacting negative emissions. Due to the delayed air-sea gas exchange, potential for premature subduction of surface water parcels and extensive horizontal transport on timescales for equilibration, the direct experimental measurement of induced CO_2 uptake remains elusive. Therefore, the problem of measurement,

5   reporting and verification (MRV) hinges on general circulation models. A number of recent studies have assessed the efficiency of OAE using different model setups and different metrics. Some models use prescribed atmospheric CO_2 levels, while others use fully coupled earth-system models. The former ignores atmospheric feedback effects, while the latter explicitly models them. In this paper it is shown that, even for very small OAE deployments, which do no substantially change atmospheric pCO_2, the change in oceanic CO_2 inventories

10   differs significantly between these methods, due to atmospheric feedback causing some ocean CO_2 offgassing. However, an analogous offgassing occurs during direct air capture (DAC). Due to these feedback effects, care must be taken to compute the correct metrics when assessing OAE efficiency with respect to determining negative emissions credits, as opposed to determining the effect on global temperatures. This paper examines the commonly used metrics of OAE efficiency, their exact physical meanings, the assumptions inherent in their

15   use and the relationship between them. It is shown that the efficiency metric $\eta(t)$, used in prescribed pCO_2^{atm} simulations, equals the equivalent schedule of a gradual direct air capture (DAC) removal in a fully coupled system.

1 Introduction

In recent years, the search for technologies capable of removing CO_2 from the atmosphere has intensified.

20   Among other approaches, there has been a rise in interest in marine carbon dioxide removal (mCDR) (NationalAcademiesPress, 2022), in particular ocean alkalinity enhancement (OAE) (Oschlies et al., 2023; Renforth and Henderson, 2017) and cultivation of algae (Ritschard, 1992). Unlike terrestrial CDR approaches, which remove CO_2 directly from the atmosphere, mCDR approaches either remove CO_2 from the surface ocean or increase the capacity of surface ocean water to hold CO_2 by adding alkalinity. Either way, the partial pressure of CO_2 (pCO_2)

25   is reduced in surface waters, which causes a subsequent transfer of CO_2 from the atmosphere to the ocean. This uptake does not happen instantly, but instead occurs gradually (He and Tyka, 2023; Bach et al., 2023), with the

potential for the CO_2 deficient water parcel to be subducted and removed from contact with the atmosphere. In
the latter case, the mCDR potential can be delayed for centuries to millennia if the water parcel does not remix
with the surface layers on timescales relevant for the CDR effort. Several studies have been published which

30 aim to quantify the equilibration dynamics, and the equilibration e-folding times (Wang et al., 2023; Tyka et al.,
2022; He and Tyka, 2023; Zhou et al., 2024; Suselj et al., 2024). It was shown that the equilibration kinetics and
completeness varies significantly depending on the induction location and season.

How much CO_2 is drawn into the ocean upon addition of some quantity of alkalinity ? Changing the al-
kalinity of seawater by a small amount ΔAlk reduces the pCO_2 by $\frac{\partial pCO_2}{\partial Alk}\Delta Alk$, while increasing DIC by a

35 small amount ΔDIC increases the pCO_2 by $\frac{\partial pCO_2}{\partial DIC}\Delta DIC$. Therefore, the relative quantity of DIC that exactly
counterbalances the pCO_2 for particular increase in alkalinity is

$$\eta_{CO_2} = \left.\frac{\partial[DIC]}{\partial[Alk]}\right|_{pCO_2} \tag{1}$$

Depending on the local state of the carbonate system $\eta_{CO_2} \approx 0.83$ (Renforth and Henderson, 2017), varying
from 0.9 closer at the poles to 0.79 at the equator (η_{CO_2} is the inverse of the isocapnic quotient, as introduced by

40 Humphreys et al. (2018)). Given that equilibration isn't instantaneous, it makes sense to define a time-dependent
OAE efficiency factor which tracks the equilibration from the moment the alkalinity is altered:

$$\eta(t) = \Delta DIC(t)/\Delta Alk, \tag{2}$$

where ΔAlk is the quantity of alkalinity added and $\Delta DIC = \sum DIC^{\text{OAE}} - \sum DIC^{\text{Ref}}$ is the difference
in the total inventory of DIC between a perturbed and a reference simulation. In other words, $\eta(t)$ tracks the

45 progress of the equilibration (Tyka et al., 2022; He and Tyka, 2023; Zhou et al., 2024; Suselj et al., 2024)
by quantifying the excess CO_2 taken up by the ocean relative to the unperturbed reference simulation. These
simulations have typically been carried out with the partial CO_2 pressure in the atmosphere (pCO_2^{atm}) held
constant or prescribed (Wang et al., 2023; Tyka et al., 2022; He and Tyka, 2023; Zhou et al., 2024; Suselj et al.,
2024; Köhler et al., 2013; Burt et al., 2021), meaning that the pCO_2^{atm} in the perturbed simulation equals that in

50 the reference.

However, in reality, the uptake of CO_2 by the ocean would be accompanied by an equal reduction of atmo-
spheric CO_2, which in turn affects the pCO_2 gradient across the sea-air interface (Jin et al., 2008; Oschlies, 2009;
Schwinger et al., 2024). This feedback acts to reduce the total transfer of CO_2 from the atmosphere to the ocean.
Additional couplings of this sort also exist as the atmosphere is further coupled with the terrestrial carbon sink

55 (Oschlies, 2009). Of course, the system relaxation observed when considering coupled reservoirs is not unique
to OAE. It applies also to direct air capture and fossil fuel emissions (Zarakas et al., 2024; Stocker et al., 2014;
Jeltsch-Thömmes et al., 2024), with coupled reservoirs acting to buffer the perturbation and reduce its magnitude
over time.

OAE simulations have also been conducted in models which include full atmosphere treatment, terrestrial
feedbacks and account for future emission scenarios and ocean dynamics in an integrated fashion (Keller et al.,
2014; González and Ilyina, 2016; Lenton et al., 2018; Köhler, 2020; Jeltsch-Thömmes et al., 2024; Schwinger
et al., 2024). In such environments, the metric $\Delta DIC(t)/\Delta Alk$ tracks a fundamentally different quantity, as
it measures the combined effect of intervention-driven CO_2 uptake and subsequent reservoir feedbacks. These
studies generally simulated the addition of large quantities of alkalinity over long periods, perhaps leading to the
impression that system feedback effects can be ignored for small, short and or local additions such as done when
calculating OAE impulse response functions (Zhou et al., 2024).

Given the central importance of models in addressing the measurement, reporting and verification (MRV)
challenge for OAE, it is worth carefully examining the physical meaning of the above metrics in the two kinds
of atmosphere treatments, in order to avoid confusion over their meaning.

Given that a prescribed atmosphere is not an accurate representation of reality, what is the physical meaning of
$\Delta DIC(t)/\Delta Alk$ obtained under prescribed pCO_2 conditions ? Is the assumption of an unresponsive atmosphere
justified when only very small quantities of alkalinity are considered, as encountered during pulse injection
studies (He and Tyka, 2023; Zhou et al., 2024; Suselj et al., 2024), because it would only cause an infinitesimally
small change in global atmospheric pCO_2 ?

This paper seeks to clarify these questions with the help of a simple numerical general circulation model and
an analytical box model, with the hope to give a more precise definition of $\eta(t)$ and establish equivalent metrics
to use in the case of fully coupled earth-system models.

2 Methods

To compare the effect of different atmosphere treatments, a simple numerical general circulation model was
run using MITgcm (Marshall et al., 1997). The purpose here is not to simulate detailed realism as would be
obtained from a full earth-system model, but to interrogate and compare the basic principles and behavior of OAE
under coupled and prescribed atmospheres. The simulation had a resolution of $2.8° \times 2.8°$ (a 128x64 worldwide
spherical polar grid) and 20 exponentially spaced depth levels, from 10m thick at the surface to 690m thick at the
sea floor. The simulation was initialized and forced as detailed in Dutkiewicz et al. (2005). The MITgcm GEOM
and DIC modules were used to simulate the soft tissue and carbonate pumps, as well as ocean-atmosphere gas
exchange. In the case of a prescribed atmosphere, the pCO_2 of the atmosphere was initialized to 415μatm and
kept constant throughout. In the case of a responsive, coupled atmosphere, it was initialized in the same way, but
the pCO_2 was continuously recalculated based on the integrated total flux through the air-sea interface at each
step. For this calculation, the total dry mass of the atmosphere was assumed to be to 5.1352×10^{18} kg (Trenberth
and Smith, 2005) with a mean molecular mass of 28.97 g/mol. The total moles of dry gas in the atmosphere was
thus 1.77×10^{20} moles, the total amount of atmospheric CO_2 was 7.35×10^{20} moles.
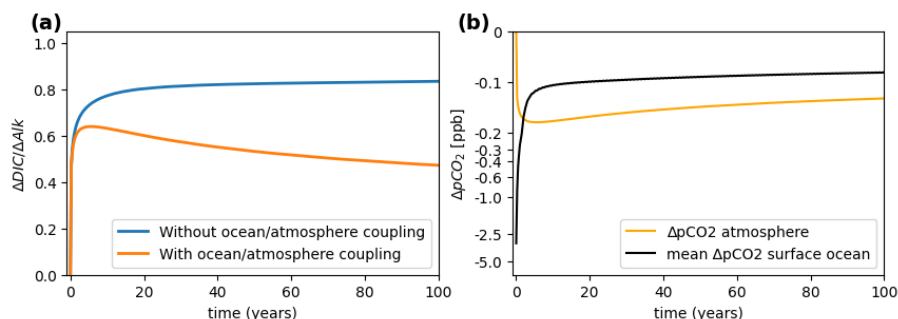
Figure 1. (a) Comparison of the increase in total ocean DIC following an ocean wide 1-month pulse of alkalinity applied to the surface layer of a total of 0.5 Tmol, under a prescribed (non-responsive) atmosphere (blue) and a coupled (responsive) atmosphere respectively (orange). Note that the total quantity of CO_2 in the atmosphere is ≈73.5 Gmol, i.e. this perturbation is tiny in comparison. **(b)** Concurrent pCO_2 changes in the atmosphere and surface ocean (under coupled simulation). The atmosphere pCO_2 decreases below that of the surface ocean after about 2 years, which the ocean off-gasses until eventual equilibrium (well beyond 100yrs).

For the pulsed OAE injections, 0.5 Tmol of alkalinity was released in a 1-month pulse similar to Zhou et al. (2024) and the total volume integrated DIC and Alk of the ocean was monitored for the rest of the simulation (100 yrs). A reference run without alkalinity addition was also conducted. Each run was repeated both with a
95 prescribed and a responsive atmosphere.

Injections were conducted as a global uniform addition as well as in patches in different locations. The uniform alkalinity additions were also conducted with different amounts (50Tmol, 500Gmol, 5Gmol), equivalent to negative emissions on the order of (170Mt, 1.7MtCO2, 170kt of CO_2). The three different point-injection locations were off the coast of Brazil (2.50°S, 37.50°W), near Iceland (61.50°N, 19.50°W) and at Hawaii'i (19.02°N,
100 155.49°E).

3 Results

3.1 Numerical circulation model

Figure 1a compares the time evolution of $\Delta DIC(t)/\Delta Alk$ for a one-month pulse release of alkalinity, simulated with a prescribed (non-responsive) and a coupled (responsive) atmosphere, respectively. It can be seen that the
105 $\eta(t)$ curve of the former approaches 0.85 as expected. In contrast, the curve obtained under responsive conditions deviates after a few years and begins to decline again, i.e. the ocean is outgassing CO_2, relative to the reference simulation. Note that the quantity of alkalinity released in these simulations was very small, just 0.5 Tmol, and the changes occurring to pCO_2^{atm} are on the order of 10^{-10} atm (Fig. 1b). Figure S2 shows results of
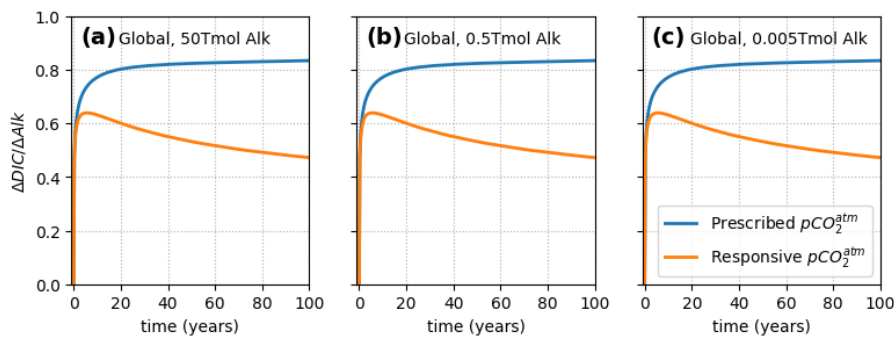
Figure 2. Increase in total ocean DIC following a worldwide 1-month pulse of alkalinity (ΔAlk) applied to the surface layer, under a prescribed (non-responsive) atmosphere (blue) and a coupled (responsive) atmosphere respectively. Three different amounts were added, between 50Tmol and 0.005Tmol. It can be seen that atmosphere feedbacks occur proportionally to the OAE perturbation size and affect $\Delta DIC(t)/\Delta Alk$ at all scales.

point injections, similar to Zhou et al. (2024) in three different point locations, with and without responsive
110 atmosphere, again showing the effect of atmosphere feedbacks on the metric $\Delta DIC/\Delta Alk$.

Figure 2 shows further simulation results but with different injection amounts. The effect of modeling a responsive atmosphere on $\Delta DIC(t)/\Delta Alk$ is observed to be the same in all cases and independent of the quantity of alkalinity released. This result confirms that under responsive atmosphere conditions, outgassing is expected (Oschlies, 2009) irrespective of the size of the alkalinity injection. This outgassing can seem counter-intuitive,
115 since the addition of alkalinity to seawater simply increases its capacity for CO_2 as calculated from the carbonate system, and begs the question why the CO_2 uptake would overshoot and then offgas, even when alkalinity is added uniformly, reducing pCO_2^{ocn} everywhere ?

This can be further illuminated when looking at the time evolution of ΔpCO_2 at the ocean surface and in the atmosphere (Figure 1b). The ΔpCO_2 of the surface ocean is maximally negative right at the moment of alkalinity
120 addition and increases back towards zero over time. This is due to both the uptake of CO_2 by the surface ocean and, critically, the dilution of alkalinized and partially equilibrated waters by mixing and subduction into depth. Or, put another way, deep water parcels, which did not receive the OAE-induced pCO_2 reduction, are now reaching the surface and outgassing to the now slightly CO_2-reduced atmosphere. The change in atmospheric ΔpCO_2 begins at zero and decreases with CO_2 transfer to the ocean. At some point during the equilibration
125 the ΔpCO_2^{atm} becomes more negative than the surface ocean, at which point a phase of outgassing occurs. As will be demonstrated later with the help of a box model, this overshoot and outgassing occurs due to continuing mixing and dilution of surface water with deep water parcels which increases surface ΔpCO_2.

Such outgassing effects caused by coupled reservoirs are of course not limited to OAE. Indeed, direct removal of CO_2 from the atmosphere (DAC) induces a similar outgassing from the ocean, similarly reducing the removal
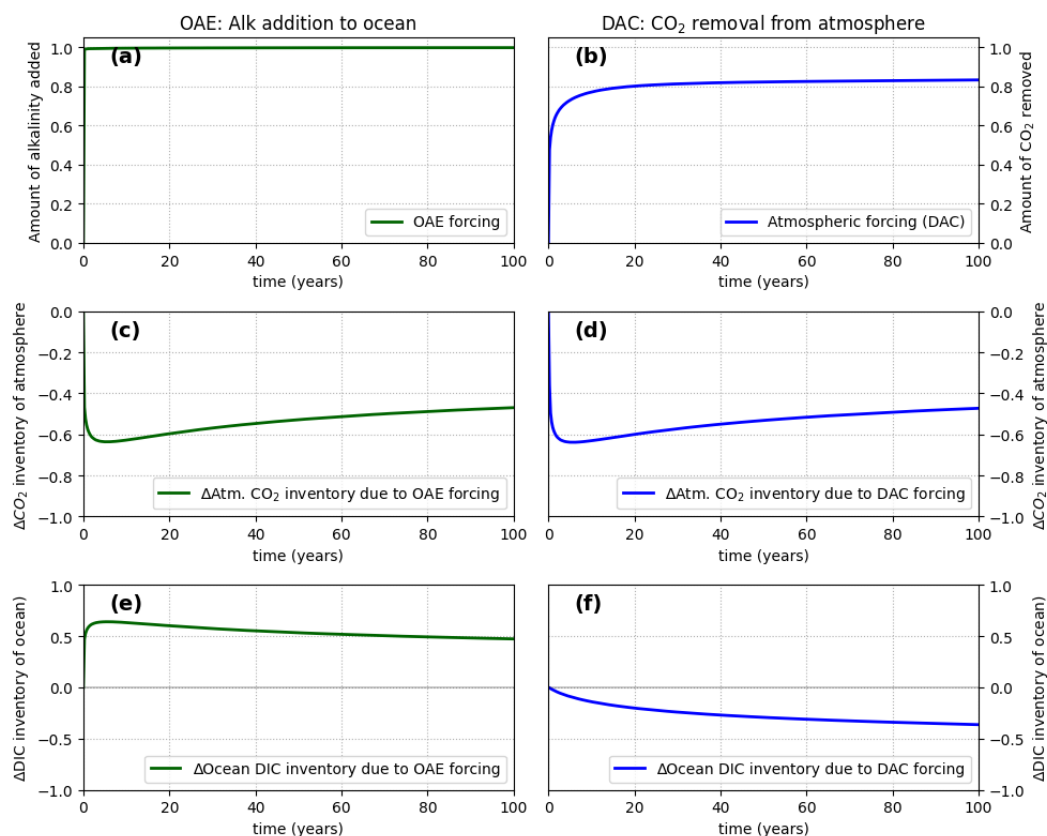
Figure 3. All simulations were conducted under responsive atmosphere conditions. **(a)** Instantaneous addition of alkalinity to the ocean (OAE pulse). **(b)** Gradual direct air capture (DAC) removal from the atmosphere. CO_2 was removed on a schedule given by the $\eta(t)$ curve corresponding to the alkalinity release done in a). Panels **(c)** and **(d)** show the respective changes in the total atmospheric CO_2 inventory under responsive atmosphere conditions. It can be seen that the perturbations in **(a)** and **(b)** lead to identical atmospheric inventory changes (panels **(c)** and **(d)**). Therefore interventions **(a)** and **(b)** can be considered equivalent negative emissions interventions from an atmospheric pCO_2 perspective. Note that the changes in the ocean inventory are not equal (panels **(e)** and **(f)**). This is because in the case of OAE, the capacity of the ocean for CO_2 is increased and thus absorbed from the atmosphere, where as in the case of DAC, CO_2 is removed from the system entirely, resulting in decreasing inventories in the atmosphere and the ocean.

130 effect on the atmosphere. Likewise, fossil fuel emissions of CO_2 fall under the same reservoir re-equilibration, with only an estimated 30% of anthropogenic emissions remaining in the atmosphere (Stocker et al., 2014).

The results above demonstrate that the metric $\Delta DIC(t)/\Delta Alk$ does not reflect the true amount of CO_2 transferred from the atmosphere to the ocean, once the feedback and coupling between the ocean and other reservoirs, such as the atmosphere, are taken into account. Do previous OAE simulations therefore overestimate

135 the effectiveness of OAE (Oschlies, 2009) or should the effectiveness of OAE be considered relative to an equivalent direct air capture removal (DAC) method (i.e. relative to emissions of fossil fuels), which are subject to the same feedback effects ? For *the purposes of assigning carbon credits*, it makes sense for the effectiveness of OAE to be measured *relative* to direct atmosphere removal (i.e DAC) or relative to fossil fuel emissions (Zarakas et al., 2024). In other words one tonne of CO_2 removal should offset the effect of one tonne of fossil

140 fuel emissions. When it comes to the slow and incomplete equilibration of surface water following an OAE deployment, the question therefore becomes: what is the equivalent CO_2 removal directly from the atmosphere compared to the removal of atmospheric CO_2 due to an alkalinity addition ? This assumes the atmosphere is comparatively rapidly mixed and the exact location of direct air removal is not important, which is a reasonable assumption, when considering the lifetime of CO_2 over which it exerts its radiative forcing effects.

145 Given the prevalence of prior studies conducted under constant pCO_2 (Wang et al., 2023; Tyka et al., 2022; He and Tyka, 2023; Zhou et al., 2024; Suselj et al., 2024; Köhler et al., 2013; Burt et al., 2021), it is important to establish the physical meaning of the quantity $\eta(t)$ when obtained under such prescribed atmospheric conditions. Since OAE removes CO_2 gradually from the atmosphere, it is a reasonable hypothesis that the $\eta(t)$ curve obtained under prescribed atmospheres gives the equivalent DAC removal. If true, one would expect that

150 under responsive atmosphere conditions the OAE deployment and a DAC removal at a rate given by $eta(t)/dt$ should yield the same reduction in atmospheric CO_2 also. To verify this hypothesis, a simulation was conducted (under responsive atmosphere conditions) in which CO_2 was removed directly from the atmosphere, at the rate of $d\eta(t)/dt \times 0.5$ Tmol. No other perturbation was made in this simulation.

The results are shown in Figure 3 with the left panels (a,c and e) show the OAE deployment and the right

155 panels (a, d and f) show the equivalent (gradual) direct atmospheric CO_2 removal simulation. It can be seen that the total change in atmospheric CO_2 inventory is the same, caused either by an instantaneous release of alkalinity (Fig 3c) or by a gradual direct CO_2 removal from the atmosphere at a schedule given by $\eta(t)$ (Fig 3 d).

The equivalence of an instantaneous OAE pulse and a gradual DAC removal can be understood by considering the following scenarios, illustrated in Figure 4, concerning an ocean reservoir coupled to an atmosphere reservoir.

160 The first scenario (Fig. 4, left column), is the instantaneous OAE forcing scenario. Here, the ocean forcing is a step function set to one (normalized): $\Delta Alk(t) = 1$, while direct atmospheric forcing (i.e. DAC) $\Delta CO_2^{force}(t) = 0$ throughout. The application of OAE to the ocean causes the ocean DIC inventory to increase by some unknown function $\varepsilon(t)$, such that $\Delta C^{ocn}(t) = \varepsilon(t)$ (relative to an unperturbed reference). Meanwhile, the atmospheric
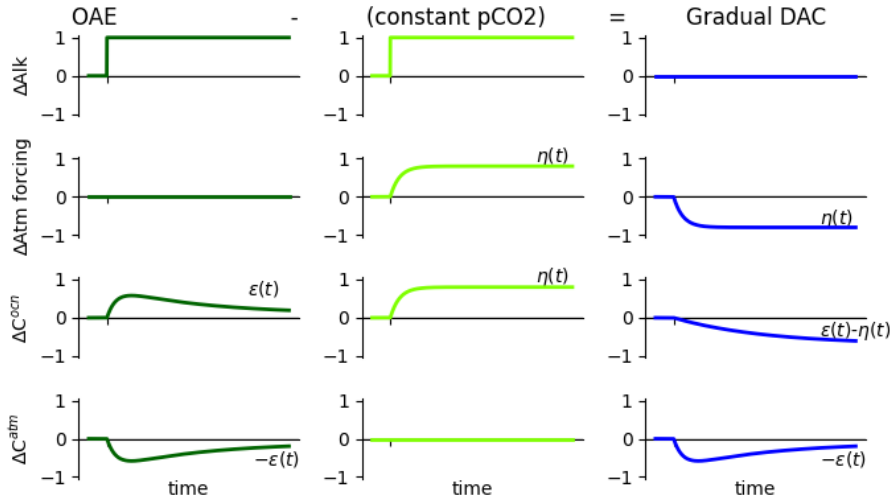
Figure 4. Diagram indicating the relationship between instantaneous OAE and gradual DAC removal, under coupled reservoirs. Left column: OAE scenario, middle column: OAE plus compensating CO_2 emission to atmosphere to keep pCO_2 constant, right column: gradual DAC. All graphs show differences to a common reference simulation.

inventory of CO_2 decreases in the same way $\Delta C^{atm}(t) = -\varepsilon(t)$. The function $\varepsilon(t)$ is the combined effect of
165 OAE-induced CO_2 uptake and atmosphere feedbacks due to the changing pCO_2.

In the second scenario (Fig. 4, middle column), additional CO_2 is emitted to the atmosphere in such a way as to cancel the effects of OAE and keep the pCO_2 and the atmospheric inventory remaining constant, i.e. $\Delta C^{atm}(t) = 0$, recreating the conditions found in prescribed pCO_2 simulations. The quantity of additional CO_2 required is exactly equal to the quantity of CO_2 taken up by the ocean under prescribed, namely $\Delta CO_2^{\text{force}}(t) =$
170 $\eta(t)$. In this scenario, the effect of OAE and the gradual addition of extra CO_2 exactly balance the pCO_2^{atm}. Since the ocean experiences the exact same atmospheric interface as in the prescribed simulation, its total DIC inventory also evolves exactly along the $\eta(t)$ curve, i.e. $\Delta C^{ocn}(t) = \eta(t)$.

If the second scenario is subtracted from the first, assuming linearity of the differential equations governing the processes, a new combined scenario is obtained (Fig. 4, right column), with the following properties:
175 $\Delta CO_2^{\text{force}}(t) = -\eta(t)$. Now CO_2 is being removed from the atmosphere gradually, on a schedule proportional to $eta(t)$, while the OAE forcing is now zero $\Delta OAE(t) = 0$. The atmospheric inventory follows the same trajectory as in the first scenario, namely $\Delta C^{atm}(t) = -\varepsilon(t)$. Finally, the ocean DIC inventory decreases slowly $\Delta C^{ocn}(t) = \varepsilon(t) - \eta(t)$.

Since $\Delta OAE(t) = 0$, this combined scenario represents the direct, albeit gradual, removal of CO_2 from the
180 atmosphere without any OAE occurring. It results in exactly the same ΔpCO_2^{atm} as the OAE scenario, showing that the two interventions are equivalent with respect to ΔpCO_2^{atm}. This argument holds for any $\varepsilon(t)$ and for
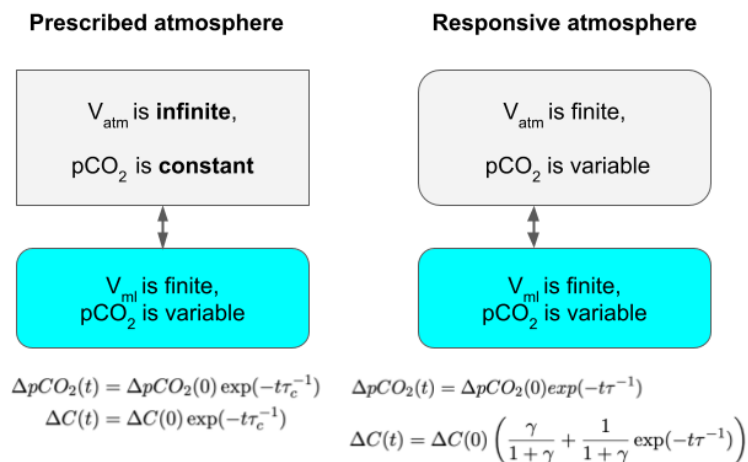
Figure 5. Two simple box models, one with a static, prescribed atmosphere and one with a responsive finite-volume atmosphere. The resulting decay laws for an initial pulse of CO_2 added to ocean ($\Delta C(0)$) and initial pulse of $pCO_2(0)$ are given below.

any shape of the uptake function $\eta(t)$, provided that the dynamical system is linear and the superposition of the two scenarios is justified.

3.2 Analytical box model

185 The equivalence of the $\eta(t)$ curve and the gradual removal of CO_2 from the atmosphere can also be shown to be analytically exact in a simple box model, as shown in Figure 5. A full derivation of the following results is given in the Supplementary material, with the following section summarizing the key results and conclusions. The model describes two coupled reservoirs, atmosphere (atm) and ocean (ocn). Each has a partial pressure of CO_2, (pCO_2^{atm} and pCO_2^{ocn}), a total (integrated) amount of CO_2 (denoted by C^{atm} and C^{ocn}) and a given volume
190 (V^{atm} and V^{ocn}).

The atmospheric partial pressure pCO_2^{atm} is directly proportional to the total amount of CO_2 in the atmosphere C^{atm} in [mol]

$$\frac{\mathrm{d}pCO_2^{atm}}{\mathrm{d}C^{atm}} = \frac{V_m p}{V_{atm}} \tag{3}$$

where V_m is the molar volume of gas (0.024 m^3/mol) and p is the atmospheric pressure. In the ocean reservoir,
195 which is in active contact with the atmosphere, specifically the mixed layer, the differential relationship between pCO_2 and C, for small changes, is

$$\frac{\mathrm{d}pCO_2^{ocn}}{\mathrm{d}C^{ocn}} = \frac{1}{\alpha V_{ml}} \frac{\partial[CO_2]}{\partial[DIC]} \tag{4}$$

where $[DIC]$ is the concentration of total dissolved carbon, α is the solubility of CO_2 in seawater [≈ 34 mol/m^3/atm] and the term $\frac{\partial[CO_2]}{\partial[DIC]}$ accounts for the vastly increased capacity of ocean water for CO_2 due to the

200 carbonate system, with a typical value of $\approx 1/20$ (Zeebe and Wolf-Gladrow, 2001).

These two reservoirs can exchange CO_2 and the flux of CO_2 across the air-water interface F_{CO_2} is typically modelled as proportional to the partial pressure difference

$$F_{CO_2} = k_w\alpha(pCO_2^{atm} - pCO_2^{ocn}) = k_w\alpha\Delta pCO_2 \tag{5}$$

where k_w is the gas transfer velocity [m/s]. Given this simple box model setup one can show that the total

205 transfer rate of CO_2, following an initial ocean DIC deficit of $\Delta C(0)$, is given by

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \Delta C(0) \left(\frac{k_w A}{V_{ocn}} \frac{\partial[CO_2]}{\partial[DIC]} \right) \exp(-t\tau^{-1}) \tag{6}$$

where the characteristic timescale of equilibration (e-folding time) is given by τ

$$\tau = \left[k_w A\alpha \left(\frac{V_m p}{V_{atm}} + \frac{1}{\alpha V_{ocn}} \frac{\partial[CO_2]}{\partial[DIC]} \right) \right]^{-1} \tag{7}$$

and A is the area over which gas exchange occurs. Integrating this rate with respect to time gives the time

210 evolution $\Delta C(t)$ of a starting DIC deficit $\Delta C(0)$ in the ocean reservoir of such a box model (details of the derivation are found in supplementary material).

$$\Delta C(t) = \Delta C(0) \left(\frac{\gamma}{1+\gamma} + \frac{1}{1+\gamma} \exp(-t\tau^{-1}) \right) \tag{8}$$

where γ expresses the ratio of the capacities of the two interacting reservoirs.

$$\gamma = \frac{V_m p\alpha V_{ocn}}{V_{atm}} \frac{\partial[DIC]}{\partial[CO_2]} \tag{9}$$

215 Note that under finite, responsive atmosphere conditions, some fraction of the initial pulse will always remain in the reservoir it was induced in, even once the pCO$_2$ values have reached equilibrium, because as the pCO$_2$ of the reservoir increases, that of the atmosphere decreases, until they are equal. Equation 8 shows that the fraction that will move to the other reservoir is $\frac{1}{1+\gamma}$, while the fraction that will remain in the ocean is $\frac{\gamma}{1+\gamma}$.

3.2.1 Simulations with prescribed pCO_2

220 The frequently taken assumption that atmospheric pCO_2 is prescribed, corresponds to the assumption that $V_{atm} = \infty$, i.e. it assumes an atmosphere which can accommodate arbitrary movement of CO_2 in or out of it, without a change in pCO_2^{atm}. In this case, the ODE for the pCO_2 difference simplifies to the often used gas-exchange expression (Zeebe and Wolf-Gladrow, 2001)

225
$$\Delta C(t) = \Delta C(0) \exp(-t\tau_c^{-1}) \tag{10}$$

where the depth of the mixed layer $z_{ml} = V_{ml}/A$ and the e-folding time, denoted here τ_c for "constant atmosphere", is

$$\tau_c = \left[\frac{k_w A}{V_{ml}} \frac{\partial[CO_2]}{\partial[DIC]} \right]^{-1} \tag{11}$$

This law results in a simple equilibration in which the initial deficit $\Delta C(0)$ is completely replenished by
230 the atmosphere and goes to zero, consistent with the fact that the atmosphere is modelled as having an infinite capacity.

This simpler equilibration law has been the basis of the $\eta(t)$ curve obtained in OAE efficiency simulations(Tyka et al., 2022; He and Tyka, 2023; Zhou et al., 2024; Suselj et al., 2024).

$$\eta(t) = 1 - \frac{\Delta C(t)}{\Delta C(0)} = 1 - \exp(-t\tau_c^{-1}) \tag{12}$$

235 How significant is the difference between Equations 8 and 10 ? Considering some reasonable values (V_{atm} =3.96x10^{18}m^3, α =34 mol m^{-3} atm^{-1}, $\frac{\partial[DIC]}{\partial[CO_2]}$=20 (from (Zeebe and Wolf-Gladrow, 2001)) and a mixed layer depth of 100m) one obtains $\gamma \approx 0.15$, meaning the fraction of an induced ocean CO_2 deficit which will remain in the ocean is $\frac{\gamma}{1+\gamma} \approx 13\%$. For example, in the case of an alkalinity addition, let's assume 1 mol of alkalinity addition creates a DIC deficit of 0.83mol (REF Renforth). At full equilibration this deficit will cause
240 0.83 × 87% = 0.72 mol of CO_2 to be absorbed by the ocean. At that point the pCO_2 of the atmosphere will have changed sufficiently to be in a new equilibrium with the surface ocean. Note that this quantity decreases when the depth (i.e. the volume) of the equilibrating ocean reservoir increases. For example, assuming a depth of 400m, the ocean would absorb only 0.52 mol CO_2

Figure 6a compares the evolution of $\eta(t)$ over time for a 100m deep ocean reservoir for a prescribed (infinite)
245 and a responsive (finite) atmosphere. Figure 6b shows the same but for a deeper, 400m reservoir. It is notable that (under responsive atmosphere) the bigger the ocean reservoir is, the less CO_2 needs to transfer to the ocean in order to match the pCO_2 across the boundary. For example, for the 400m deep ocean reservoir, for every 1 mol of DIC deficit induced, the ocean would take up only 0.63 mol of CO_2 before the pCO_2 values are in equilibrium.
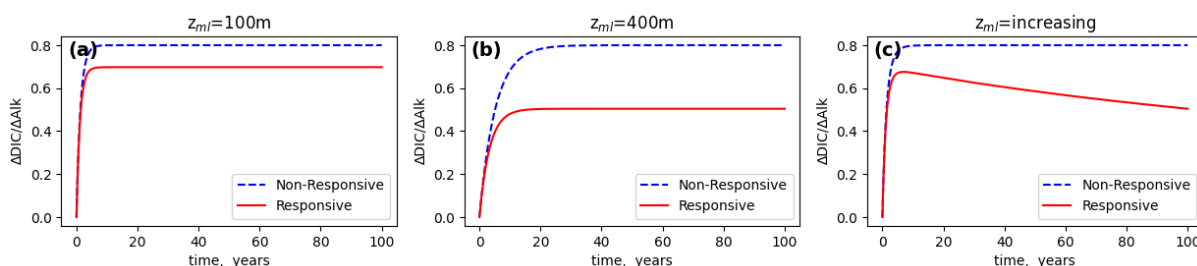
Figure 6. Box model comparison of $\eta(t)$ over 100 years, under different mixed layer assumptions. For simplicity, $\partial[DIC]/\partial[Alk]$ is assumed to be 0.8. The ocean carbon uptake is calculated with Equation 10 (non-responsive atmosphere) or Equation 8(responsive atmosphere) respectively. **(a)** Mixed layer depth z_{ml} =100m, **(b)** Mixed layer depth z_{ml} =400m, **(c)** Linear interpolation of z_{ml} = from 100m to 400m over 100 years.

Now, consider what happens when the ocean reservoir slowly increases in depth. A DIC deficit induced at the surface will initially equilibrate just from the relatively thin mixed layer, which experiences rapid mixing. Over time, however, slower mixing processes exchange water parcels between the mixed layer and deeper layers. If one considers this, crudely, as a gradual deepening of the reservoir which is exchanging with the atmosphere on longer timescales, one can express the effective exchanging ocean volume V_{ml} as a function which increases in time. Figure 6c shows how $\eta(t)$ evolves in time when V_{ml} is a linearly increasing from 100m to 400m in a span of 100 years. Initially the equilibration occurs from a shallow reservoir and $\eta(t)$ rises quickly and reaches relatively high values as in Figure 6a. Over time, however, as the equilibration slowly proceeds to deeper layers, the equilibrium situation begins resembling Figure 6b. Because the carbon uptake initially overshoots relative to the eventual equilibrium point, a process of net out-gassing occurs. This sort of out-gassing has been previously described by other authors (Oschlies, 2009). Despite our crude assumptions here about the linear subduction of the excess alkalinity, the behaviour of the curve matches qualitatively that observed in the numerical simulation (Fig 1 and Fig 2).

3.2.2 Equivalent removal from the Atmosphere

We have shown earlier that the function $\eta(t) = \Delta DIC(t)/\Delta Alk$, determined under constant pCO_2^{atm} conditions, does not properly describe the actual movement of CO_2 from the atmosphere into the ocean under realistic conditions (where feedback of the atmosphere is taken into account). This raises the question, what physical quantity does $\eta(t)$ represent, if anything ? To illuminate this question, consider the following scenario. How would the total inventory of CO_2 in the atmosphere evolve, under realistic responsive-atmosphere conditions, if CO_2 was directly removed from the atmosphere at a rate proportional to $d\eta(t)/dt$, using a terrestrial technology like DAC, instead of indirectly, by applying an alkalinity pulse to the ocean?

270   Specifically, the rate of carbon removal out of the atmosphere would be

$$\frac{\mathrm{d}\Delta C^{atm}}{\mathrm{d}t} = \Delta C(0)\frac{\mathrm{d}\eta(t)}{\mathrm{d}t} = \Delta C(0)\tau_c^{-1}\exp(-t\tau_c^{-1}) \tag{13}$$

    where $\Delta C(0)$ is a scaling factor that sets the total, eventual amount of CO_2 removed.

    This steady removal of CO_2 from the atmosphere lowers the $p\mathrm{CO}_2$ of the atmosphere. Since the atmosphere now develops a ΔpCO_2 deficit, relative to the ocean, the ocean reacts and degases into the atmosphere (re-

275 member all Δs are differences between a reference and a perturbed simulation). What is the combined effect on total atmospheric CO_2 inventory, i.e. the sum of direct removal and ocean reactance ? The total rate of change is the sum of the direct CO_2 removal rate (Equation 13) and the rate due to gas exchange between ocean and atmosphere (due to the imbalance of ΔpCO_2):

$$\frac{\mathrm{d}\Delta C^{atm}}{\mathrm{d}t} = \Delta C(0)\tau_c^{-1}\exp(-t\tau_c^{-1}) - k_w A\alpha\Delta pCO_2(t) \tag{14}$$

280   Through substitution of $\Delta pCO_2^{atm}(t)$ the above equation can be shown to equal the following expression (for full derivation, see Supplement).

$$\frac{\mathrm{d}\Delta C^{atm}}{\mathrm{d}t} = \Delta C(0)\left[\frac{k_w A}{V_{ml}}\frac{\partial[CO_2]}{\partial[DIC]}\right]\exp(-t\tau^{-1}) \tag{15}$$

    This equation for the net rate of change in atmospheric carbon inventory equals precisely that obtained earlier when considering a pulsed DIC deficit in the ocean, Equation (6). This result reveals the exact meaning of the $\eta(t)$

285 OAE efficiency curve: The OAE curve of an *instantaneously* induced ocean-based DIC deficit (obtained under artificial, non-responsive conditions), gives the progression of the equivalent *gradual* removal of CO_2 directly from the atmosphere (under real, responsive conditions); both result in the same reduction in net atmospheric carbon inventory.

3.3   Measuring $\eta(t)$ in coupled models

290 Practical OAE deployments will rely on modeling to estimate the amount of carbon removal credits they generate over time, especially in the far-field, where the induced changes in $p\mathrm{CO}_2$ are diluted far below experimental detection thresholds(Ho et al., 2023), but where the majority of the excess CO_2 uptake will take place (Zhou et al., 2024; He and Tyka, 2023). While one way to calculate the amount of credits is to keep pCO_2^{atm} prescribed, future modeling efforts will likely want to employ more accurate full earth system models, with forward-looking

295 ocean state prediction, which will require the inclusion of atmosphere coupling and consideration of different emission scenarios, which have the potential to change ocean circulation and therefore affect $\eta(t)$. How can the quantity $\eta(t)$ be calculated in such a model ?

    Fundamentally $\eta(t)$ expresses the efficiency of OAE relative to direct air removal. Therefore, the reference state should not be an unperturbed model run, but one that reflects an equivalent DAC removal. The simplest

300 approach would be to run a simulation in which an amount of atmospheric CO_2 is removed at the beginning,

equimolar to the amount of alkalinity added during OAE. The difference in atmospheric CO_2 inventory, $\eta \approx 1 - \frac{\sum CO_2^{\mathrm{OAE}} - \sum CO_2^{\mathrm{DAC}}}{\Delta Alk}$, would then capture the efficiency of an OAE deployment relative to a straightforward direct removal of CO_2 from the atmosphere. However, this comparison is not quite exact, because the true equivalent DAC removal is a gradual one, not a sudden DAC pulse, as shown earlier. Instead, a simple and elegant

305 way to create a suitable reference state was suggested by (Schwinger et al., 2024). First, the OAE-perturbed simulation is carried out with a fully coupled model. Then, one conducts an additional reference simulation (Ref^*) in which the atmosphere pCO_2 is prescribed at the exact trajectory obtained in the earlier fully-coupled simulation with the OAE intervention. However, in the new reference simulation no OAE is performed - only the atmospheric pCO_2 is prescribed. The difference in the ocean inventories between these two simulations then

310 is equivalent to the $\eta(t)$ obtained in a prescribed simulation

$$\eta(t) = \frac{\sum DIC^{\mathrm{OAE}} - \sum DIC^{\mathrm{Ref}^*}}{\Delta Alk} \tag{16}$$

In the case of the two-box model used earlier, it can be shown that this equivalence is mathematically exact (see supplementary material for a proof). The disadvantage is that for every OAE simulation, a separate reference simulation must be run, since the CO_2 feedback depends on the trajectory of the OAE perturbation. This approach

315 works perfectly, if the atmosphere is the only reservoir directly coupled to the ocean. Any additional reservoirs which are coupled only to the atmosphere (such as the terrestrial reservoir) are also handled automatically by this approach, as the prescribed pCO_2 in the reference run includes any indirect ocean coupling via the atmosphere. However, other reservoirs which couple directly to ocean pCO_2 would not be exactly covered by this approach. For example, if the model includes biological productivity which removes further DIC, and this productivity is

320 dependent on ocean DIC concentration, then this constitutes essentially a coupled reservoir with its own feedback effects (which may be linear or non-linear). In that case, the altered growth rates would also need to be prescribed in the reference state. Similarly, ocean carbonate precipitation and dissolution depend on ocean pCO_2 and are influenced by all OAE methods and should be factored out when calculating relative efficiencies. Of course, in the case that the total capacity of such additional reservoirs is small, they may not make a significant difference,

325 but this would need to be confirmed in future studies.

4 Conclusions

Emissions of CO_2 to the atmosphere and removals of CO_2 from the atmosphere (via DAC) both induce a rebalancing of CO_2 from or to the atmosphere into other coupled reservoirs. However, as these feedback effects are approximately symmetrical, the impact on atmospheric pCO_2 is the same for emissions and removals, except

330 for the sign. Therefore, when accounting negative emissions, such CO_2 removals are always counted relative to tailpipe emission of CO_2, in other words, the removal of 1kg of CO_2 using direct air removal (DAC) offsets the emission of 1kg of CO_2 elsewhere. When applying metrics to evaluate negative emission technologies which do

not remove CO_2 directly from the atmosphere, but indirectly and with time delay, the desired metric should thus represent the equivalent DAC removal over time, due to some initial perturbation.

335   To obtain this metric, which should exclude the effects of reservoir feedbacks common to DAC and OAE, one needs to be careful in using the correct counterfactual reference depending on whether reservoir feedbacks are accounted for in the simulation or not.

     We have shown that in simulations which use a prescribed atmospheric pCO_2, the quantity $\eta(t) = \Delta DIC(t)/\Delta Alk$ yields the desired metric, i.e. $\eta(t)$ is the equivalent, gradual removal of CO_2 from the atmosphere, if it were con-

340 ducted using the direct air capture method, under responsive atmosphere conditions and other couplings. In other words, η captures the efficiency of OAE relative to direct atmosphere removal, and ignores reservoir feedbacks common to all negative emission technologies. It should be noted that there exists no instantaneous DAC removal pulse which causes the same evolution of atmospheric pCO_2 as an instantaneous release of alkalinity, due to the different timescales of CO_2 equilibration and reservoir feedbacks.

345   For OAE, $\eta(t)$ is expected to equilibrate over a period of a few years to decades following an alkalinity addition and ultimately asymptote around 0.85 mol C/mol Alk, unless significant quantities of alkalinity were subducted into the deep ocean before air-sea gas exchange was completed (Zhou et al., 2024).

     It is important to realize that $\eta(t)$ does not quantify the excess amount of CO_2 taken up by the ocean due to an OAE deployment, since that includes reservoir feedbacks. Consequently, to avoid confusion, it is most precise

350 to say that 1 mol of alkalinity can offset up to 0.85mol of emissions, rather than say it can cause the uptake of up to 0.85mol of CO_2.

     Conversely, we propose to follow nomenclature by Jeltsch-Thömmes et al. (2024) to denote as $\varepsilon(t)$ the efficiency of OAE with respect to its ability to reduce atmospheric carbon inventories under fully coupled earth-system models, which includes all the reservoir feedbacks. This quantity is relevant to calculating the reduction

355 of future radiative forcing and global temperatures due to OAE deployments. Prior work has shown that ε can reach values almost as high as $\eta(t)$ in the short term but is expected to eventually decrease to around 0.35 mol C/ mol Alk on longer timescales Jeltsch-Thömmes et al. (2024). However, ε is less useful for assigning or comparing carbon credits because its value is dependent on future emission scenarios, changes to landsink capacities, etc., which are independent of the OAE intervention and common among all CDR efforts. On the other hand, if

360 one wishes to calculate the long-term counterfactual effects of an OAE deployment on ocean variables (such as ΔpH or $\Delta\Omega$), the use of a fully coupled-model is necessary, because the feedback effects influence the behavior of such variables. For example, the OAE effect on pH is greater in a fully coupled model, because less CO_2 enters the ocean to neutralize the excess alkalinity than would be calculated under a prescribed CO_2 atmosphere. However, for short-term and near-field effects, dominated by the effect of alkalinity addition before it has had

365 time to disperse and dilute, the use of simpler models yields reasonable approximations, since the buffering effect of coupled reservoirs is comparatively slow and non-local. An alternative way to compare negative technologies and to measure credits would be to focus on expected GWP50 or GWP100 of a given NET deployment, under

a given future emission scenario. The advantage is that NET interventions that remove CO_2 immediately at purchase time (e.g. DAC), and those that remove it gradually (e.g. OAE, enhanced weathering, reforestation, etc.)
370   could be compared more directly.

Code and data availability.   Code and data will be made available upon publication

Author contributions.   M.D.T. Conceived of the work, ran the simulations and wrote the manuscript.

Competing interests.   The author declares no competing interest.

Acknowledgements.   The author would like to express their gratitude to Lennart Bach, Freya Chay, Jörg Schwinger and Chris
375   Van Arsdale for many helpful discussions and comments on the manuscript.

References

Bach, L. T., Ho, D. T., Boyd, P. W., and Tyka, M. D.: Toward a consensus framework to evaluate air-sea CO2 equilibration for marine CO2 removal, Limnology and Oceanography Letters, 8, 685–691, https://doi.org/https://doi.org/10.1002/lol2.10330, 2023.

380 Burt, D. J., Fröb, F., and Ilyina, T.: The Sensitivity of the Marine Carbonate System to Regional Ocean Alkalinity Enhancement, Frontiers in Climate, 3, https://doi.org/10.3389/fclim.2021.624075, 2021.

Dutkiewicz, S., Sokolov, A., Scott, J., and Stone, P.: A three-dimensional ocean-seaice-carbon cycle model and its coupling to a two dimensional atmospheric model: Uses in climate change studies. Report 122, MIT Joint Program on the Science and Policy of Global Change, [Online; accessed 20-April-2021], 2005.

385 González, M. F. and Ilyina, T.: Impacts of artificial ocean alkalinization on the carbon cycle and climate in Earth system simulations, Geophys. Res. Lett., 43, 6493–6502, https://doi.org/10.1002/2016gl068576, 2016.

He, J. and Tyka, M. D.: Limits and CO_2 equilibration of near-coast alkalinity enhancement, Biogeosciences, 20, 27–43, https://doi.org/10.5194/bg-20-27-2023, 2023.

Ho, D. T., Bopp, L., Palter, J. B., Long, M. C., Boyd, P. W., Neukermans, G., and Bach, L. T.: Monitoring, reporting, and
390 verification for ocean alkalinity enhancement, State of the Planet, 2-oae2023, 12, https://doi.org/10.5194/sp-2-oae2023-12-2023, 2023.

Humphreys, M. P., Daniels, C. J., Wolf-Gladrow, D. A., Tyrrell, T., and Achterberg, E. P.: On the influence of marine biogeochemical processes over CO2 exchange between the atmosphere and ocean, Marine Chemistry, 199, 1–11, https://doi.org/https://doi.org/10.1016/j.marchem.2017.12.006, 2018.

395 Jeltsch-Thömmes, A., Tran, G., Lienert, S., Keller, D., Oschlies, A., and Joos, F.: Earth system responses to carbon dioxide removal as exemplified by ocean alkalinity enhancement: tradeoffs and lags, Environmental Research Letters, http://iopscience.iop.org/article/10.1088/1748-9326/ad4401, 2024.

Jin, X., Gruber, N., Frenzel, H., Doney, S. C., and McWilliams, J. C.: The impact on atmospheric CO_2 of iron fertilization induced changes in the ocean's biological pump, Biogeosciences, 5, 385–406, https://doi.org/10.5194/bg-5-385-2008,
400 2008.

Keller, D. P., Feng, E. Y., and Oschlies, A.: Potential climate engineering effectiveness and side effects during a high carbon dioxide-emission scenario, Nature Communications, 5, 3304, 2014.

Köhler, P.: Anthropogenic CO2 of High Emission Scenario Compensated After 3500 Years of Ocean Alkalinization With an Annually Constant Dissolution of 5 Pg of Olivine, Frontiers in Climate, 2, https://doi.org/10.3389/fclim.2020.575744,
405 2020.

Köhler, P., Abrams, J. F., Völker, C., Hauck, J., and Wolf-Gladrow, D. A.: Geoengineering impact of open ocean dissolution of olivine on atmospheric CO2, surface ocean pH and marine biology, Environ. Res. Lett., 8, 014 009, https://doi.org/10.1088/1748-9326/8/1/014009, 2013.

Lenton, A., Matear, R. J., Keller, D. P., Scott, V., and Vaughan, N. E.: Assessing carbon dioxide removal through
410 global and regional ocean alkalinization under high and low emission pathways, Earth Syst. Dynam., 9, 339–357, https://doi.org/10.5194/esd-9-339-2018, 2018.

Marshall, J., Adcroft, A., Hill, C., Perelman, L., and Heisey, C.: A finite-volume, incompressible Navier Stokes model for studies of the ocean on parallel computers, Journal of Geophysical Research: Oceans, 102, 5753–5766, https://doi.org/https://doi.org/10.1029/96JC02775, 1997.

415 NationalAcademiesPress: A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration, National Academies Press, https://doi.org/10.17226/26278, 2022.

Oschlies, A.: Impact of atmospheric and terrestrial CO_2 feedbacks on fertilization-induced marine carbon uptake, Biogeosciences, 6, 1603–1613, https://doi.org/10.5194/bg-6-1603-2009, 2009.

Oschlies, A., Stevenson, A., Bach, L., Fennel, K., Rickaby, R. E. M., Satterfield, T., Webb, R., and Gattuso, J.: Guide to

420 Best Practices in Ocean Alkalinity Enhancement Research, State of the Planet, 2-oae2023, 3, https://doi.org/10.5194/sp-2-oae2023-3-2023, 2023.

Renforth, P. and Henderson, G.: Assessing ocean alkalinity for carbon sequestration, Reviews of Geophysics, 55, 636–674, https://doi.org/10.1002/2016rg000533, 2017.

Ritschard, R. L.: Marine algae as a co2 sink, Water, Air, and Soil Pollution, 64, 289–303,

425 https://doi.org/10.1007/BF00477107, 1992.

Schwinger, J., Bourgeois, T., and Rickels, W.: On the emission-path dependency of the efficiency of ocean alkalinity enhancement, Environmental Research Letters, 19, 074 067, https://doi.org/10.1088/1748-9326/ad5a27, 2024.

Stocker, T. F., Plattner, G.-K., and Dahe, Q.: IPCC Climate Change 2013: The Physical Science Basis - Findings and Lessons Learned, https://api.semanticscholar.org/CorpusID:220600282, 2014.

430 Suselj, K., Carroll, D., Menemenlis, D., Zhang, H., Beatty, N., Savage, A., and Whitt, D.: Quantifying Regional Efficiency of Marine Carbon1 Dioxide Removal (mCDR) via Alkalinity Enhancement2 using the ECCO-Darwin Ocean Biogeochemistry State3 Estimate and an Idealized Vertical 1-D Model, submitted to Global Biogeochemical Cycles, 123, 123–123, 2024.

Trenberth, K. E. and Smith, L.: The Mass of the Atmosphere: A Constraint on Global Analyses, https://doi.org/10.1175/jcli-

435 3299.1, 2005.

Tyka, M. D., Van Arsdale, C., and Platt, J. C.: CO2 capture by pumping surface acidity to the deep ocean, Energy Environ. Sci., 15, 786–798, https://doi.org/10.1039/D1EE01532J, 2022.

Wang, H., Pilcher, D. J., Kearney, K. A., Cross, J. N., Shugart, O. M., Eisaman, M. D., and Carter, B. R.: Simulated Impact of Ocean Alkalinity Enhancement on Atmospheric CO2 Removal in the Bering Sea, Earth's Future, 11, e2022EF002 816,

440 https://doi.org/https://doi.org/10.1029/2022EF002816, e2022EF002816 2022EF002816, 2023.

Zarakas, C., Badgley, G., and Chay, F.: Comparing carbon removal at different timescales https://carbonplan.org/research/cdr-timescale-accounting, https://carbonplan.org/research/cdr-timescale-accounting, 2024.

Zeebe, R. E. and Wolf-Gladrow, D. A.: CO2 in seawater: Equilibrium, kinetics, isotopes: Volume 65, Elsevier Oceanography Series, Elsevier Science, London, England, ISBN 9780444509468, 2001.

445 Zhou, M., Tyka, M. D., Ho, D. T., Yankovsky, E., Bachman, S., Nicholas, T., Karspeck, A. R., and Long, M. C.: Mapping the global variation in the efficiency of ocean alkalinity enhancement for carbon dioxide removal, Submitted to Nat. Clim. Change, 123, 123–123, 2024.