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A comprehensive assessment of electrochemical ocean alkalinity enhancement in seawater: kinetics, efficiency, and precipitation thresholds

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Abstract

Ocean alkalinity enhancement (OAE) is a promising approach to marine carbon dioxide removal (mCDR) that leverages the large surface area and carbon storage capacity of the oceans to sequester atmospheric CO_2 as dissolved bicarbonate (HCO_3^-). The SEA MATE (Safe Elevation of Alkalinity for the Mitigation of Acidification Through Electrochemistry) process uses electrochemistry to convert some of the salt (NaCl) in seawater or brine into aqueous acid (HCl), which is removed from the system, and base (NaOH), which is returned to the ocean with the remaining seawater. The resulting increase in seawater pH and alkalinity causes a shift in dissolved inorganic carbon (DIC) speciation toward carbonate and a decrease in the surface-ocean pCO_2. The shift in the pCO_2 results in enhanced CO_2 uptake or reduced CO_2 loss by the seawater due to gas exchange. The net result of this process is the increase of surface-ocean DIC, where it is durably stored as mostly bicarbonate and some carbonate. In this study, we systematically test the efficiency of CO_2 uptake in seawater treated with NaOH at beaker (1L), aquaria (15L), and tank (6000L) scales to establish operational boundaries for safety and efficiency in scaling up to field experiments. Preliminary results show CO_2 equilibration occurred on order of weeks to months, depending on circulation, air forcing, and air bubbling conditions within the test tanks. An increase of ~0.7-0.9 mol DIC/ mol added alkalinity (in the form of NaOH) was observed through analysis of seawater bottle samples and pH sensor data, consistent with the value expected given the values of the carbonate system equilibrium calculations for the range of salinities and temperatures tested. Mineral precipitation occurred when the bulk seawater pH exceeded 10.0 and $\Omega_{aragonite}$ exceeded 30.0. This precipitation was dominated by $Mg(OH)_2$ over hours to 1 day before shifting to $CaCO_{3,\ aragonite}$ precipitation. These data, combined with models of the dilution and advection of alkaline plumes, will allow for estimation of the amount of carbon dioxide removal expected from OAE pilot studies. Future experiments should better approximate field conditions including sediment interactions, biological activity, ocean circulation, air-sea gas exchange rates, and mixing-zone dynamics.

Keywords

Ocean Alkalinity Enhancement (OAE); marine carbon dioxide removal (mCDR); ocean carbon dioxide removal (ocean CDR)

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1 Introduction

The Sixth Assessment Report of the Intergovernmental Panel on Climate Change reported that in addition to a drastic decrease in CO_2 emissions, active removal of 5.5 Gt of atmospheric CO_2 per year by 2100 is necessary to constrain average global warming to less than 1.5 - 2 °C (IPCC, 2022; Rogelj, 2018). A wide variety of negative emissions technologies (NETs) are under development to meet this enormous challenge (Minx et al., 2018; NASEM, 2019; NASEM, 2022; Rueda et al., 2021; Vitillo et al., 2022).

A suite of promising approaches to CO_2 removal termed ocean or marine carbon dioxide removal (ocean CDR or mCDR, respectively) leverage the enormous surface area and carbon storage capacity of the ocean (Boettecher et al., 2019; NASEM, 2021). Ocean alkalinity enhancement (OAE) is an mCDR method that aims to store atmospheric CO_2 in a dissolved phase in the ocean as bicarbonate ions (HCO_3^-), thereby accelerating a natural planetary CO_2 regulation mechanism, the carbonate-silicate cycle (Berner, 1983; Isson et al., 2020). OAE has the potential to scale to gigatons of CO_2 removal per year (He and Tyka, 2023), but development of this approach requires careful consideration of: the methods and materials used to source and process alkalinity; the form and method of delivery of alkalinity to the surface ocean (for example, aqueous or solid phase); and selection of appropriate geographic sites for alkalinity dispersal (Oschlies et al., 2023). OAE methods under exploration include: mining and crushing alkaline minerals (e.g., olivine, basalts) to be spread via ship or in coastal environments (e.g., beach restoration, or salt marsh distribution) (Feng et al., 2017; Köhler, Hartmann, and Wolf-Gladrow, 2010; Monserrat et al., 2018; Rigopoulos et al., 2018); the mining or industrial production of $Mg(OH)_2$ or mining $CaCO_3$ and calcining it to CaO or $Ca(OH)_2$, with the $Mg(OH)_2$ or $Ca(OH)_2$ spread via ship or coastal outfall pipe (Harvey, 2008; Ilyina et al., 2013; Kheshgi, 1995; La Plante, 2023; Moras et al., 2022; Nduagu, 2012; Rau, 2008; Renforth and Henderson, 2017; Shaw, 2022); and the electrochemical conversion of saltwater into aqueous hydroxides and dispersal via coastal outfalls (de Lannoy et al., 2018; Eisaman et al., 2018; Lu et al., 2022; Tyka, Van Arsdale, and Platt, 2022; Eisaman et al., 2023).

Many of these approaches and technologies are at a nascent stage and we must move quickly to quantitatively test and characterize their performance to determine which, if any, justify larger-scale deployment. The electrochemical conversion of salt (NaCl) into aqueous alkalinity (NaOH) has many potential advantages in scaling considerations, including simplified distribution of a liquid product to the ocean, avoidance of mining and the transportation of the alkalinity source over long distances, and avoidance of potentially harmful impurities present in mined alkalinity sources (NASEM, 2021; Caserini, Storni, and Grosso, 2022).

Figure 1 summarizes a specific OAE approach in which electrochemical processing of seawater or brine rearranges the hydrogen (H^+), hydroxide (OH^-), sodium (Na^+), and chloride (Cl^-) ions to produce acidic (HCl) and basic (NaOH) solutions. From a molecular point of view, since the Na+ and OH- ions come from the seawater itself, the net result of this process is the removal of H^+ and Cl^- ions from the input seawater, that is the removal of HCl acid. Nothing new is added to the ocean in this process, but rather H^+ and Cl^- ions are removed from seawater.

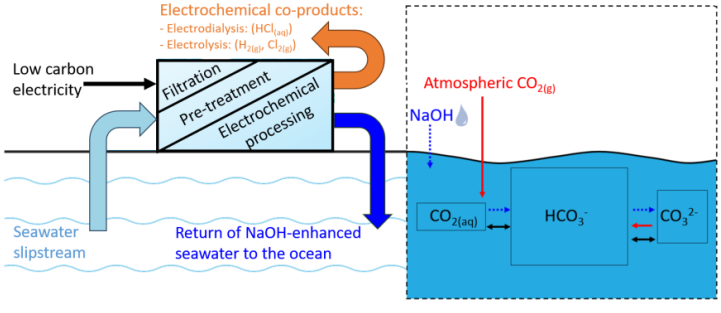

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Figure 1: Low-carbon electricity and a slipstream of seawater are the inputs to electrochemical OAE. Various process-specific filtration and pretreatment steps allow for membrane-based electrochemical processing, resulting in the removal of H^+ and Cl^- ions from seawater. The NaOH-enhanced seawater is returned to the ocean, resulting in the invasion of CO_2 into seawater and durable storage as mostly HCO_3^- and some CO_3^{2-}.

In the process shown in Fig. 1, a portion of the salt (NaCl) in the seawater is electrochemically separated into its constituent acid (HCl) and base (NaOH). The acid is removed, but the base is remixed with the seawater enhancing the alkalinity of the resulting seawater that is then returned to the ocean. In the case where bipolar membrane electrodialysis is used to generate the acid and base, water (H_2O) is dissociated into H^+ and OH^- ions at the junction of the bipolar membranes inside the electrochemical system (Eisaman et al. 2012). This operation alone does not change the alkalinity. But a voltage applied across a stack of ion-selective membranes then separates the H^+ and OH^- ions from each other and from the seawater, with Cl^- ions (in HCl) and Na^+ ions (in NaOH) providing the charge balance. Remixing the NaOH with the seawater but retaining the HCl results in a treated seawater solution an increased OH^- concentration $[OH^-]$ compared to the input seawater.

Total alkalinity (TA) is defined as the excess of proton acceptors over proton donors in an aqueous solution (Eq. 1), where ellipses represent neglected acids and bases (Dickson 1981; Dickson 1992; Wolf-Gladrow et al., 2007). A higher TA value for a seawater sample indicates that it has a higher buffering capacity than a sample with a lower TA value. That is, for sample with a higher TA value, the addition of a given amount of acid to the sample will decrease its pH less than for a sample with a lower TA value.

$$TA = [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2\,[PO_4^{3-}] + \ldots - [H^+] - [HSO_4^-] - \ldots \quad (1)$$

From Eq. (1), we see the increased OH^- concentration in a treated seawater solution corresponds to a salt solution with increased alkalinity relative to the starting salt solution. The reason that the H^+ concentration remains the same even though H^+ ions were removed is that both the H^+ and OH^- started as bound in an H_2O molecule, which was then dissociated into free H^+ and OH^- ions at the bipolar membrane junction. Therefore, upon removing the H^+ ions but remixing the OH^- ions, the H^+ ion concentration is the same as prior to H_2O dissociation, while the OH^- ion concentration is increased. This increase in OH^- ion concentration rapidly increases the seawater pH upon mixing, resulting in a shift of the dissolved inorganic carbon (DIC) speciation towards carbonate (Eisaman et al., 2023):

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-} \quad (2a)$$
$$OH^- + CO_{2,aq} \rightarrow HCO_3^- \quad (2b)$$

The concentration of dissolved CO_2 gas ($CO_{2,aq}$) in this alkalinity-enhanced seawater is less than it would be if it were in equilibrium with atmospheric CO_2 (Equation 2b). Over the longer timescale required for air-sea gas exchange - weeks to months (Wang et al., 2023) or months to years (He and Tyka, 2023) depending on location - the disequilibrium in the surface ocean resulting from the alkalinity addition drives the invasion of atmospheric CO_2 into seawater (or lessens the outgassing of CO_2 from the surface ocean to the atmosphere), where it reacts with carbonate and is stored primarily in the stable bicarbonate phase (Jones et al., 2014; Bach et al., 2023; Renforth and Henderson, 2017; Eisaman et al., 2023).

$$CO_{2,g} \rightarrow CO_{2,aq}$$
(3a)
$$CO_{2,aq} + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \quad (3b)$$

Once equilibrium has been reached, the net reaction can be written as equation 4 (Eisaman et al., 2023):

$$OH^- + aCO_{2,aq} \rightarrow bHCO_3^- + cCO_3^{2-} + dOH^- + eH_2O \quad (4)$$

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where the coefficients a-e depend on seawater properties such as temperature, pressure, and pH through the dependence of the equilibrium constants on these variables. Under typical ocean conditions, after equilibrium has been reached, OAE results in an increase in the DIC in seawater on the order of 0.7-0.9 moles of DIC per mole of NaOH added, with a slightly increased pH relative to the initial value (He and Tyka, 2023). For common surface ocean conditions (e.g., 20°C, salinity 35, and initial TA of 2000 µmol kg^{-1}) at complete equilibrium, calculated values of a=0.84, b=0.71, c=0.13, d=0.002, e≈1 can be obtained, which would correspond to 0.84 moles of DIC per mole of NaOH.

It is possible that air-sea gas exchange will not completely drive the seawater pCO_2 to the initial unperturbed value before the seawater sinks into the ocean interior and loses contact with the atmosphere for hundreds to thousands of years. Therefore, the DIC anomaly relative to the alkalinity anomaly present when the seawater sinks into the ocean interior may be used to assess the effective impact of the OAE for capturing atmospheric CO_2 on the 0-100 year timescales that are most important for climate interventions.

In addition to the storage of atmospheric CO_2 in the form of DIC, this process may have the potential to locally mitigate ocean acidification. In a water body with a finite seawater exchange rate with the ocean, such as a semi-protected estuary or bay, alkalinity could be added in a controlled manner such that the combination of the rapid reactions described by Eq.(1) and the exchange/flushing rate with the open ocean result in the bay being held in steady-state at a target pH or aragonite saturation state value that is higher than its equilibrium value under conditions of ocean acidification. As this added alkalinity diffuses through the bay and makes its way to the open ocean, CO_2 removal and storage as DIC would occur. Even once equilibrium has been achieved, the pH and the carbonate ion concentration in the open ocean remains slightly higher than before the alkaline discharge. By metering the rate of alkalinity addition to the bay to match the flushing rate, the pH or saturation state of the bay can be held at a constant target value. We refer to this approach as the SEA MATE process: the Safe Elevation of Alkalinity for the Mitigation of Acidification Through Electrochemistry.

Deploying SEA MATE in the ocean or coastal waters will require an understanding of carbonate chemistry in seawater in the ocean volume under consideration, as well as thresholds for safe operation. For example, at the point of alkaline dispersal where there is the maximum change in seawater chemistry, SEA MATE must control the rate of alkalinity addition relative to the rate of mixing and dilution in the ocean to avoid the precipitation of $Mg(OH)_2$ or $CaCO_3$ (Hartmann et al., 2023; Moras et al., 2022). While $Mg(OH)_2$ readily redissolves, an increase in turbidity due to precipitation may negatively affect marine organisms (Bainbridge et al., 2018; Broderson et al., 2017; Dutertre et al., 2009). By contrast, $CaCO_3$ will generally not redissolve in the surface ocean without biological mediation, and runaway precipitation, where alkalinity removed by precipitation exceeds that added by the OAE treatment, can occur under conditions of increased aragonite saturation state and increased nucleation sites in the water column (Moras et al., 2022). $CaCO_3$ precipitation could counteract the intended effect of the OAE intervention by removing alkalinity from the surface ocean and releasing CO_2 gas via Eq. 5 (Zeebe and Wolf-Gladrow, 2001):

$$Ca^{+} + 2HCO_3^{-} \rightarrow CaCO_3(s) + CO_2(g) + H_2O \quad (5)$$

Upon dispersal to the ocean through a coastal outfall pipe, the added alkalinity is advected and diffuses away from the point source, becoming increasingly diluted through the mixing zone. Because the timescale for air-sea gas exchange and re-equilibration described by Eq. (2) is longer than the characteristic timescale for dilution driven by tides, currents, and weather, most of the CO_2 removal occurs far from the mixing zone. Dilution will spread the impacts over a broad area, to an extent that it is unlikely that the impacts on the DIC distribution can be quantified using only direct measurements, given current instrument resolution and the typical dynamic range of natural variability (Wang et al., 2023). In general, options for measurement, reporting, and verification (MRV) of OAE will therefore rely on (Ho et al., 2023): experimentation in laboratory and mesocosm settings, such as the work we describe here, to establish CO_2 removal dynamics under conditions of OAE; direct monitoring of the rate and

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characteristics of alkalinity addition into seawater; monitoring the seawater carbonate and environmental chemistry in the immediate vicinity of the outfall via sensors and sampling (Cyronak et al., 2023; Schulz et al., 2023); and ocean modeling to estimate CDR beyond the range of direct detection (Fennel et al., 2023).

While some work has investigated various aspects of NaOH-based ocean alkalinity enhancement in microcosms (Ferderer et al., 2022; Hartmann et al., 2023), in mesocosms (Groen et al., 2023), and over natural coral reefs (Albright et al., 2016), a systematic characterization of the efficiency and kinetics of OAE as a function of key process parameters has not yet been performed. Here we report the first tank-scale tests of OAE that use aqueous hydroxide (NaOH) to enhance the alkalinity of natural seawater, a process that mimics OAE via the electrochemical brine-to-alkalinity conversion used in the SEA MATE process. Our experiments, conducted in 6,000 liter tanks using seawater pumped from Flax Pond on Long Island Sound in Stony Brook NY, quantify the magnitude and timescale of the CO_2 removal from the air and storage as seawater DIC by monitoring the air-seawater re-equilibration after an initial alkalinity perturbation. In addition, our use of both laboratory-processed bottle samples and field-deployable sensors to measure and over-constrain the carbonate chemistry response allows us to assess the suitability of certain sensing platforms for MRV. Finally, we investigate safe thresholds for the rate and concentration of alkalinity addition to avoid: (1) the precipitation and redissolution of $Mg(OH)_2$ that can lead to local, temporary increases in turbidity; and (2) the precipitation of $CaCO_3$, which partially reverses the intended OAE effect by removing alkalinity from, and releasing CO_2 gas into, the surrounding seawater.

Using this approach, we address the following key questions:

(1) How much additional atmospheric CO_2 is stored in seawater as DIC in response to a given alkalinity perturbation?

(2) What is the timescale for CO_2 removal from the air, and how does it depend on pH and the magnitude of alkalinity enhancement?

(3) If $Mg(OH)_2$ precipitates upon addition of NaOH to seawater, on what spatial and temporal scales does it redissolve?

(4) What are the threshold values for pH and aragonite saturation state beyond which undesired $CaCO_3$ precipitation will occur?

Answering these questions is key to assessing the viability of this approach and to optimizing its eventual deployment.

2. Methods

2.1 Experimental procedure

We investigated the carbonate chemistry changes resulting from the addition of $NaOH_{(aq)}$ to natural seawater over timescales ranging from 2 weeks to 2 months in a series of experiments at two scales: (1) two large (~6200 L) indoor tanks, and (2) multiple 15 L aquaria (Fig. 2).

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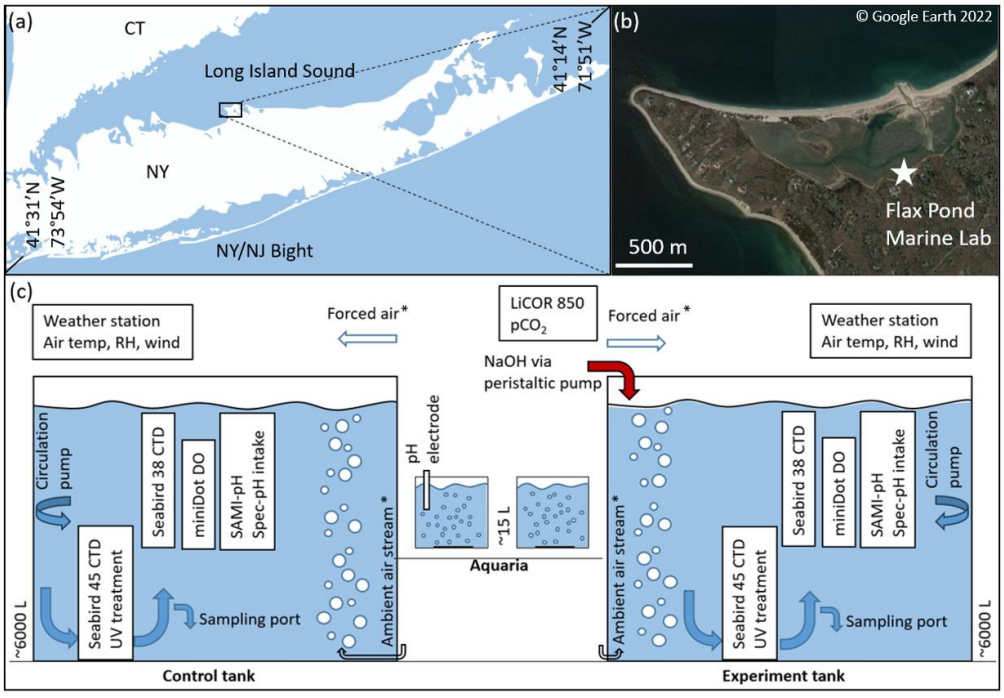

Figure 2: (*a, b*) Flax Pond Marine Laboratory is located on Long Island Sound, New York, USA (© Google Earth 2022). (*c*) The ~6000 L control and experiment tanks were instrumented with a series of oceanographic sensors and sampled routinely for DIC/ TA analyses to allow for measurement of carbon uptake over time following an addition of alkalinity in the form of NaOH. The ~15 L aquaria were instrumented with standard pH electrodes and monitored with routine TA analyses. The Forced air* and Ambient air streams* indicate their use in some but not all experiments, as noted in later sections.

This study was conducted at the Flax Pond Marine Laboratory at Stony Brook University, NY. All experiments used natural seawater collected from Flax Pond, part of a 128-acre salt marsh tidal wetlands connected to the Long Island Sound. The surface areas of the tanks and aquaria were ~4.6 m^2 and ~0.1 m^2, respectively. The tanks had a diameter of 0.24 m, a total height of 1.52 m, and were typically filled to a height of ~1.35 m, allowing for a corresponding seawater volume of 6185 L. The large tank volumes were chosen to limit interactions with walls while increasing the air-seawater boundary, and to allow for in-situ oceanographic sensor deployment and frequent bottle sampling while retaining semi-controlled temperature, mixing, filtration, and biological control. The inherent limitations of these tank tests include limited air-sea interaction, unrealistic light levels and circulation, and biological responses that are not a perfect representation of natural seawater in the ocean, but serve as a stepping stone to mesocosm and eventual field experiments. On average, the large (~6,000 L) tank experiments took ~6.5 weeks after dosing with NaOH to reach 90% of the calculated or extrapolated asymptotic ΔDIC/TA addition ratio indicative of full air-seawater equilibrium, as will be discussed in Section 3. Therefore, in addition to the large tank tests, we conducted a series of smaller aquaria alkalinity additions to increase our capacity for experimental test cases. The limitations of the aquaria include limited sensor options, unrealistic circulation, and limited biological control.

2.1.1 Tank experiments

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Seawater was pumped into the tanks at high tide through a series of sock filters to exclude macroscopic biology. The tanks were then dosed to 40 ppm bleach (sodium hypochlorite) and the shock-treated seawater was allowed to circulate through the tanks for ~1 day to limit biological growth. The seawater was then circulated through UV light arrays to break down the bleach over ~1-2 weeks, as assessed by a standard Hach test kit for free chlorine. During this period, seawater was pumped between the two large test tanks (~25 L/min) to increase mixing of the bleach and to homogenize the tanks to similar initial conditions. For the remainder of each experiment, the seawater was continually pumped through the UV sterilizers.

Oceanographic sensors and discrete daily bottle sampling, as described in Sections 2.2 and 2.3, respectively, were deployed for carbonate chemistry analysis for several days prior to the alkalinity addition to understand the initial baseline conditions in both tanks. Two submerged pumps were used for water circulation within each tank: the first pump (Current eFlux DC Flow Pump, 210 GPH) cycled seawater through the UV arrays with an estimated overturning time of the bulk tank on order of 1 day, and a second (Kedsum Submersible pump, 260 GPH), mounted at an angle halfway down the tank wall, allowed for subsurface circulation within the tank to reduce the occurrence of unmixed 'dead zones ' and subsequent non-homogenous biological growth, as assessed visually on the surface of the water and/or tank lining. With exceptions discussed in Section 2.4, the surface of each tank was still throughout the experiments.

After baselining, one tank (referred to as the "experimental tank") was dosed with enough 0.5 M NaOH (see Supplementary Materials) to raise the bulk seawater pH to the target pH of interest for a given experiment, and the same volume of DI water was added to the other tank (referred to as the "control tank"). NaOH additions were typically dosed into the tank via peristaltic pump at a low enough rate (~50 mL/min) that a steady increase in bulk tank pH was observed, but local pH measured just below the NaOH introduction never exceeded a pH of 9.0. A pump (~25 L/min) was placed just below the NaOH stream to speed the mixing of NaOH into the bulk tank, increase dilution from the point source, and to prevent the immediate precipitation of $Mg(OH)_2$ upon contact of the NaOH with seawater. This pump was removed after the full volume of NaOH was mixed into the tank.

After the alkalinity addition, the tanks were left to equilibrate with the atmosphere and were monitored by sensors and sampling as described in Sections 2.2 and 2.3. The tanks were indoors in the wet laboratory at Flax Pond Marine Lab, such that temperature and CO_2 concentration were moderated by the building's HVAC system, but varied throughout days and seasons depending on other uses of the lab space. The experiments were concluded when the observed pH or DIC (calculated from daily pH and frequent TA measurements) appeared to stabilize (e.g., ΔpH ±0.05% or ΔDIC ±10 μmol kg^{-1} per day) over several days. The continuous improvement of experimental methods during this study resulted in some minor variations among the methods used for each experiment, including methods of NaOH dosing, tank circulation, and biological control, as discussed where necessary in Section 3 and in the Supplementary Materials.

2.1.2 Aquaria experiments

A series of polycarbonate aquaria were filled with 15 L of seawater taken from the large control tank just after the described bleaching and bleach breakdown procedure was completed. NaOH was dosed into each aquaria to reach a targeted bulk pH_T, with a corresponding volume of DI H_2O added to the control aquaria, and then the seawater was allowed to equilibrate with atmospheric pCO_2 over days to weeks. The aquaria did not have either UV light arrays for biological control or aquarium pumps for internal circulation. In most cases, the aquaria were bubbled with air (~4 L/min) via a standard aquarium bubbling bar spanning the center diameter of each aquarium to reduce the equilibration time of these experiments compared to the large tank experiments for all initial pH conditions investigated. No sensors were deployed in the aquaria due to their limited size, and seawater chemistry was established via discrete pH_T and TA measurements (Sect. 2.2).

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As shown in Eq. (6), we define the dimensionless 'Carbon-to-Alkalinity Ratio' (CAR) for our experiments as the molar ratio of the increase in *n*DIC (in units of µmol/kg, normalized to the system's initial salinity to account for evaporation) to the magnitude of the TA increase (ΔTA, in units of µmol/kg). $nDIC_{equ}$ is the measured (via direct titration) or calculated (via CO2SYS using measured TA and pH_T) DIC value that the system reached at the end of an experiment (Pierrot et al., 2006; Van Heuven et al., 2011). Some experiments were left long enough to achieve equilibration with atmospheric CO_2, but others were halted early. In these cases, a CO2SYS calculation was used to estimate the DIC increase expected at equilibration given initial seawater conditions, and the difference between this value and the final recorded $nDIC_{equ}$ was used to estimate the overall percent equilibration for a given experiment. Depending on experimental constraints described in later sections, $nDIC_i$ may represent either: (1) the final *n*DIC measured (via titration of bottle samples) or calculated (via CO2SYS using seawater TA and pH) in the control tank, or (2) the 'baseline' *n*DIC before the addition of NaOH to a given aquaria experiment, for cases where a corresponding control case may not be available. Note that because we are reporting CAR values where the measured DIC has reached or has been estimated at equilibrium, the CAR values we measure and report reflect the ratio of ΔDIC to ΔTA that would be expected given sufficient time for air-sea exchange to reach equilibrium, and so are equivalent to directly measuring the value of the "TA addition potential impact ratio" as defined by Wang et al., 2023.

$$\text{Carbon-to-Alkalinity Ratio (CAR)} = (nDIC_{equ} - nDIC_i) / \Delta TA \quad (6)$$

2.2 Oceanographic sensors

Each tank was instrumented with a series of sensors placed halfway down the wall of the tank near the inlet of the UV circulation pump. A Seabird 38 Digital Oceanographic Thermometer and Seabird 45 MicroTSG Thermosalinograph continuously monitored seawater temperature and salinity, respectively. Dissolved oxygen was measured by a PME miniDOT Logger at 10 min resolution. pH_T was monitored daily by a SAMI-pH (manufacturer specified accuracy/precision ~ 0.003/0.001, though this accuracy is likely an underestimate of the uncertainty given known challenges for the calibration of the pH_T measurements) and by a semi-automated spectrophotometric (spec-pH) pH unit (~± 0.0055/0.0004) as described by Carter et al. (2013). CRM measurements were taken by each pH system at the beginning and end of each experiment and were used alongside discrete samples of DIC and TA as described in Section 2.3 to constrain the stability of each sensor. The SAMI-pH measurements were recorded at ambient seawater temperature and corrected for in-situ salinity as recorded by the Seabird Thermosalinograph following best practices from the manufacturer. The spec-pH analyses occurred in a jacketed cuvette held at 20 °C (regulated via water bath) and were corrected to the in-situ bulk tank temperature and salinity as recorded by the Seabird Thermometer and Thermosalinograph. Both the SAMI-pH and spec-pH rely on spectrophotometric analysis of metacresol purple indicator dye, which allows for pH measurement within the pH_T range of approximately 7 to 9. For experiments in which enough NaOH was dosed into seawater to raise pH above these limits, a Thermo Scientific Orion ROSS Ultra pH/ATC Triode combination electrode (8157BNUMD) was used to monitor pH_{NBS} at the surface of the tank (±0.01 precision), which was then converted to pH_T for comparison with the other pH sensor systems.

A LiCOR LI-850 sensor was used to analyze atmospheric pCO_2 (±1.5% accuracy) above the tanks. The inlet to this sensor was periodically moved between tanks to ensure that atmospheric pCO_2 in the vicinity of the control and experiment tanks was the same. AcuRite Iris weather stations were mounted on the side of each tank to monitor air temperature (±2 °C), relative humidity (±3%), and air speed (±0.8 m s^{-1}). All data were compiled on an hourly basis in a custom R package.

2.3 Discrete sampling

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Two types of discrete sampling were used to constrain carbonate chemistry throughout these experiments. First, 500 mL of seawater was collected and preserved from each tank, typically on a daily basis, and as frequently as hourly during the addition of NaOH, following best practices laid out by Dickson (2007) including overflowing of the sample bottles during collection and addition of 0.2 mL of saturated mercuric chloride ($HgCl_2$) as a preservative. These bottle samples were analyzed for DIC and TA at NOAA Pacific Marine Environmental Laboratory (NOAA/PMEL). DIC concentrations were measured using a coulometer (UIC Inc.) and Single Operator Multiparameter Metabolic Analyzer (SOMMA) (Johnson et al., 1985; 1993). TA was determined by an open-cell acidimetric titration (Dickson et al. SOP 3b, 2007). The accuracy of DIC and TA measurements was assessed with Certified Reference Materials (CRMs, supplied by the Dickson laboratory at Scripps Institution of Oceanography), and overall uncertainty for both DIC and TA was typically ± 0.1% (~2 µmol/kg).

In addition, discrete seawater samples were analyzed for TA via open-cell potentiometric titration at Stony Brook University. A Thermo Scientific Orion ROSS Ultra pH/ATC Triode combination electrode (8157BNUMD), calibrated using three buffer solutions (pH_{NBS} 4.01, 7, and 10.01) was used to track the titration of a ~20 mL seawater sample with a dilute HCl solution (~0.1 M in 0.7 M NaCl, calibrated daily with CRM or a secondary seawater standard) following a modified Gran titration procedure using a Kloehn digital syringe pump (Song et al., 2020; Wang and Cai, 2004). The precision of TA measurements was ~±5-10 µmol/kg. This TA data was corrected to that of the bottle samples analyzed via titration at NOAA PMEL where available (see Supplementary Materials).

There are several differences between the aquaria experiments and the larger tank experiments. First, the aquaria experiments were monitored daily to every few days by discrete measurement of TA at Stony Brook University and pH_{NBS} via Thermo Scientific Orion ROSS Ultra pH/ATC Triode combination electrode (8157BNUMD) (±0.01 precision), which was then converted to pH_T and corrected against the other pH sensor systems via occasional bottle samples for DIC and TA analysis at NOAA PMEL. Variations between these experiments are noted in Section 3 where necessary and in the Supplementary Materials.

In either tank or aquaria cases where mineral precipitation was observed, 0.5 – 1 L of seawater was vacuum filtered through a 0.45 µm Whatman GF/F filter via vacuum pump and the solids were rinsed with DI water 3 times to remove NaCl. The precipitate was dried in an oven at 90 °C, then crushed into a uniform powder via mortar and pestle. Samples were analyzed via Hitachi 4800 Scanning Electron Microscopy (SEM) (5 kV) and Rigaku SmartLab X-ray Diffraction (XRD) (Cu Kα, 1.5406 Å, 10 - 100° 2 θ at 4°/min) at Brookhaven National Laboratory at the Materials Synthesis and Characterization Facility of the Center for Functional Nanomaterials.

2.4 Evaluation of CO_2 uptake by seawater in response to NaOH perturbation

Seawater carbonate chemistry measurements were used to analyze the uptake of CO_2 in each tank, primarily relying on calculations from the NOAA/PMEL DIC and TA analyses of bottle samples when available and using sensor pH and Stony Brook TA measurements for cross-verification or to fill in between discrete DIC samples. Carbonate chemistry calculations were performed using CO2SYS (Lewis and Wallace, 1998), with Leuker et al. (2000) carbonate constants, Dickson (1990) for KSO_4, and Lee et al. (2010) for total boron. Wherever possible, a combination of CRM analyses and comparisons between simultaneous pH sensor and NOAA PMEL bottle samples were used to correct SAMI-pH and spectrophotometric pH sensor data for drift. DIC and TA data were normalized to the salinity at the start of a given experiment to account for evaporation (Friis et al., 2003).

Changes in the seawater carbonate chemistry over time were analyzed with respect to shifts away from the baseline within a single control or experiment tank, as well as with respect to the differences between the control and experimental tanks.

3 Results and Discussion

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3.1 Large tank experiments

A summary of the range of oceanographic variables measured by sensors and bottle samples, calculated via CO2SYS, or extrapolated to equilibration conditions during the large tank experiments is provided in Table 1. This summary includes 6 experiments including 3 targeting pH_T 8.5 (still surface water, with forced air, and with forced air and air bubbling) and one (each) targeting pH_T values of 8.7 (still surface water), 9.5 (with forced air and air bubbling), and 10.3 (still surface water). In two early experiments in which bulk pH_T was raised from the initial condition to 8.3 and to 8.7, the initial pH_T and TA varied between the control and experiment tanks as seawater was pumped from multiple reservoirs and unevenly distributed between the tanks. The experiments were subsequently refined to allow for several days of cross-pumping between tanks to homogenize the control and experiment seawater before NaOH was added at the start of an experiment. More details on experimental variations and a larger summary table are available in the Supplementary Materials.

The initial pH_T, TA, and DIC varied across experiments as seawater was collected between March 2022 and May 2023, ranging from pH 7.66 (December 2022) – 7.95 (May 2023), TA 2001 (May 2023) – 2176 (March 2023) µmol/kg, and DIC 1847 (May 2023) – 2021 (March 2023) µmol/kg. Both measured and CO2SYS -calculated DIC and TA values were normalized to salinity to account for evaporation, which drove salinity increases ranging from 0.2 – 7.1 across these experiments.

After the addition of NaOH, the control and experiment tanks were allowed to equilibrate with atmospheric CO_2. While refinements in the experimental design allowed for complete or near-complete equilibration in later experiments, as determined by the stabilization of nDIC at some asymptotic value, early experiments were terminated before full equilibration. In all experiments, the absorption of atmospheric CO_2 began immediately after the NaOH addition, as determined by decreasing pH and Ω_{arag} and increasing DIC and seawater pCO_2. nTA was fairly stable or increasing (+10 - 60 µmol kg^{-1}) after the NaOH addition in all cases except the pH_T = 10.3 experiment, where nTA and DIC rapidly decreased due to runaway $CaCO_3$ precipitation. A stable TA value is an indicator that no significant persistent mineral precipitation (e.g., $Mg(OH)_2$ or $CaCO_3$) has occurred. In the absence of active mixing or bubbling, $Mg(OH)_2$ precipitation occurred immediately upon the introduction of NaOH to seawater, however the precipitation can be rapidly dissolved by turbulence (i.e., pumping NaOH directly above a strong circulation pump and/or stream of air bubbles). No $CaCO_3$ precipitation was observed in the tanks or aquaria for which the bulk seawater pH_T was <10.0. The pH_T = 10.3 experiment was designed to induce $CaCO_3$ runaway precipitation, as described in Section 3.3.

Ω_{arag} ranged from 1.4 - 2.5 in the control tanks with minimal variation over the course of any given experiment. During the three experiments in which bulk pH_T was increased to ~8.5, Ω_{arag} increased immediately to 6.0 - 6.3 at the peak of the experiments, before slowly decreasing to 2.8 - 3.0 as the seawater equilibrated with atmospheric CO_2. For the bulk pH_T 9.5 experiment, Ω_{arag} increased to 20.2 and slowly decreased to 5.0 when the experiment was ended at full equilibration. Mineral precipitation was observed in the bulk pH_T 10.3 experiment, where Ω_{arag} was increased to 30.3 and rapidly (<1 week) fell to 5.2 after the addition of NaOH.

The results of one representative set of time-series measurements from the control and experiment tanks are shown in Figure 3 for the case where pH_T of the bulk experiment tank was raised to 8.5 then allowed to relax into equilibration with the atmosphere without the addition of surface air forcing or bubbling. Time-series plots for the other tank-scale experiments are available in the Supplementary Materials.

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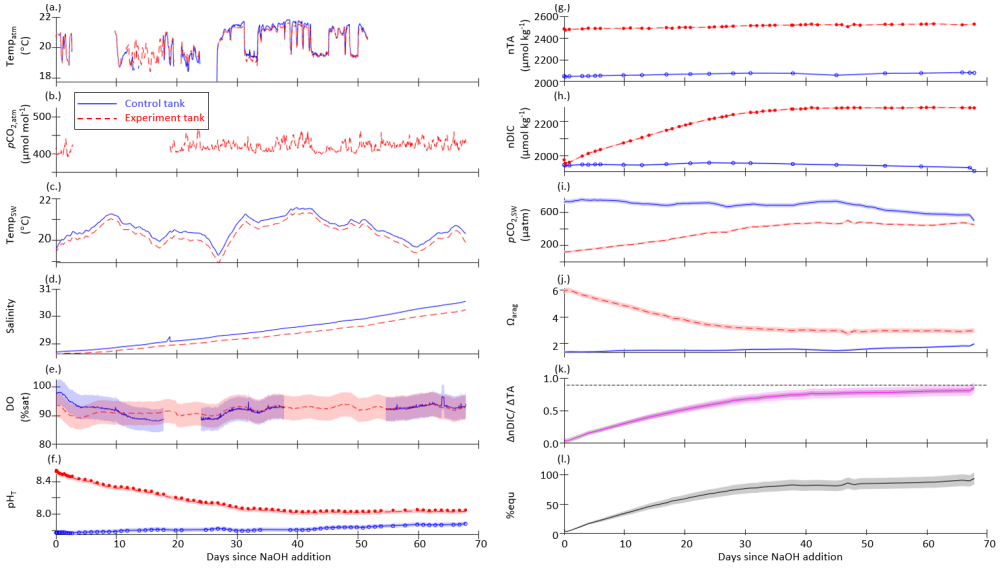

Figure 3: Time-series data for the case where pH_T of the bulk experiment tank was raised to 8.5 with no forced air flow and no bubbling (still surface) for control (blue, solid) and experiment (red, dashed) tanks: (*a*) continuously measured air temperature, (*b*) atmospheric pCO_2, (*c*) seawater temperature, (*d*) salinity, and (*e*) dissolved oxygen; (*f*) pH_T measured by the SAMI-pH (*circles*) and interpolated from the spec-pH (*line*), corrected to bottle sample and CRM data; (*g*) NOAA/PMEL-measured TA and (*h*) DIC from bottle samples and normalized to salinity; (*i*) seawater pCO_2 and (*j*) saturation state of aragonite (Ω_{arag}) calculated from interpolated nDIC and nTA data via CO2SYS; (*k*) the observed carbon uptake ratio (CAR) as (nDIC$_{exp}$ – nDIC$_{control}$) / $\Delta TA_{NaOH\ addition}$ (*solid*) and the theoretical CAR (*dashed*) from a CO2SYS calculation using measured TA and the average $pCO2_{atm}$ to estimate the equilibrium change in DIC (*dashed*); (*l*) the percent equilibration estimated between the observed and theoretical CAR. Data gaps in panels *a*, *b*, and *e* are due to connectivity issues while offloading sensor data.

The ΔnTA and ΔnDIC values calculated between the control and experiment tanks are summarized in Figure 4, where nTA and nDIC were interpolated between bottle samples measured at NOAA-PMEL, and/or were calculated via CO2SYS using sensor pH_T and TA measured at Stony Brook University corrected to less frequent NOAA-PMEL TA and DIC bottle samples. The ratio of the ΔnDIC to the addition of alkalinity in the form of NaOH, or ΔnTA, is included in Figure 4 for all experiments except that of the bulk pH_T increase to 10.3. Neglecting experiments that were terminated before full equilibration, the final observed CAR ranged from 0.75 ± 0.04 to 0.87 ± 0.08 (Table 1).

Henry's law and CO2SYS calculations were used to estimate the initial and final equilibration condition of each tank experiment. LiCOR $pCO_{2,atm}$ measurements were averaged across experiments to a representative value of 421 ± 14 ppm, which was used with the initial seawater temperature and salinity to estimate $pCO_{2,seawater}$ at the beginning of each experiment. This initial $pCO_{2,seawater}$ was in all cases greater than the atmospheric $pCO_{2,seawater}$, indicating that the seawater was not fully equilibrated with the atmosphere at the time when NaOH was added, likely due to respiration and decomposition of biology removed during the bleaching step (Section 2.1), and as such, the tanks should outgas CO_2. The initial equilibrium DIC was estimated from a CO2SYS calculation using the $pCO_{2,seawater}$ and nTA$_i$, which in all cases was less than the initial nDIC measured or calculated from nTA$_i$ and $pH_{T,i}$ (by 29 – 108 µmol kg^{-1}). These observations underscore the importance of having a control tank to capture natural dynamics of CO_2 ingassing and outgassing to ensure that changes in DIC attributed to OAE are correctly accounted for.

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The final equilibrium *n*DIC was estimated from a CO2SYS calculation using the same $pCO_{2,seawater}$ and the *n*TA measured just after the NaOH addition, corrected for the linear increase in salinity over the course of the experiment. The ratio of the expected ΔnDIC calculated at equilibrium with the atmosphere to the addition of alkalinity provides a simple estimate of the expected CO_2 storage capacity for a given experiment. The percent equilibration for each experiment was then estimated from the measured and expected values for CAR. Within the series of experiments with a targeted pH_T of 8.5, the timeline to reach an estimated 90% CO_2 equilibration decreased from 65 days (with internal circulation but still water at the surface of the tank), to 50 days (with the addition of forced air movement across the surface of the tank) to 22 days (with the addition of air bubbling). We note that only the two cases (targeted pH_T of 8.5 and 9.5) with the addition of air bubbling reached full equilibration with the atmosphere.

Table 1: Range of variables measured, calculated, or extrapolated in large tank experiments, where M denotes direct measurement, C denotes calculation via CO2SYS, and E denotes extrapolation to equilibrium conditions. Subscripts *i* and *f* refer to initial and final conditions, and 'peak' refers to the time point immediately after the addition of NaOH.

pH target	-	8.5		8.5		8.5		8.7		9.5		10.3	
Surface condition	-	Still		Forced Air		Forced Air and Air Bubbles		Still		Forced Air and Air Bubbles		Still	
Tank (C = control, E = experiment)	-	C	E	C	E	C	E	C	E	C	E	C	E
ΔTA = NaOH addition (± 10 µmol/kg)	M	0	409	0	462	0	375	0	626	0	1406	0	3305
$Salinity_i$ (g/kg)	M	28.7	28.7	30.2	30.2	30.4	30.4	26.9	26.8	26.9	26.9	28.5	28.4
$Salinity_f$ (g/kg)	M	30.5	30.2	37.3	36.6	34.7	33.7	27.6	27.6	29.0	29.2	28.6	28.6
$pH_{T,i}$ (± 0.005)	M	7.76	7.76	7.73	7.73	7.93	7.93	7.92	7.75	7.95	7.95	7.70	7.75
$pH_{T,peak}$ (± 0.005)	M	-	8.54	-	8.58	-	8.49	-	8.68	-	9.51	-	10.10
$pH_{T,f}$ (± 0.005)	M	7.88	8.05	7.85	7.99	7.99	8.01	7.84	8.26	8.01	8.21	7.75	9.52
nTA_i (± 10 µmol/kg)	M	2049	2049	2069	2069	2248	2248	2075	2075	2007	2007	2023	2025
nTA_{peak} (± 10 µmol/kg)	M	-	2458	-	2531	-	2623	-	2701	-	3414	-	5330
nTA_f (± 10 µmol/kg)	M	2080	2528	2235	2674	2246	2624	2095	2696	2014	3363	2041	1253
$nDIC_i$ (µmol/kg)	M	1944	1947	1957	1996	2082	2087	1897	1975	1852	1852	1928	1938
$nDIC_f$ (µmol/kg)	M	1908	2280	2084	2433	2027	2365	1937	2336	1832	2977	1947	720
$\Omega_{aragonite,i}$	C	1.39	1.37	1.4	1.1	2.0	2.0	2.4	2.4	1.9	1.9	1.4	1.3
$\Omega_{aragonite,peak}$	C	-	5.9	-	6.0	-	6.2	-	8.8	-	19.3	-	30.3
$\Omega_{aragonite,f}$	C	2.0	3.0	1.7	2.8	2.5	3.0	1.9	4.4	2.1	4.9	1.4	5.2
CAR_f	C	-	0.85 ± 0.04	-	0.75 ± 0.04	-	0.87 ± 0.08	-	0.52 ± 0.07	-	0.82 ± 0.09	-	-
$CAR_{equilibrium}$	E	-	0.89	-	0.85	-	0.85	-	0.84	-	0.81	-	-
% equilibration (time elapsed in days)	E	-	95 ± 10 (67)	-	92 ± 10 (63)	-	102 ± 12 (45)	-	79 ± 6 (42)	-	104 ± 7 (74)	-	(13)

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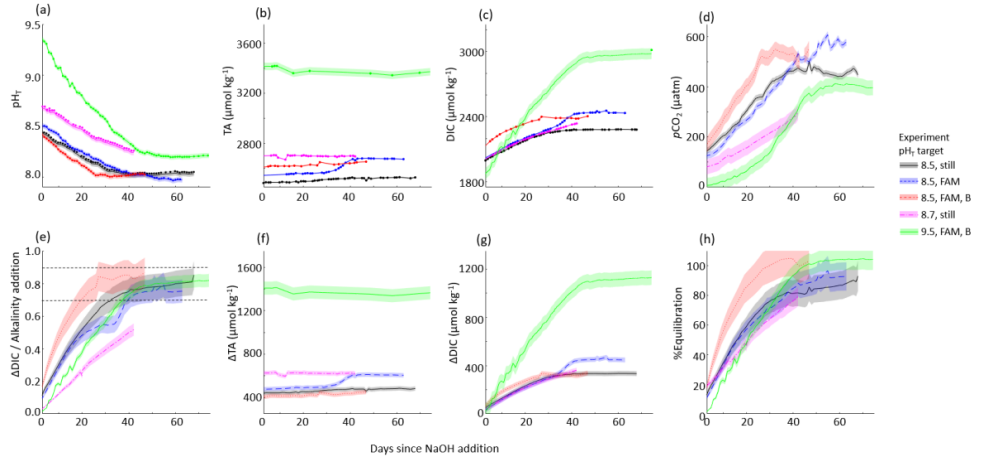

Figure 4: Results of 5 tank-scale experiments in which enough NaOH was added to each tank to raise the bulk pH_T to 8.3 – 9.7. pH_T decreased rapidly in all cases in which air bubbling sped equilibration with atmospheric CO_2. Results include: (a) measured pH_T, (b) measured TA, (c) measured DIC or CO2SYS calculated (for pH_T 9.5 case only), (d) CO2SYS -calculated pCO_2, (e) the observed carbon uptake ratio (CAR) as $(DIC_{exp} - DIC_{control}) / \Delta TA_{NaOH\ addition}$ with horizontal dashed lines representing the expected range of 0.7-0.9 mol CO_2 uptake / mol NaOH added to seawater, the change in (f) TA and (g) DIC compared to the baseline measurements before the addition of NaOH, and the percent equilibration estimated between the observed and theoretical CAR.

3.2 Aquaria experiments

The large volume of tank experiments allowed for precise measurement of the seawater carbonate chemistry via bottle sampling (1L each, sent to NOAA/PMEL for analysis) with high sampling frequency. To compliment these measurements, we also performed a series of experiments in smaller aquaria (15 L each), which enabled a larger number of replicates and a faster time to equilibrium when bubbled with air. Table 2 provides a summary of the range of oceanographic variables quantified for the aquaria experiments.

Table 2: Range of variables measured, calculated, or extrapolated in aquaria experiments, where M denotes direct measurement, C denotes calculation via CO2SYS, and E denotes estimation within specified equilibration conditions. Subscripts *i* and *f* refer to initial and final conditions, and 'peak' refers to the time point immediately after the addition of NaOH.

pH target	-	0 Control	8.3	8.5	8.5 Without air bubbles	8.7	9.3	9.5	9.7	9.9	10.0	10.1	10.2	10.3
ΔTA = NaOH addition (± 10 µmol/kg)	M	0	187	331	362	543	1409	1679	2037	2216	2276	2504	2796	3829
$pH_{T,i}$ (± 0.005)	M	7.94	7.97	7.90	7.86	7.95	7.98	7.98	7.98	8.06	8.04	8.04	8.04	7.95
$pH_{T,peak}$ (± 0.005)	M	-	8.28	8.41	8.40	8.63	9.22	9.43	9.64	9.83	9.91	10.23	10.32	10.20
$pH_{T,f}$ (± 0.005)	M	8.06	8.03	8.07	8.11	8.08	9.21	9.02	8.23	8.65	8.96	8.72	9.46	7.99
TA_i (± 10 µmol/kg)	M	2265	2262	2250	2250	2250	2393	2393	2393	2531	2531	2531	2531	2250
TA_{peak} (± 10 µmol/kg)	M	-	2449	2582	2611	2793	3801	4072	4430	4748	-	-	-	4608

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TA_f (± 10 µmol/kg)	M	2323	2476	2640	2645	2822	3837	4110	4420	4462	1702	1835	1537	2202
DIC_i (µmol/kg)	C	2089	2073	2091	2107	2070	2192	2192	2192	2282	2287	2287	2287	2067
DIC_f (µmol/kg)	C	2113	2246	2377	2382	2540	3372	3486	3877	3389	992	1244	671	2003
$\Omega_{aragonite,i}$	C	2.1	2.2	1.9	1.8	2.1	2.34	2.4	2.4	2.9	2.8	2.8	2.8	2.1
$\Omega_{aragonite,peak}$	C	-	4.2	5.5	5.5	8.1	19.5	23.1	27.0	29.8	30.2	30.9	32.4	38.9
$\Omega_{aragonite,f}$	C	2.4	2.7	3.1	3.1	3.4	5.9	7.9	7.1	13.7	6.5	5.7	7.0	2.2
CAR_f	C	-	0.92 ± 0.10	0.87 ± 0.06	0.76 ± 0.05	0.87 ± 0.04	0.84 ± 0.02	0.86 ± 0.02	0.84 ± 0.02	0.50	-	-	-	-
$CAR_{equilibrium}$	E	-	0.69	0.67	0.64	0.77	0.80	0.80	0.80	0.81	-	-	-	-
% equilibration (time elapsed in days)	E	(40)	130 (16)	126 (18)	116 (40)	111 (16)	104 (18)	106 (18)	104 (18)	62 (1)	(1)	(1)	(1)	(16)
$CaCO_3$ precipitation?	M	-	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes

The aquaria experiments are not directly comparable to the control stated in Table 2. This is because seawater for these experiments was collected in three batches between March and May 2023, with 4-6 aquaria experiments running in parallel within each set of experiments. One control aquarium was monitored for pH_T and TA changes beginning in March 2023 and concluding in May 2023. The CAR for each aquaria experiment was calculated from changes in DIC and TA between the initial 'baseline' and after the NaOH was added within a given aquarium, rather than between the experiment and control cases. The CAR ranged between 0.76 ± 0.05 and 0.92 ± 0.10, excluding cases where mineral precipitation was evident and for the pH_T 9.9 case where the experiment ended after one day due to a sensor logging failure. This wide range in ΔDIC/ ΔTA is likely due to the low temporal resolution of pH_T and TA samples, and the imprecision of electrode-based pH_T measurements relative to the SAMI-pH and spec-pH based measurements used in the large tank experiments.

With the exception of a single target pH_T 8.5 experiment, all aquaria were bubbled with ambient air, allowing for rapid CO_2 exchange, and an optically clear lid was placed on each aquarium to reduce evaporation and splashing onto nearby equipment. Some evaporation was evident from the rising TA throughout these experiments, but was not resolvable within the resolution of a handheld salinometer used for these experiments, which ranged from values of 30 - 31 during the experiments. Therefore, DIC and TA were not normalized to salinity in these cases. Temperature was discretely recorded from a combination Ross pH electrode, and temperature values ranged from 19 - 21 °C during the experiments.

After the addition of NaOH, the aquaria were allowed to equilibrate with atmospheric CO_2. Similar to the large tank experiments, we used Henry's law and CO2SYS calculations to estimate the initial and final equilibration condition of each aquaria experiment. The same average $pCO_{2,atm}$ of 421 ± 14 ppm was used with the initial seawater temperature and salinity to estimate $pCO_{2,seawater}$ at the beginning of each experiment. The initial equilibrium DIC was estimated from a CO2SYS calculation using this $pCO_{2,seawater}$ and TA_i, which in all cases was less than the initial DIC calculated from TA_i and $pH_{T,i}$ (by 36 – 36 µmol kg^{-1}). This indicates that the seawater was not fully equilibrated with the atmosphere at the time when NaOH was added, likely due to respiration and decomposition of biology removed during the bleaching step (Section 2.1), and as such, the aquaria should outgas CO_2. The final equilibrium DIC was estimated from a CO2SYS calculation using the same $pCO_{2,seawater}$ and the TA measured just after the NaOH addition. The percent equilibration for each experiment was then estimated between the measured and predicted values for ΔDIC/ ΔTA. Due to the air bubbling, most experiments approached equilibrium with the atmosphere within 1-7 days, with the exception of the non-bubbled pH_T 8.5 experiment that took ~20 days. The surface water of this non-bubbled experiment was stagnant, and the water was only mixed via stirring just before taking pH and TA samples. Absorption of atmospheric CO_2 began immediately after the NaOH addition, as determined by decreasing pH_T. We note that there are significant uncertainties in these equilibrium estimates, and

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that more continuous seawater carbonate chemistry measurements and finer control of bubbling and diffusion rates are necessary to define the timeline for equilibration within the aquaria.

Each aquaria was gently stirred during the addition of NaOH to prevent $Mg(OH)_2$ precipitation. No $CaCO_3$ precipitation was observed in the tanks below a bulk seawater pH_T of 10.0, and TA remained stable in each of these experiments with the exception of some increase driven by minor evaporation on the order of +2 umol/kg per day. Experiments where $CaCO_3$ precipitation was induced by increasing the starting pH to values above 10 are discussed in Section 3.3.

The aquaria experiments with target pH_T from 8.3 – 9.9 are summarized in Figure 5.

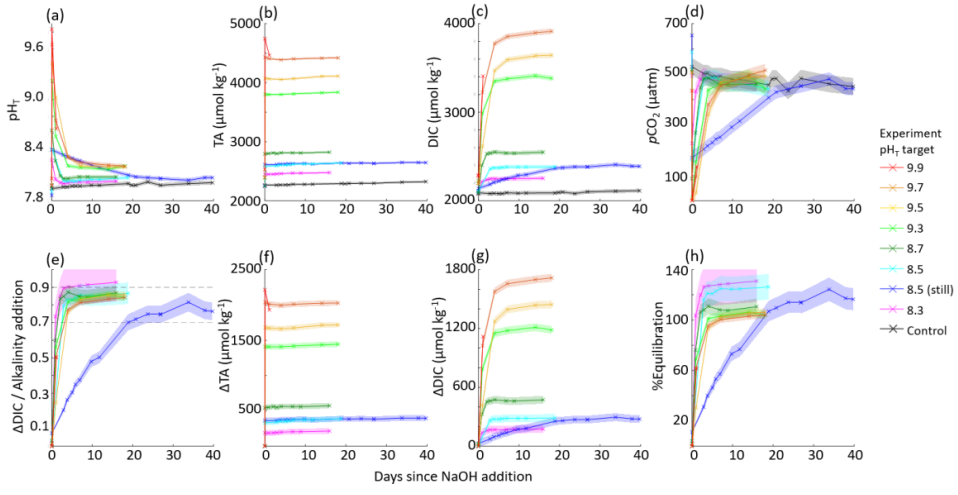

Figure 5: Results of 9 aquaria experiments in which enough NaOH was added to each aquaria to raise the bulk pH_T to 8.3 – 9.9. pH_T decreased rapidly in all cases in which air bubbling sped equilibration with atmospheric CO_2. Results include: (a) measured pH_T, (b) measured TA, (c) CO2SYS-calculated DIC, (d) CO2SYS-calculated pCO_2, (e) the observed carbon uptake ratio (CAR) as $(DIC_{exp} - DIC_{baseline}) / \Delta TA_{NaOH\ addition}$ with horizontal dashed lines representing the expected range of 0.7-0.9 mol CO_2 uptake / mol NaOH added to seawater, the change in (f) TA and (g) DIC compared to the baseline measurements before the addition of NaOH, and the percent equilibration estimated between the observed and theoretical CAR.

In general, the large tanks and aquaria showed reasonable agreement in achieving values for CAR within the expected range of 0.7-0.9 (He and Tyka, 2023). While the use of aquaria bubbled with air to speed equilibration allowed for a greater range of data collection within a constrained experiment timeline, the quality of this data is limited by the lack of appropriate sensors to fit into these small 15 L aquaria and fewer bottle samples due to the reduced quantity of seawater. However, while the large tanks allow for a larger range of oceanographic sampling and sensing techniques, it is more challenging to fully quantify mixing and circulation rates in the current large tank experimental setup.

Figure 6 shows the dependence of the equilibrium values of ΔDIC, CAR, and $\Delta pH_T = (pH_{final} - pH_{initial})$ as a function of the target starting pH_T value after alkalinity addition for both tank and aquaria experiments. Higher starting pH values correspond to a greater alkalinity addition, resulting in larger values of ΔDIC relative to lower starting pH values. The CAR is observed for all experiments to fall within the range typical for seawater with the temperature and salinity values used in these tests. As expected from calculations of the response of the seawater carbonate

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buffer system to additions of alkalinity, the pH_T at equilibrium exceeds the initial pH_T value prior to the addition of alkalinity. That is, even once equilibrium in the alkalinity enhanced experiment tank has been reached, the ending pH value is slightly elevated relative to the starting pH value.

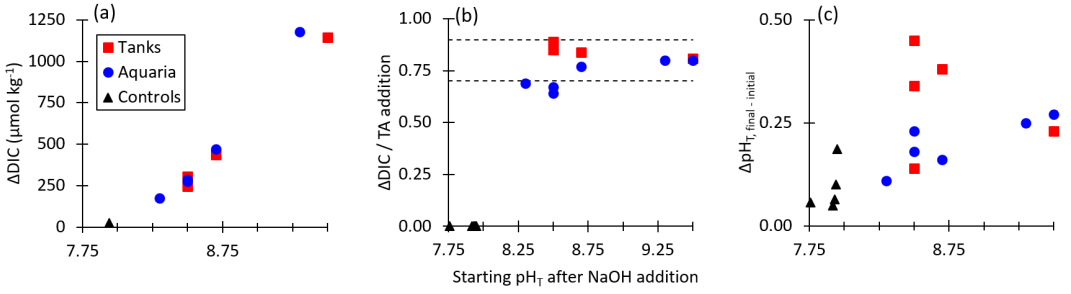

Figure 6: (a) The change in final CO2SYS-predicted DIC relative to the initial conditions for tank, aquaria, and control experiments increases with increasing NaOH additions. (b) CO2SYS-predicted CAR (ΔDIC / Alkalinity addition) at air-sea equilibrium conditions for tank, aquaria, and control experiments, with horizontal dashed lines representing the expected range of 0.7-0.9 mol CO_2 uptake / mol NaOH added to seawater. (c) The CO2SYS-predicted $\Delta pH_T = (pH_{final} - pH_{initial})$ increases as a function of the target pH_T value after alkalinity addition for both tank and aquaria experiments.

3.3 Experiments exceeding the $CaCO_3$ precipitation threshold

While $Mg(OH)_2$ precipitation occurs immediately upon introduction of NaOH to still seawater, it may be rapidly dissolved or avoided entirely by gentle mixing, including via the use of stirrers, circulation pumps, or air bubblers. This precipitation and redissolution happened rapidly enough that it was not identified in any TA or other variables measured in the aquaria and tank tests. However, in cases where enough NaOH was added to raise the bulk seawater pH_T to greater than 10.0 (i.e. in one large tank test with a target pH_T of 10.3, and in 4 aquaria experiments ranging from pH_T 10.0-10.3), runaway precipitation of $Mg(OH)_2$ and $CaCO_3$ was observed. This was characterized by a sharp reduction in both TA and DIC and an increase in turbidity.

In both the tank and aquarium pH_T 10.3 cases, discrete samples of the precipitate were collected at seven different times after the bulk pH_T value reached 10.3 (0h, 3h, 24h, 49h, 71h, 145h, 167h - see Fig. 6) for XRD and SEM analysis. At each timepoint, 0.5 – 1 L seawater was collected from the tank sampling port or from the center of the aquaria. In cases where precipitation had visibly settled at the bottom of the aquaria, this material was stirred into the water column before sampling. We note that material that settled to the bottom of the large tanks was not directly collected, and that only a subset of precipitation was collected at each time point, such that later timepoints may include solids that had precipitated at the beginning of the experiment. The filtered seawater was immediately analyzed for TA and pH via Ross electrode because the heightened pH was out of the range of spectrophotometric methods. Bottle samples of filtered seawater were not able to be analyzed at NOAA PMEL due to the continued precipitation of $CaCO_3$ after filtration and preservation. Both XRD and SEM results showed the dominance of $Mg(OH)_2$ precipitation immediately after the alkalinity addition and the corresponding increase in pH and $\Omega_{aragonite}$ (to a value of around 30), though this signal was partially obscured by the presence of other salts. The $Mg(OH)_2$ precipitation at this stage was thick, slurry-like, and difficult to appropriately rinse. Within hours of the NaOH addition, the runaway $CaCO_3$ precipitation began, characterized by fine, light particulates in the water column and a sharp increase in turbidity. Within ~24 hours of the NaOH addition, most $Mg(OH)_2$ signals had disappeared, leaving only aragonite and calcite peaks in the XRD. The results of the XRD analysis for the tank experiment are summarized in Figure 7, and the aquarium experiment showed similar results. TA decreased throughout the precipitation of $Mg(OH)_2$ and $CaCO_3$, and was below that of the initial seawater within 24 hours of the NaOH addition. In the tank experiment, the initial TA (2025 μmol/kg) was raised by 3305 μmol/kg. Within 3 days the TA

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had decreased to 1583 µmol/kg and continued to decrease through the termination of the experiment to 1253 µmol/kg 10 days after the addition of NaOH. The DIC, which was initially measured at 1938 µmol/kg, decreased to 720 µmol/kg by the end of the experiment. This experiment shows that runaway $CaCO_3$ can result in a significant loss of both efficiency of alkalinity dosing for OAE projects and of storage of carbon in the form of DIC. A figure of time-series data collected during the tank experiment is available in the supplementary materials.

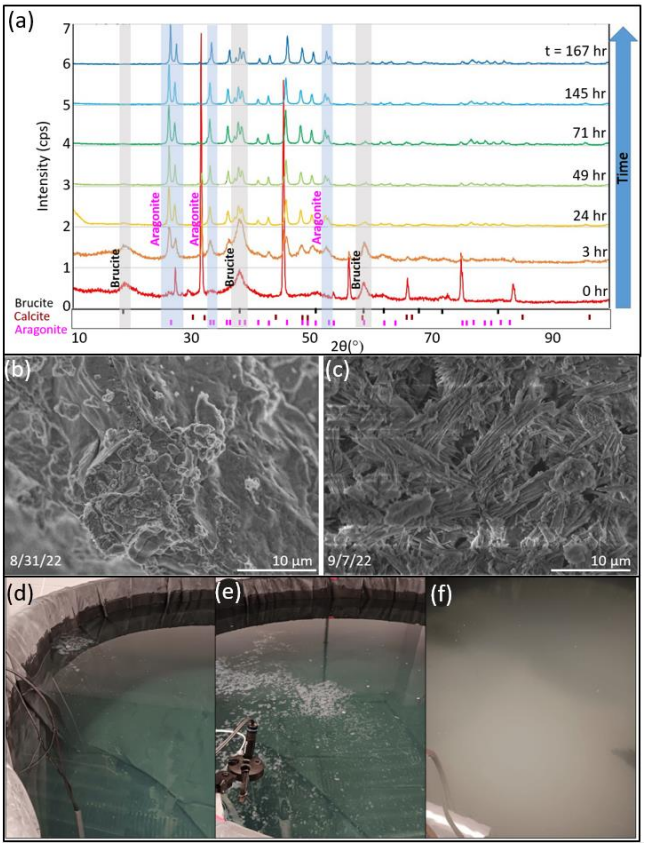

Figure 7: (*a*) XRD analysis (top) of particulates filtered from seawater after the addition of enough NaOH to raise the bulk seawater pH_T to 10.3 showed mineral precipitation initially dominated by $Mg(OH)_2$ before it was overtaken by $CaCO_{3,arag}$. The shaded grey vertical bars highlight peaks characteristic of brucite which typically disappear after 24 hours, and the shaded blue bars represent several aragonite peaks which appear between 3 and 24 hours. Representative SEM images show (*b*) $Mg(OH)_2$ captured ~3 hours after the NaOH addition, and (*c*) $CaCO_{3,arag}$ at the end of the experiment. Photographs of the tank experiment show seawater (*d*) before NaOH addition, (*e*) during NaOH addition into still water (i.e., without the use of stirrers, circulation pumps, or air bubblers to break up and redissolve $Mg(OH)_2$), and (*f*) ~3 hours after the NaOH addition, when runaway $CaCO_3$ precipitation became visually apparent.

In summary, the presence and duration of brucite precipitation upon addition of 0.5 M aqueous NaOH depends on the ratio of the NaOH addition rate to the local dilution rate in the receiving waters. Future research using flow through tanks could help identify thresholds below which brucite precipitation can be avoided or limited. At the given initial seawater conditions, the threshold for aragonite precipitation begins at an Ω_{arag} of 30, corresponding to

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pH_T > 10.0. The potential for this precipitation may be reduced by active mixing at the point of NaOH introduction, maintaining a mixing volume below bulk seawater pH_T of 10.0, and allowing for appropriate dilution in flow-through conditions.

5 Summary

These results demonstrate that ocean alkalinity enhancement using aqueous sodium hydroxide in seawater results in CO_2 removal from air at an efficiency of 0.75 (± 0.04) – 0.92 (± 0.10), with 90% equilibration typically achieved within 7 - 9 weeks (still surface water with ~16 L/min subsurface circulation through UV arrays) to 3 - 5 weeks (with the addition of ambient air bubbling into the bottom of each tank) of the initial addition when performed in ~6000 L tanks with seawater-air contact areas of around 4.6 m^2. Here, uncertainties are driven by sensor precision and temporal resolution in discrete DIC and TA sampling, the limited number of experiments with minimal opportunities for duplicates or replicates, and poorly constrained data on mixing, circulation, and air bubbling rates. Ongoing experiments seek to improve each of these conditions and should particularly focus on constraining the movement of water within a given tank to improve air-sea equilibration estimates and to allow for better extrapolation from tank to field experiments. In addition, a focus of ongoing and future work is to provide rate estimates for the uptake of atmospheric CO_2 in response to an NaOH addition, allowing for fitting and extrapolation of a shortened experiment to equilibration with the atmosphere.

We relied on several methods to constrain seawater carbonate chemistry. The tank-scale experiments primarily relied on discrete (<= daily) DIC and TA sampling (NOAA PMEL), paired with daily measurements from spectrophotometric pH systems (SAMI-pH and a semi-automated benchtop spec-pH system following Carter et al. (2013)) and local TA measurements. With appropriate calibration or correction of the spec-pH systems relative to CRM, there was no significant difference in carbonate calculations using the NOAA PMEL DIC-TA or spec-pH-local TA pairings, though the latter case typically produced larger uncertainties. Aquaria experiments relied on a standard glass pH electrode (< daily, corrected to spectrophotometric systems) with discrete (< daily) TA measurements, which provided reasonable data relative to the tank experiments. As a result, ongoing tank-scale experiments have limited the volume of discrete DIC and TA samples collected for analysis at NOAA PMEL to allow for faster and less expensive monitoring via spec-pH and local TA titrations. However, we note that the major limitation in this measurement pathway lies in the spec-pH method, which is typically limited to pH_T measurements ranging from 7 – 9 for the meta-cresol purple indicator dye used. While our measurements retained some sensitivity up to pH_T 9.5, such a method should typically be considered unreliable at these pH_T values, and we relied on frequent correction to CRM and comparison with DIC/TA samples. Thymol blue is an alternative spectrophotometric pH_T indicator dye with sensitivity over the higher pH_T conditions observed during these initial trials and will be assessed for future experiments.

Aqueous NaOH with concentrations as high as 0.5 M can be added directly to turbulent seawater with only limited observable precipitation of $Mg(OH)_2$. In these conditions this precipitated mineral rapidly redissolves on the timescales of minutes to seconds. Improved control over the NaOH dosing rate (in our tank experiments, ~50 mL NaOH/min) and the turbulence of the receiving water through metered flow through experiments will be valuable in extrapolating to field conditions. This precipitation is detectable both visually and through turbidity measurements and implies that straightforward measurement of pH and turbidity at the dispersal site can be used to adjust the alkalinity dispersal rate according to local mixing conditions such that $Mg(OH)_2$ precipitation is avoided and/or redissolves when it occurs. No significant $CaCO_3$ precipitation was observed at pH <10.0 or $\Omega_{aragonite}$ < 30.0. Runaway $CaCO_3$ precipitation was observed above these thresholds, where a massive precipitation and settling of $Mg(OH)_2$ and $CaCO_3$ solids results in less alkalinity in the overlying water than at the starting condition. pH and turbidity sensing combined with discrete TA measurements could be used as a feedback signal for alkalinity dosing into seawater to ensure that the local maximum thresholds at the dispersal location do not approach or exceed conditions that promote significant $CaCO_3$ precipitation. We note that future investigations seeking to better

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approximate field conditions should take into account seasonal and tidal shifts in temperature and salinity, and varying conditions of suspended sediment in the water column, including that of aerial dust, terrestrial runoff, and resuspended bottom sediments.

In these experiments, the seawater was filtered and bleach treated prior to experiments to limit biological growth, and both tank and aquaria experiments were conducted indoors with limited light. Nevertheless, in most experiments, biological growth was observed after a few weeks, including cyanobacteria and coccolithophores. A series of experiments are underway to test the difference in CO_2 removal efficiency for two side-by-side tanks, both of which are dosed with NaOH, but only one of which was bleached. Preliminary results show minimal difference between the bleached and unbleached tanks, indicating these experiments are applicable to real-world conditions, at least for regions with biological communities similar to that of Long Island Sound, but further investigation is warranted.

A focus of future work is to consider the potential impact of the SEAMATE process on local ocean acidification mitigation efforts. We note that in each constrained tank and aquaria experiment, the pH_T at equilibrium exceeds the initial pH_T value prior to the addition of alkalinity. A controlled release of alkalinity could theoretically be configured to maintain a locally elevated pH_T value relative to pre-alkaline conditions, with potential uses in aquaculture and hatchery environments.

These results provide clear and practical guidelines for MRV for OAE implementations employing aqueous alkalinity. First, carbonate chemistry and turbidity measurements at the alkalinity dispersal location can ensure that seawater parameters such as pH and $\Omega_{aragonite}$ remain within pre-determined safe bounds and that unwanted precipitation is avoided. Second, for a given OAE deployment, where ocean models provide a reasonable certainty about the fraction of the alkalinity plume remaining in the surface over weeks to months, the CO_2 removal efficiency and timescale for air-seawater equilibration provided by our experiments can place a lower bound on the amount of CO_2 removal expected from that OAE intervention. Expanding these studies from tank scale to mesocosm and field experiments will be crucial to understanding biological impacts and constraining realistic air-sea interactions in response to this type of OAE.

Data availability

Data are described in the manuscript and provided Supplementary Materials, which includes a .csv file with processed sensor and sample time-series data at hourly resolution.

Author contribution

MDE and BRC designed the experiments and MCR carried them out with support from NH, CS, and XL. JH provided support on experimental setup and instrumentation. MCR prepared the manuscript with contributions from all co-authors.

Competing interests

MCR is Lead Oceanographer and Head of MRV at Ebb Carbon, Inc. MDE is Co-Founder and Chief Scientific Advisor at Ebb Carbon, Inc.

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References

Albright, R., Caldeira, L., Hosfelt, J., Kwiatkowski. L., Maclaren, J.K., Mason, B.M., Nebuchina, Y. et al.: Reversal of ocean acidification enhances net coral reef calcification. Nature, 531, no. 7594: 362-365, 2016.

Bach, L. T., Gill, S.J., Rickaby, R.E.M., Gore, S., and Renforth, P.: CO_2 removal with enhanced weathering and ocean alkalinity enhancement: potential risks and co-benefits for marine pelagic ecosystems. Frontiers in Climate, 1, 7, 2019.

Berner, R. A., Lasaga, A.C., and Garrels, R.M.: Carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. Am. J. Sci.;(United States) 283, no. 7, 1983.

Boettcher, M., Chai, F. Cullen, J., Goeschl, T., Lampitt, R., Lenton, A., Oschlies, A. et al.: High level review of a wide range of proposed marine geoengineering techniques. GESAMP Working Group Reports and Studies, 41, 2019.

Carter, B. R., J. A. Radich, H. L. Doyle, and A. G. Dickson.: An automated system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11, no. 1: 16-27, 2013.

Caserini, S., Storni, N., & Grosso, M.: The availability of limestone and other raw materials for ocean alkalinity enhancement. Global Biogeochemical Cycles, 36, e2021GB007246. https://doi. org/10.1029/2021GB007246, 2022.

Cyronak, T., Albright, R., and Bach, L.: Chapter 4.5: Field Experiments, State Planet Discuss. [preprint], https://doi.org/10.5194/sp-2023-9, in review, 2023.

de Lannoy, C.-F., Eisaman, M.D., Jose, A., Karnitz, S.D., DeVaul, R.W., Hannun, K., and Rivest, J.L.B.: Indirect ocean capture of atmospheric CO_2: Part I. Prototype of a negative emissions technology. International journal of greenhouse gas control, 70: 243-253, 2018.

Dickson, A. G.: An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep Sea Research Part A. Oceanographic Research Papers, 28(6), 609–623, 1981.

Dickson, A. G.: The development of the alkalinity concept in marine chemistry. Marine Chemistry, 40(1–2), 49–63, 1992.

Dickson, A.G.: Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. Deep Sea Research Part A. Oceanographic Research Papers, 37, no. 5: 755-766, 1990.

Dickson, A.G., Sabine, C.L., and Christian, J.R.: Guide to best practices for ocean CO_2 measurements. North Pacific Marine Science Organization, 2007.

Eisaman, M. D., Parajuly, K., Tuganov, A., Eldershaw, C., Chang, N., Littau, K. A. CO_2 Extraction from Seawater Using Bipolar Membrane Electrodialysis, Energy Environ. Sci., 5: 7346. https://doi.org/10.1039/c2ee03393c, 2012.

Eisaman, M. D.; Rivest, J. L. B.; Karnitz, S. D.; De Lannoy, C.-F.; Jose, A.; DeVaul, R. W.; Hannun, K. Indirect Ocean Capture of Atmospheric CO_2: Part II. Understanding the Cost of Negative Emissions. International Journal of Greenhouse Gas Control, 70: 254–261, https://doi.org/10.1016/j.ijggc.2018.02.020, 2018.

Eisaman, M. D., Geilert, S., Renforth, P., Bastianini, L., Campbell, J., Dale, A. W., Foteinis, S., Grasse, P., Hawrot, O., Löscher, C. R., Rau, G. H., and Rønning, J.: Assessing the technical aspects of ocean-alkalinity-enhancement approaches, in: Guide to Best Practices in Ocean Alkalinity Enhancement Research, edited by: Oschlies, A., Stevenson, A., Bach, L. T., Fennel, K., Rickaby, R. E. M., Satterfield, T., Webb, R., and Gattuso, J.-P., Copernicus Publications, State Planet, 2-oae2023, 3, https://doi.org/10.5194/sp-2-oae2023-3-2023, 2023.

https://doi.org/10.5194/egusphere-2024-108
Preprint. Discussion started: 22 January 2024

692 Feely, R.A., Alin, S., Carter, B., Bednaršek, N., Hales, B., Chan, F., Hill, T.M., Gaylord, B., Sanford, E., Byrne,
693 R.H., Sabine, C.L., Greeley, D., Juranek, L., Chemical and biological impacts of ocean acidification along the
694 west coast of North America, Estuarine, Coastal and Shelf Science, doi: 10.1016/j.ecss.2016.08.043, 2016.
695 Feng, E. Y., Koeve, W., Keller, D.P., and Oschlies, A.: Model-Based Assessment of the CO_2 Sequestration Potential
696 of Coastal Ocean Alkalinization. Earth's Future, 5, no. 12: 1252-1266, 2017.
697 Fennel, K., Long, M. C., Algar, C., Carter, B., Keller, D., Laurent, A., Mattern, J. P., Musgrave, R., Oschlies, A.,
698 Ostiguy, J., Palter, J., and Whitt, D. B.: Modeling considerations for research on Ocean Alkalinity Enhancement
699 (OAE), State Planet Discuss. [preprint], https://doi.org/10.5194/sp-2023-10, in review, 2023.
700 Ferderer, A., Chase, Z., Kennedy, F., Schulz, K.G., and Bach, L.T..: Assessing the influence of ocean alkalinity
701 enhancement on a coastal phytoplankton community. Biogeosciences 19, no. 23: 5375-5399, 2022.
702 Friis, K.; Körtzinger, A.; Wallace, D. W. R. The Salinity Normalization of Marine Inorganic Carbon Chemistry
703 Data. Geophys. Res. Lett., 30 (2). https://doi.org/10.1029/2002GL015898, 2003.
704 Hartmann, J., Suitner, N., Lim, C., Schneider, J., Marín-Samper, L., Arístegui, J., Renforth, P., Taucher, J., and
705 Riebesell, U.: Stability of alkalinity in ocean alkalinity enhancement (OAE) approaches–consequences for
706 durability of CO_2 storage. Biogeosciences 20, no. 4: 781-802, 2023.
707 Harvey, L.: Mitigating the atmospheric CO_2 increase and ocean acidification by adding limestone powder to
708 upwelling regions, Journal of 640 Geophysical Research: Oceans, 113, 2008.
709 He, J. and Tyka, M. D.: Limits and CO_2 equilibration of near-coast alkalinity enhancement, Biogeosciences, 20, 27–
710 43, https://doi.org/10.5194/bg-20-27-2023, 2023.
711 Ho, D. T., Bopp, L., Palter, J. B., Long, M. C., Boyd, P., Neukermans, G., and Bach, L.: Chapter 6: Monitoring,
712 Reporting, and Verification for Ocean Alkalinity Enhancement, State Planet Discuss. [preprint],
713 https://doi.org/10.5194/sp-2023-2, in review, 2023.
714 Ilyina, T., Wolf-Gladrow, D., Munhoven, G., and Heinze, C.: Assessing the potential of calcium-based artificial
715 ocean alkalinization to mitigate rising atmospheric CO_2 and ocean acidification, Geophysical Research Letters,
716 40, 5909-5914, 2013.
717 IPCC: Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis, Contribution of Working
718 Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Masson-
719 Delmotte, V., Zhai, P., Pirani, A., Connors, S. L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis,
720 M. I., Huang, M., Leitzell, K., Lonnoy, E., Matthews, J. B. R., Maycock, T. K., Waterfield, T., Yelekçi, O., Yu,
721 R., and Zhou, B.: Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 3–32,
722 https://doi.org/10.1017/9781009157896.001, 2022.
723 Isson, T. T., Planavsky, N. J., Coogan, L. A., Stewart, E. M., Ague, J. J., Bolton, E. W., et al.: Evolution of the
724 global carbon cycle and climate regulation on earth. Global Biogeochemical Cycles, 34, e2018GB006061.
725 https://doi.org/ 10.1029/2018GB006061, 2020.
726 Jones, D.C., Ito, T., Takano, Y., and C.-W Hsu, C.-W.: Spatial and seasonal variability of the air-sea equilibration
727 timescale of carbon dioxide. Global Biogeochemical Cycles, 28(11), 1163–1178,
728 https://doi.org/10.1002/2014GB004813, 2014.
729 Kheshgi, H. S.: Sequestering atmospheric carbon dioxide by increasing ocean alkalinity, Energy, 20, 915-922, 1995.
730 Köhler, P., Hartmann, J., and Wolf-Gladrow, D.A.: Geoengineering potential of artificially enhanced silicate
731 weathering of olivine. Proceedings of the National Academy of Sciences 107, no. 47: 20228-20233, 2010.
732 La Plante, E., Chen, X., Bustillos, S., Bouissonnie, A., Traynor, T., Jassby, D., Corsini, L., Simonetti, D., and Sant,
733 G.: Electrolytic seawater mineralization and the mass balances that demonstrate carbon dioxide removal. ACS
734 EST Engg. https://doi.org/10.1021/acsestengg.3c00004, 2023.
735 Lee, K., Kim, T.-W., Byrne, R.H., Millero, F.J., Feely, R.A., and Liu, Y.-M.: The universal ratio of boron to
736 chlorinity for the North Pacific and North Atlantic oceans. Geochimica et Cosmochimica Acta 74, no. 6: 1801-
737 1811, 2010.
738 Lewis, E., Wallace, D., & Allison, L. J.: Program developed for CO_2 system calculations.
739 https://doi.org/10.2172/639712, 1998.
740 Lu, X., Ringham, M., Hirtle, N., Hillis, K., Shaw, C., Herndon, J., Carter, B.R., and Eisaman, M.D.:
741 Characterization of an Electrochemical Approach to Ocean Alkalinity Enhancement. In AGU Fall Meeting
742 Abstracts, vol. 2022, pp. GC31C-01. 2022.
743 Lueker, T.J., Dickson, A.G., and Keeling, C.D.: Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity,
744 and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at
745 equilibrium. Marine chemistry 70, no. 1-3: 105-119, 2000.
746 Minx, J.C., Lamb, W.F., Callaghan, M.W., Fuss, S., Hilaire, J., Creutzig, F., Amann, T., et al.: Negative
747 emissions—Part 1: Research landscape and synthesis. Environmental Research Letters 13, no. 6: 063001, 2018.

https://doi.org/10.5194/egusphere-2024-108
Preprint. Discussion started: 22 January 2024

Montserrat, F., Renforth, P., Hartmann, J., Leermakers, M., Knops, P., and Meysman, F.J.R.: Olivine dissolution in seawater: implications for CO_2 sequestration through enhanced weathering in coastal environments. *Environmental Science & Technology* 51, no. 7: 3960-3972, 2017.

Moras, C.A., Bach, L.T., Cyronak, T., Joannes-Boyau, R., and Schulz., K.G.: Ocean alkalinity enhancement–avoiding runaway $CaCO_3$ precipitation during quick and hydrated lime dissolution. Biogeosciences 19, no. 15: 3537-3557, 2022.

National Academies of Sciences, Engineering, and Medicine. A research strategy for ocean-based carbon dioxide removal and sequestration. 2021.

National Academies of Sciences, Engineering, and Medicine. Negative Emissions Technologies and Reliable Sequestration: A Research Agenda. 2018.

Nduagu, E."Production of $Mg(OH)_2$ from Mg-silicate rock for CO_2 mineral sequestration. Dissertation for Abo Akademi University, 2012.

Oschlies, A., Bach, L., Rickaby, R., Satterfield, T., Webb, R. M., and Gattuso, J.-P.: Climate targets, carbon dioxide removal and the potential role of Ocean Alkalinity Enhancement, State Planet Discuss. [preprint], https://doi.org/10.5194/sp-2023-13, in review, 2023.

Pierrot, D., Lewis, E., and Wallace, D.W.R.: MS Excel program developed for CO_2 system calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 2006.

Rau, G.H.: Electrochemical splitting of calcium carbonate to increase solution alkalinity: Implications for mitigation of carbon dioxide and ocean acidity. Environmental science & technology 42, no. 23: 8935-8940, 2008.

Renforth, P., and Henderson, G.: Assessing ocean alkalinity for carbon sequestration. Reviews of Geophysics 55, no. 3: 636-674, 2017.

Rigopoulos, I., Harrison, A.L., Delimitis, A., Ioannou, I., Efstathiou, A.M., Kyratsi, T., and Oelkers, E.H. : Carbon sequestration via enhanced weathering of peridotites and basalts in seawater. Applied Geochemistry 91: 197-207, 2018.

Rueda, O., Mogollón, J.M., Tukker, A., and Scherer, L.: Negative-emissions technology portfolios to meet the 1.5° C target. Global Environmental Change 67: 102238, 2021.

Rogelj, J., Popp, A., Calvin, K. V., Luderer, G., Emmerling, J., Gernaat, D., Fujimori, S., Strefler, J., Hasegawa, T., Marangoni, G., Krey, V., Kriegler, E., Riahi, K., van Vuuren, D. P., Doelman, J., Drouet, L., Edmonds, J., Fricko, O., Harmsen, M., Havlík, P., Humpenöder, F., Stehfest, E., and Tavoni, M.: Scenarios towards limiting global mean temperature increase below 1.5 °C, Nat. Clim. Change, 8, 325–332, https://doi.org/10.1038/s41558-018-0091-3, 2018.

Schulz, K. G., Bach, L. T., and Dickson, A. G.: Seawater carbonate system considerations for ocean alkalinity enhancement research, State Planet Discuss. [preprint], https://doi.org/10.5194/sp-2023-12, in review, 2023.

Shaw, C., Ringham, M.C., Lu, X., Carter, B.R., Eisaman, M.D., and Tyka, M.: Understanding the Kinetics of Electrochemically derived Magnesium Hydroxide for Ocean Alkalinity Enhancement. In AGU Fall Meeting Abstracts, vol. 2022, pp. GC32I-0713. 2022.

Song, S., Wang, Z.A., Gonneea, M.E., Kroeger, K.D., Chu, S.N., Li, D., and Liang, H.: An important biogeochemical link between organic and inorganic carbon cycling: Effects of organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt marshes. Geochimica et Cosmochimica Acta 275:123-139, 2020.

Tyka, M.D., Arsdale, C.V., and Platt, J.C.: CO_2 capture by pumping surface acidity to the deep ocean. Energy & Environmental Science 15, no. 2: 786-798, 2022.

Van Heuven, S., Pierrot, D., Rae, J., Lewis, E., & Wallace, D.: MATLAB program developed for CO_2 system calculations. ORNL/CDIAC-105b, 530, 2011.

Vitillo, J. G., Eisaman, M.D., Aradóttir, E.S.P., Passarini, F., Wang, T., and Sheehan, S.W.: The role of carbon capture, utilization and storage for economic pathways that limit global warming to below 1.5° C." Iscience: 104237, 2022.

Wang, Z. A. and Cai, W. J.: Carbon dioxide degassing and inorganic carbon export from a marsh-dominated estuary (the Duplin River): A marsh CO_2 pump. Limnol. Oceanogr. 49, 341–354, 2004.

Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., & Dickson, A. G.: Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Marine Chemistry, 106(1–2), 287–300, 2007.

Wang, H., Pilcher, D. J., Kearney, K. A., Cross, J. N., Shugart, O. M., Eisaman, M. D., & Carter, B. R.: Simulated impact of ocean alkalinity enhancement on atmospheric CO2 removal in the Bering Sea. Earth's Future, 11(1), e2022EF002816, 2023