An assessment of ocean alkalinity enhancement using aqueous hydroxides: kinetics, efficiency, and precipitation thresholds

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Abstract

Ocean alkalinity enhancement (OAE) is an 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^-). One OAE method involves the production of an acid (HCl) and a base (NaOH) from seawater, the return of the base to the ocean, and the removal or neutralization of the acid. 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 net uptake of atmospheric CO_2 by the seawater due to gas exchange. In this study, we systematically test the efficiency of CO_2 uptake in seawater treated with NaOH at aquaria (15L) and tank (6000L) scales to establish operational boundaries for safety and efficiency in advance of mesocosm studies and scaling up to field experiments. 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_T (total scale pH) exceeded 10 and $\Omega_{aragonite}$ exceeded 30. 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)

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 5-15 Gt of atmospheric CO_2 per year by 2100 is necessary to constrain average global warming to less than 1.5 - 2 °C (noting that the magnitude of carbon removals varies by

climate scenario: 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, 2021; 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 (Boettcher 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; Eisaman, 2024).

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).

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.

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

Most of the OH^- from NaOH addition rapidly reacts with other molecules in seawater, but Eq. (1) is formulated so the total remains unchanged through these reactions. From Eq. (1), we see the additional OH^- in a treated seawater solution corresponds to a salt solution with increased alkalinity relative to the starting salt solution. The OH^- reacts with and consumes free H^+, thereby increasing the seawater pH. The OH^- also accepts protons from bicarbonate and the carbonic acid formed from the reaction with CO_2 and H_2O, resulting in a shift of the dissolved inorganic carbon (DIC) speciation towards carbonate according to the net reactions:

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

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

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).

$$CO_{2,g} \rightarrow CO_{2,aq} \quad (3a)$$

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

As net reaction (2b) takes significantly longer than net reaction (2a), this process may have the potential to locally and transiently mitigate the elevated pCO_2 and loss of carbonate ions associated with ocean acidification (NASEM, 2021; Cross et al., 2023; Butenschön et al., 2021) even though most of the carbonate ion that is initially produced (in Eq. 2a) is eventually consumed (in Eq. 3b). 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, depending on seawater conditions. Following equilibration after OAE, the final pH and carbonate ion concentrations are slightly increased relative to the initial values (He and Tyka, 2023).

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. Deploying this OAE process 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, the rate of alkalinity addition must be controlled 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). 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 in the presence of mineral 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 mixed away from the point source, becoming increasingly diluted over time. 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 sufficiently broad area 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 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), and mesocosms (Groen et al., 2023), and other work has studied the

release of NaOH over natural coral reefs as a method of local ocean acidification mitigation (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 electrochemical brine-to-alkalinity conversion. 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 for these tanks, and how does it depend on the pH_T following OAE and the magnitude of alkalinity enhancement?

(3) What are the conditions for $Mg(OH)_2$ precipitation upon addition of NaOH to seawater?

(4) What are the threshold values for pH_T 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. The large tank experiments presented in this manuscript provide a stepping stone between bench-scale experiments and in-situ mesocosms or field pilots, and are among the largest experiments that can be conducted with a control seawater reference reservoir. Even if these experiments simply confirm stoichiometric and modeled expectations, this is critical information in the design and implementation of OAE deployments. This work is a necessary part of the growing scientific body that will allow for field trials to progress.

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. 1).

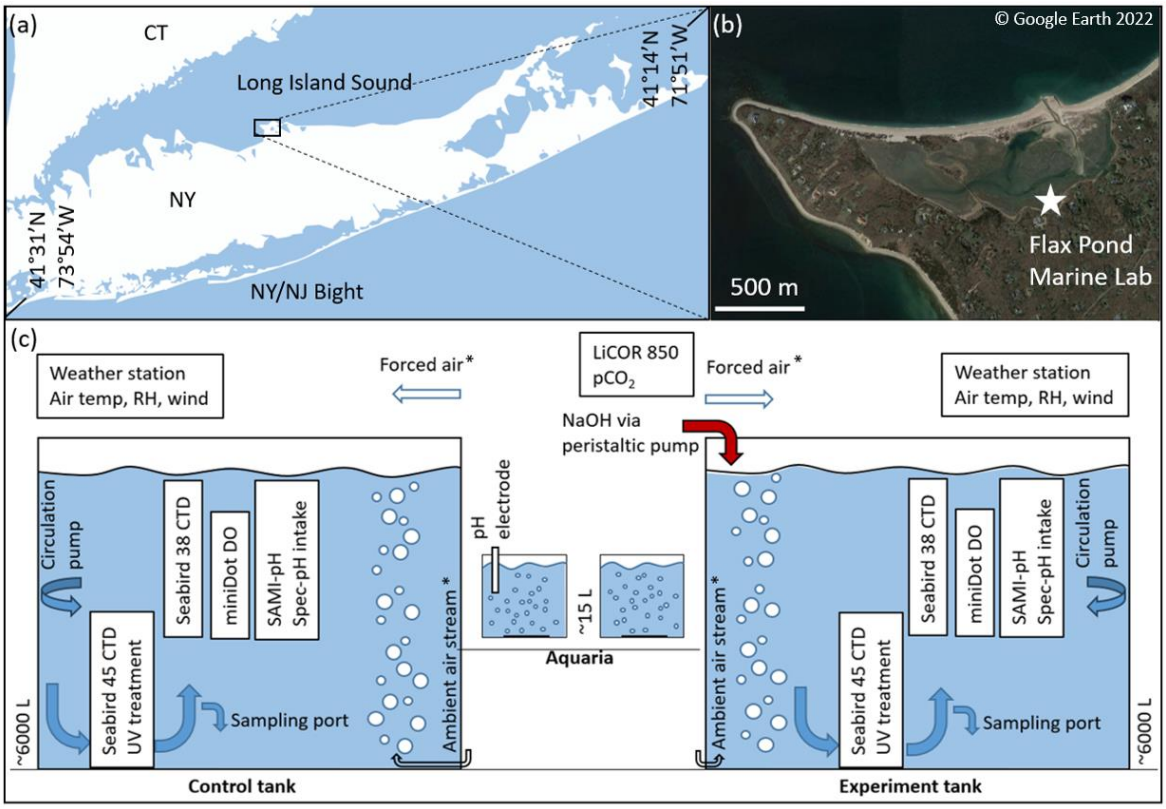

Figure 1: (*a*, *b*) Flax Pond Marine Laboratory is located on Long Island Sound, New York, USA (© Google Earth 2022). (*c*) The ~6000 L control and experiment tanks were instrumented with a series of oceanographic sensors and sampled routinely for DIC/ TA analyses to allow for measurement of carbon uptake over time following an addition of alkalinity in the form of NaOH. The ~15 L aquaria were instrumented with standard glass 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 2.4 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 aquaria had a diameter of 0.3 m and were typically filled to a height of ~0.23 m, for a total seawater volume of 15 L. The large tank volumes were chosen to limit interactions with walls while increasing the air-seawater boundary, and to lose a smaller fraction of their volume to evaporation. These tanks 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. While it is expected that equilibration occurs more rapidly in the small aquaria than in the large tanks, the results from these cases should be similar after both experiment types have been allowed to fully equilibrate CO_2 across the air-seawater boundary. However, we

note that some variation is expected due to limited sensing and sampling options in the smaller aquaria and the greater potential for biological growth in the large tanks over longer timescales.

2.1.1 Tank experiments

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. Measurements of total alkalinity showed no significant differences in the bulk seawater TA before and after the bleaching process in any experiment or control tank.

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. Initial tank experiments were conducted with a still surface condition, i.e., with no visible water movement across the surface of each tank. As experiments progressed, forced air movement was added across the surface of each tank using a stationary fan with a wind speed of ~5 kph. This was done to control for potential variations in the laboratory HVAC system and to potentially reduce the time to equilibration for the experiments by increasing the rate of air-sea CO_2 equilibration. In later experiments, air was bubbled into the bottom of each tank at a rate of ~ 30 L min^{-1} with an estimated surface area of ~ 0.3 m^2, with a goal of further increasing the rate of equilibration to allow for more rapid throughput of experiments. These variations are further discussed in Section 2.4.

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_T to the target pH_T 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_T was observed, but local pH_T measured just below the NaOH introduction never exceeded a pH_T 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_T or DIC (calculated from daily pH_T and frequent TA measurements) appeared to stabilize (e.g., ΔpH_T $\pm 0.05\%$ or ΔDIC ± 10 μmol kg^{-1} per day) over several days, though we note that early experiments were terminated before full equilibration. 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.

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 (described in Section 2.3) and using sensor pH_T and Stony Brook TA measurements for cross-verification or to fill in between discrete DIC samples. DIC and TA data were normalized to the salinity at the start of a given experiment to account for evaporation (Friis et al., 2003). Carbonate chemistry calculations were then performed using CO2SYS (Lewis and Wallace, 1998), with Lueker 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_T sensor and NOAA PMEL bottle samples were used to correct SAMI-pH and spectrophotometric pH_T sensor data for drift.

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. 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 (421 ± 14 ppm), which 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 the $pCO_{2,seawater}$ and nTA_i. The final equilibrium nDIC was estimated from a CO2SYS calculation using the same $pCO_{2,seawater}$ and the nTA 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.

2.1.2 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. 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^{-1}) 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_T conditions investigated. There was no fine control on air bubbling, but the surface area of all air bubbles in a given aquarium at any point in time was estimated at ~0.01 m^2. 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).

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 nDIC (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 nDIC 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.

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

Not all aquaria experiments were directly comparable to the aquaria control. Seawater for one control aquarium was collected in March 2023 and was monitored for pH_T and TA changes beginning in March 2023 and concluding in May 2023. Seawater for the experimental aquaria was collected in three batches between March, April, and May 2023, with only 4-6 aquaria experiments running in parallel within each set of experiments due to space and analytical throughput constraints. Because of this, the experiments started in March 2023 could be compared directly to the control (target pH_T 8.3, 8.5, 8.5 still, and 8.7), but the rest of the experiments used different initial seawater than the control aquaria. The CAR for each aquaria experiment was therefore calculated from changes in DIC and TA between the initial 'baseline' condition and after the NaOH was added within a given aquarium, rather than between the experiment and control cases.

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.

Each aquaria was gently stirred during the addition of NaOH to prevent $Mg(OH)_2$ precipitation. 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. 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_T and TA samples.

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_T unit (~± 0.0055/0.0004) as described by Carter et al. (2013). CRM measurements were taken by each pH_T 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_T 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_T rely on spectrophotometric analysis of metacresol purple indicator dye, which allows for pH_T measurement within the pH_T range of approximately 7 to 9. For experiments in which enough NaOH was dosed into seawater to raise pH_T 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_T measurement 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

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). 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_T 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.

Samples of mineral precipitation were collected as follows: In the tank pH_T 10.3 case, 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 and 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. 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. Mineral samples from aquaria experiments were collected less frequently due to the volume of seawater required. If precipitation had visibly settled at the bottom of the aquaria, this material was stirred into the water column before sampling from the center of the aquaria. 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.

3 Results and Discussion

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. While the initial seawater conditions were similar between the control and experiment tanks, we note that these cases are not entirely comparable after the termination of cross-pumping between tanks and the subsequent addition of alkalinity. While tanks were initially bleached, eventually some biological growth was noted in each tank with potential differences in spatial and temporal distribution as well as species and community differences. Herein, we assume that differences between the control and experiment cases are due to the addition of alkalinity alone, but we note that characterization of other potential confounding factors is a subject for future work.

The initial pH_T, TA, and DIC varied across experiments as seawater was collected between March 2022 and May 2023, ranging from pH_T 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.

In all experiments, the absorption of atmospheric CO_2 began immediately after the NaOH addition, as determined by decreasing pH_T 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 2 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.

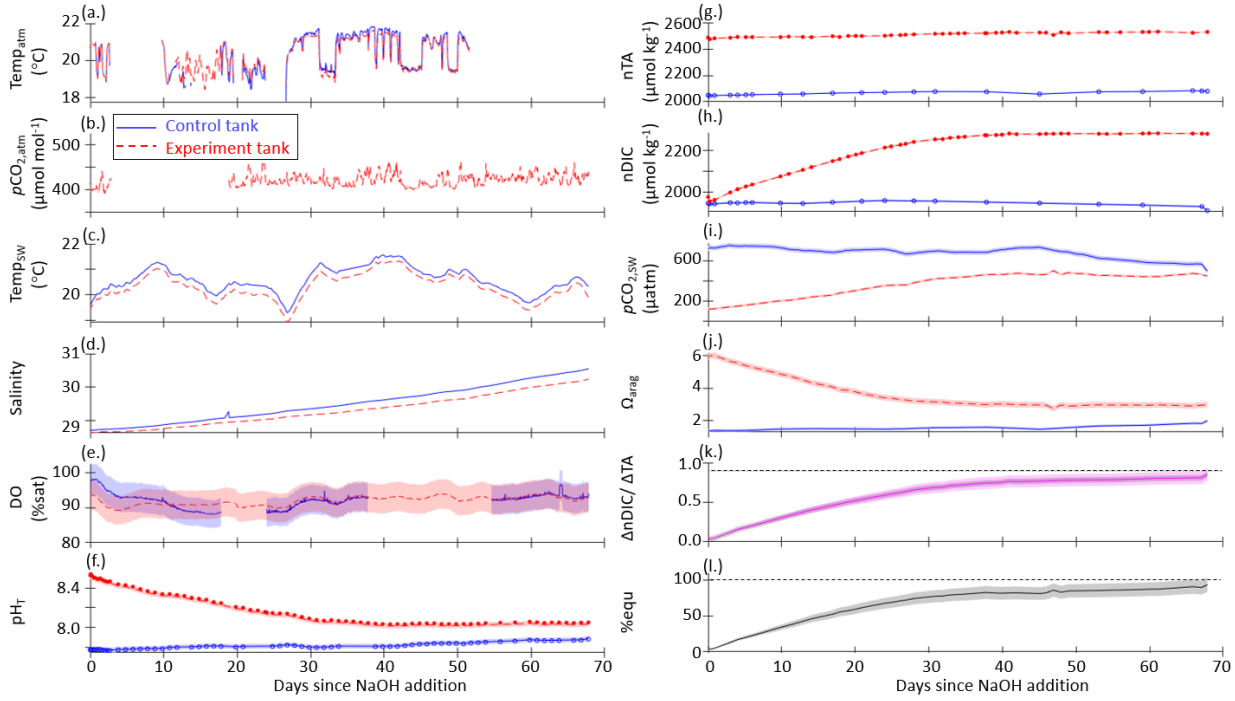

Figure 2: Time-series data for the case where pH_T of the bulk experiment tank was raised to 8.5 with no forced air flow and no bubbling (still surface) for control (blue, solid) and experiment (red, dashed) tanks: (*a*) continuously measured air temperature, (*b*) atmospheric pCO_2, (*c*) seawater temperature, (*d*) salinity, and (*e*) dissolved oxygen; (*f*) pH_T measured by the SAMI-pH (*circles*) and interpolated from the spec-pH_T (*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 3 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 3 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).

An anomalous event was noted in both the experiment and control cases for the target pH_T 8.5 experiment with forced air movement across the surface of the tank, wherein an increase in TA and DIC was noted around day 30 of the experiment. The cause of this event is unclear but could include biological changes in both tanks, the introduction of alkalinity from environmental contaminants, or the anomalous delayed release of alkalinity from suspended solids. This event was not observed in any other case, and highlights the importance of using controls to understand complex interactions in these experiments. A time-series including this event is available in the Supplementary Materials.

The initial CO2SYS-calculated $pCO_{2,seawater}$ 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 estimated from a CO2SYS calculation using the $pCO_{2,seawater}$ and nTA_i was in all cases 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.

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_T 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)

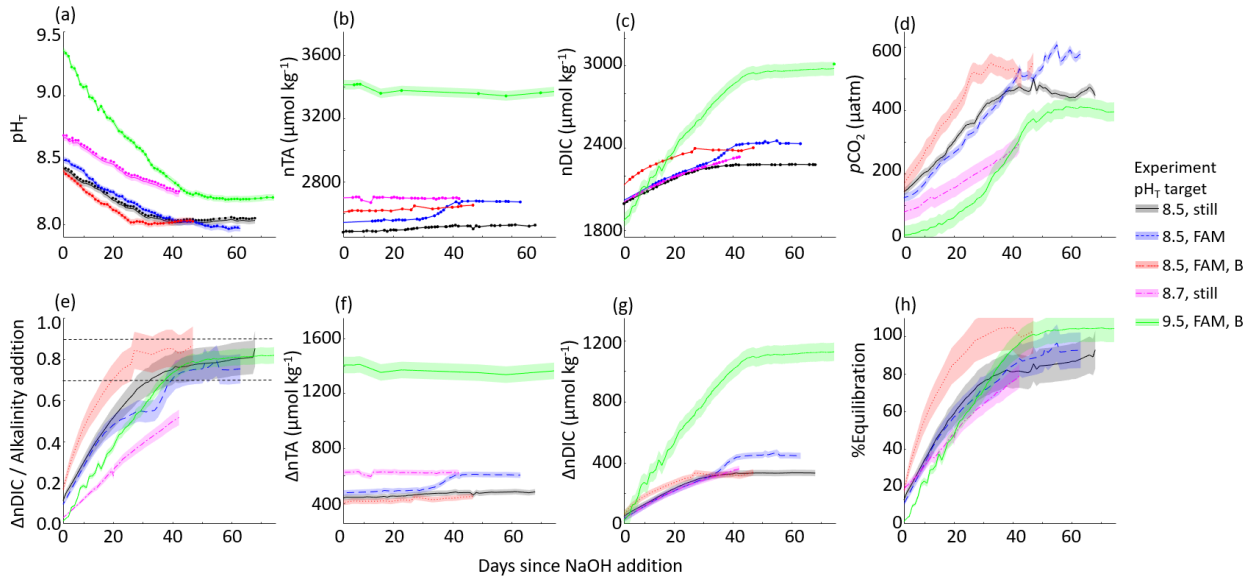

Figure 3: Results of 5 tank-scale experiments in which enough NaOH was added to each tank to raise the bulk pH_T to 8.3 – 9.7. pH_T decreased rapidly in all cases in which air bubbling sped equilibration with atmospheric CO_2. Results include: (a) measured pH_T, (b) measured *n*TA, (c) measured *n*DIC or CO2SYS calculated (for pH_T 9.5 case only), (d) CO2SYS -calculated pCO_2, (e) the observed carbon uptake ratio (CAR) as ($nDIC_{exp}$ - $nDIC_{control}$) / $\Delta nTA_{NaOH\ addition}$ 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) *n*TA and (g) *n*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

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_T target	-	0 Control	8.3	8.5	8.5	8.7	9.3	9.5	9.7	9.9	10.0	10.1	10.2	10.3

					Without air bubbles									
ΔTA = NaOH addition (± 10 μmol/kg)	M	0	187	331	362	543	1409	1679	2037	2216	2276	2504	2796	3829
$pH_{T,i}$ (± 0.1)	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
$pH_{T,peak}$ (± 0.1)	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
$pH_{T,f}$ (± 0.1)	M	8.06	8.03	8.07	8.11	8.08	8.21	8.20	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
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 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 lack of a control for aquaria experiments, limited number of TA samples collected throughout these experiments (daily at best with no duplicates due to the limited volume), and the imprecision of electrode-based pH_T measurements relative to the SAMI-pH and spec-pH_T based measurements used in the large tank experiments.

The initial CO2SYS-estimated equilibrium DIC was in all cases less than the initial DIC calculated from TA_i and $pH_{T,i}$ (by 16 – 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 would be expected to outgas CO_2 if NaOH were not added. 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 leading to estimates of >100% equilibration. These estimates would be better constrained with more continuous carbonate chemistry measurements, particularly seawater and atmosphere pCO_2 throughout the experiments that would allow for more direct calculation of air-sea CO_2 flux and equilibration, and finer control of bubbling and diffusion rates are necessary to define the timeline for equilibration within the aquaria.

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_T 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 4.

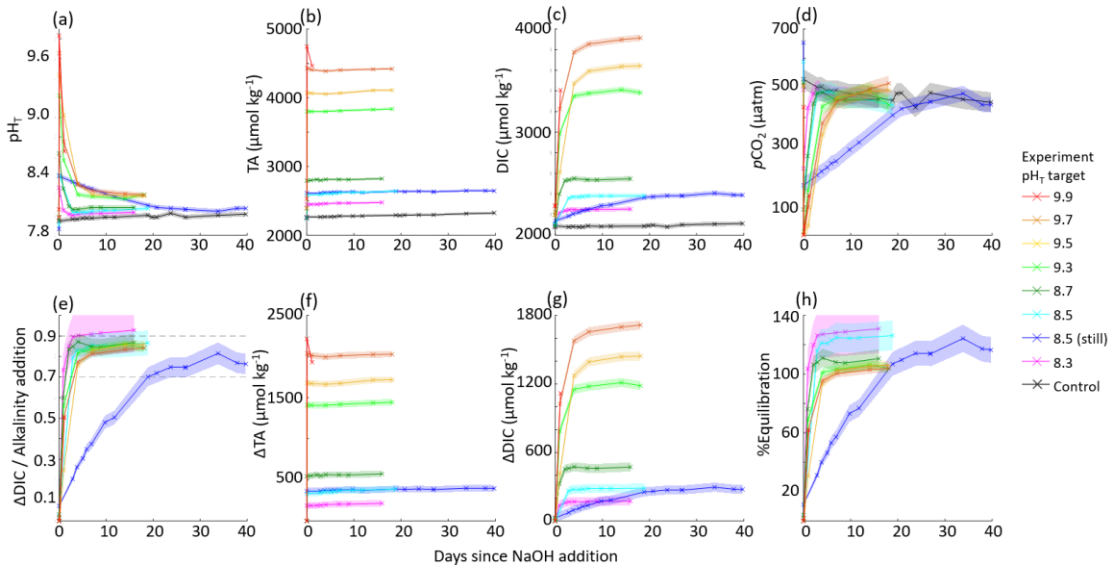

Figure 4: Results of 9 aquaria experiments in which enough NaOH was added to each aquaria to raise the bulk pH_T to 8.3 – 9.9. pH_T decreased rapidly in all cases in which air bubbling sped equilibration with atmospheric CO_2. Results include: (a) measured pH_T, (b) measured TA, (c) CO2SYS-calculated 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; Burt et al., 2021; Wang et al., 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, challenges with establishing control conditions, 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 5 shows the dependence of the equilibrium values of ΔDIC, CAR, and $\Delta pH_T = (pH_{final} - pH_{initial})$ as a function of the alkalinity addition for both tank and aquaria experiments in which the final percent equilibration for CO_2 was estimated at greater than 90%. Results for tank and aquaria experiments aligned well, with increasing ΔDIC for increasing alkalinity additions. The CAR was observed for all experiments to fall within the range expected for seawater with the temperature and salinity values used in these tests. As expected from calculations of the response of the seawater carbonate buffer system to additions of alkalinity, the final pH_T at equilibrium exceeded the pH_T of the control tank or aquaria at the same timepoint. That is, even once equilibrium in the alkalinity enhanced experiment tank had been reached, the ending pH value was slightly elevated relative to both the starting pH_T value and the pH_T of the control. While not all of these experiments resulted in complete equilibration, a line fit to the aquarium experiments has a slope of 0.0001 which is similar to the slope of the line that is expected from CO2SYS when assuming complete equilibration with a 421 ppm CO_2 atmosphere.

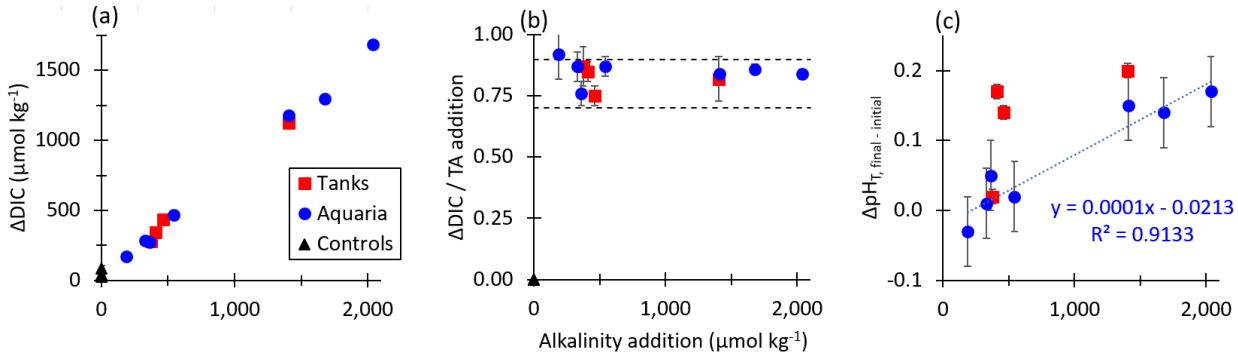

Figure 5: (a) The change in final CO2SYS-predicted DIC relative to the initial conditions for tank, aquaria, and control experiments increases with increasing NaOH additions for cases where the air-sea CO_2 equilibration was estimated at >90% at the termination of each experiment. (b) CO2SYS-predicted 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 measured ΔpH_T = ($pH_{final,\ experiment} - pH_{final,\ control}$) increases with 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 concentrated (i.e., ~0.5 M) 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, and a continued depletion of DIC and slow removal of TA as atmospheric CO_2 from gas exchange was converted to additional $CaCO_3$. Runaway precipitation has been described as a condition in which more alkalinity is removed from seawater by mineral precipitation than was initially added until a new steady state is achieved (Moras et al., 2022; Hartmann et al., 2023; Suitner et al., 2023). This can significantly reduce the efficiency of OAE, and has implications for biological productivity, as increased turbidity may impact photosynthesis or predator-prey interactions.

Both XRD and SEM results of the mineral precipitation 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 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 to be 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.

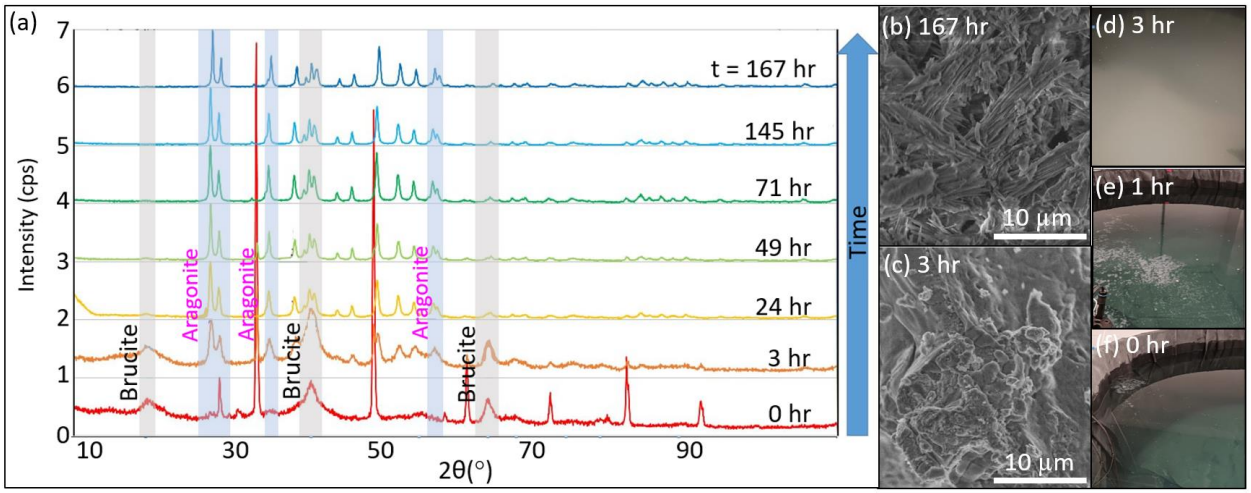

Figure 6: (*a*) XRD analysis (top) of particulates filtered from seawater after the addition of enough NaOH to raise the bulk seawater pH_T to 10.3 showed mineral precipitation initially dominated by $Mg(OH)_2$ before it was overtaken by $CaCO_{3,arag}$. The shaded grey vertical bars highlight peaks 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*) $CaCO_{3,arag}$ at the end of the experiment, and (*c*) $Mg(OH)_2$ captured ~3 hours after the NaOH addition. Photographs of the tank experiment show seawater (*d*) ~3 hours after the NaOH addition, when runaway $CaCO_3$ precipitation became visually apparent, (*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*) before NaOH addition.

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, and the immediate formation of $Mg(OH)_2$ may be reversible, as also noted by Suitner et al. (2023) and Cyronak et al. (2023). At the given initial seawater conditions, the threshold for aragonite precipitation began at an Ω_{arag} of 30, corresponding to pH_T > 10.0, and continued as Ω_{arag} decreased to ~5.2. This threshold corresponded to an increase in TA of >2270 µmol/kg. The potential for runaway aragonite 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, particularly on timescales of hours after alkalinity addition.

Characterization of runaway precipitation thresholds at varying temperatures, salinities, and suspended particulate conditions will allow for OAE implementation designs that best avoid this potential risk to OAE efficiency and ecosystem perturbation. We note that these results are only valid for open experiments using an aqueous hydroxide feedstock for alkalinity, and may not be comparable to bench-scale experiments such as closed bottle incubations, where increased surface area, edge effects, and sustained conditions of high Ω_{arag} may result in precipitation at different thresholds. We also note that we do not assume zero aragonite precipitation at conditions below the stated thresholds, but that potential precipitation is not readily detectable with our experimental setup. For example, heterogeneous $CaCO_3$ precipitation events, such as may occur on suspended sediments in the water column, have been suggested through characteristic changes in seawater TA/DIC ratios in cases of riverine inputs and bottom sediment resuspension (Bustos-Serrano et al., 2009; Wurgaft et al., 2016; 2021). Suspended sediments in the context of OAE project sites could influence OAE efficiency and the potential for runaway precipitation and should be included in future studies (Bach, 2023). The thresholds determined in this study are significantly higher than those of some mineral-based OAE studies, including precipitation after an increase in TA of ~500 µmol/kg using CaO and

$Ca(OH)_2$ mineral additions (Moras et al., 2022). Hartmann et al. (2022) noted precipitation resulting from alkalinity additions of >600 μmol/kg $Mg(OH)_2$, and found that aqueous alkaline solutions avoided carbonate precipitation better than reactive alkaline particle additions to seawater. Suitner et al. (2023) suggested that alkalinity additions > 2000 μmol/kg could be achievable given sufficient dilution to avoid runaway precipitation. Together, these studies highlight the need to expand research into runaway precipitation to characterize potential inefficiencies in OAE, particularly in in-situ experiments to establish relationships applicable to ocean environments.

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. These results are in general agreement with ratios noted in Burt et al. (2021), He and Tyka (2023), and Wang et al., (2023), and thus give no reason to doubt the air-sea equilibrium dynamics used in these model based OAE studies. 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. While the tank-to-atmosphere exchange rate is unlikely to be generalizable to the ocean sea-to-air kinetics, it is essential information for the storage of high TA solutions (which will be a common element of many OAE field trials) and for the subset of proposed approaches that plan to conduct partial pre-equilibration of high-TA seawater mixtures before discharge (typically to avoid creating high-pH environmental conditions).

We relied on several methods to constrain seawater carbonate chemistry. The tank-scale experiments primarily relied on discrete (at most 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 (at most daily, corrected to spectrophotometric systems) with discrete (at most 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 (Zhang and Byrne, 1996; Liu et al., 2006).

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 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 electrochemical OAE 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 (see Fig. 5c). 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 shallow-depth experiments can place an upper 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 (Oschlies et al., 2023).

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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