

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

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1: Sodium Hydroxide source

In scaled field operations, electrochemical OAE aims to generate aqueous alkalinity from seawater through the removal of HCl (Figure 1). This results in a treated seawater solution with similar H⁺ ion concentration but an increased OH⁻ concentration [OH⁻] compared to the input seawater. In our experiments and in the absence of this electrochemical alkalinity stream, we add 0.5 M NaOH to seawater to simulate the electrochemical effluent. This 0.5 M NaOH is mixed from concentrated commercial aqueous NaOH (10N/ Certified, Fisher Chemical 1310-73-2) diluted with DI H₂O immediately before introduction to seawater to reduce the potential for atmospheric CO₂ uptake directly into the alkalinity source before the beginning of an experiment. We note that an electrochemically-generated alkalinity effluent may have additional differences from 0.5 M NaOH: pretreatment steps can require stripping of some Mg²⁺ and Ca²⁺ ions from seawater, most of which will be returned to seawater. Depending on the configuration of an electrochemical system, concentrated brine may be premixed with the aqueous alkalinity stream before release to seawater, or they may be released in tandem. Some electrochemical systems may reduce the dissolved oxygen in the effluent. Ongoing investigation of these factors and adaptation of laboratory research using aqueous NaOH in OAE studies to better reflect electrochemical operations will improve our understanding of potential impacts in scaling this process.

S2: Stony Brook University Total Alkalinity (TA) titrations

The highest quality seawater carbonate chemistry data generated throughout this study came from discrete DIC and TA titrations completed at NOAA PMEL, as reported in Section 2.3, with reported uncertainties of $\pm 0.1\%$ (~1-2 $\mu\text{mol/kg}$). Because these analyses are constrained by manual sample collection, analytical time, and cost, these samples were collected at most daily in early experiments and less than weekly in later experiments. To fill in the sampling gap, we tested our process with automated pH sensors and filled in where possible with semi-automated open-cell potentiometric TA titrations completed at Stony Brook University. These titrations were corrected to CRM with a precision of $\pm 5 \mu\text{mol/kg}$. 97 samples were collected within 1 hour of each other for both NOAA PMEL and Stony Brook TA analysis. The residuals between these samples are shown against the NOAA PMEL-determined TA values in Figure SM1, with an average and standard deviation of 3.5 and 6.5 $\mu\text{mol/kg}$, respectively.

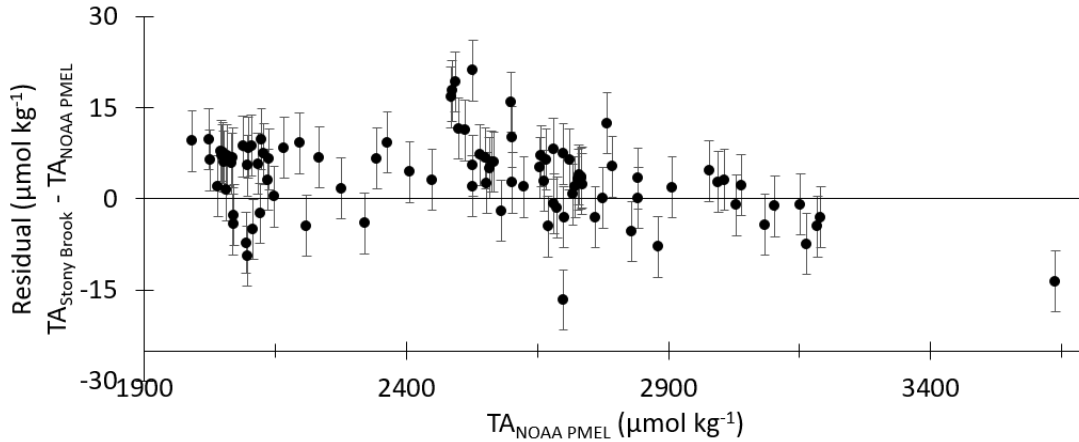


Figure S1: Residuals between TA measured at NOAA PMEL and with the semi-automated open-cell titrator at Stony Brook University. Horizontal error bars of $\pm 0.1\%$ ($\sim 1\text{--}2 \mu\text{mol/kg}$) are too small to be seen behind the data. Vertical error bars represent estimated Stony Brook titrator precision as determined against CRM (i.e., $5 \mu\text{mol/kg}$).

S3: Full tank and aquaria summary tables

Table 1 in the main text provides a short summary of the 6 tank experiments described. A complete summary table is provided below.

Table S1: 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	
Dates	-	9/23/22-11/29/22		12/20/22-02/20/23		03/22/23-05/07/23		06/30/22-08/09/22		05/25/23 – 07/07/23		08/26/22 – 09/05/22	
Duration (days after NaOH addition)	-	67		63		45		42		74		13	
Tank (C = control, E = experiment)	-	C	E	C	E	C	E	C	E	C	E	C	E
$\Delta\text{TA} = \text{NaOH}$ addition ($\pm 10 \mu\text{mol/kg}$)	M	0	409	0	462	0	375	0	626	0	1406	0	3305
Air temperature range ($^{\circ}\text{C}$)	M	17.8 - 21.8	18.1 - 21.6	19.2 - 22.9	19.2 - 22.9	20.2 - 23.4	19.9 - 23.4	-	-	18.7-26.0	19.1-25.5	19.1 - 20.3	18.6 - 20.7
Wind speed (km/hr)	M	0	0	5	5	5	5	-	-	5	5	0	0
Average atmospheric $p\text{CO}_2$ ($\pm 3 \text{ ppm}$)	M	421	420	-	426	-	-	420	421	-	-	-	418
Surface condition	-	Still	Still	Forced air	Forced air	Forced air + bubbles	Forced air + bubbles	Still	Still	Forced air + bubbles	Forced air + bubbles	Still	Still
Water temperature range ($^{\circ}\text{C}$)	M	19.1 – 21.3	19.4 – 21.2	16.0 – 19.5	16.0 – 19.0	19.1 – 20.4	18.3 – 20.8	19.8 – 21.8	20.0 – 21.8	18.5 – 21.3	19.3 – 21.3	20.3 – 20.9	20.2 – 20.7
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
<i>n</i> TA _i (± 10 μmol/kg)	M	2049	2049	2069	2069	2248	2248	2075	2075	2007	2007	2023	2025
<i>n</i> TA _{peak} (± 10 μmol/kg)	M	-	2458	-	2531	-	2623	-	2701	-	3414	-	5330
<i>n</i> TA _f (± 10 μmol/kg)	M	2080	2528	2235	2674	2246	2624	2095	2696	2014	3363	2041	1253
<i>n</i> DIC _i (μmol/kg)	M	1944	1947	1957	1996	2082	2087	1897	1975	1852	1852	1928	1938
<i>n</i> DIC _i (μmol/kg) predicted from TA and <i>p</i> CO ₂ (atm,avg) by CO2SYS	C	1868	1868	1885	1885	2033	2035	1877	1881	1834	1834	1874	1874
<i>n</i> DIC _f (μmol/kg)	M	1908	2280	2084	2433	2027	2365	1937	2336	1832	2977	1947	720
<i>n</i> DIC _f (μmol/kg) predicted from TA and <i>p</i> CO ₂ (atm,avg) by CO2SYS	C	1868	2254	1998	2280	2017	2332	1881	2411	1835	2977	-	4630
Ω _{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
Ω _{aragonite,peak}	C	-	5.9	-	6.0	-	6.2	-	8.8	-	19.3	-	30.3
Ω _{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 assuming equilibrium with <i>p</i> CO ₂ (atm,avg)	E	-	0.89	-	0.85	-	0.85	-	0.84	-	0.81	-	-
Estimated % equilibration at termination of experiment	E	-	95 ± 10	-	92 ± 10	-	102 ± 12	-	79 ± 6	-	104 ± 7	-	-

Table 2 in the main text provides a short summary of the aquaria experiments described. A complete summary table is provided below.

Table S2: 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
Dates	-	40	16	18	40	16	18	18	18	1	1	1	1	16

Duration (days after NaOH addition)														
$\Delta TA = \text{NaOH addition } (\pm 10 \mu\text{mol/kg})$	M	0	187	331	362	543	1409	1679	2037	2216	2276	2504	2796	3829
$pH_{T,i} (\pm 0.005)$	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
$pH_{T,\text{peak}} (\pm 0.005)$	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
$pH_{T,f}$ predicted from TA and pCO_2 (atm,avg) by CO2SYS	E	8.04	8.06	8.08	8.09	8.11	8.23	8.25	8.28	8.31	8.31	8.33	8.35	8.39
$pH_{T,f} (\pm 0.005)$	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
$nTA_i (\pm 10 \mu\text{mol/kg})$	M	2265	2262	2250	2250	2250	2393	2393	2393	2531	2531	2531	2531	2250
$nTA_{\text{peak}} (\pm 10 \mu\text{mol/kg})$	M	-	2449	2582	2611	2793	3801	4072	4430	4748	-	-	-	4608
$nTA_f (\pm 10 \mu\text{mol/kg})$	M	2323	2476	2640	2645	2822	3837	4110	4420	4462	1702	1835	1537	2202
$DIC_i (\mu\text{mol/kg})$	C	2089	2073	2091	2107	2070	2192	2192	2192	2282	2287	2287	2287	2067
$DIC_i (\mu\text{mol/kg})$ predicted from TA and pCO_2 (atm,avg) by CO2SYS	E	2040	2037	2028	2028	2028	2149	2149	2149	2266	2266	2266	2266	2028
$DIC_f (\mu\text{mol/kg})$	C	2113	2246	2377	2382	2540	3372	3486	3877	3389	992	1244	671	2003
$DIC_f (\mu\text{mol/kg})$ predicted from TA and pCO_2 (atm,avg) by CO2SYS	E	2041	2212	2324	2350	2503	3338	3559	3848	4102	4118	4298	4527	5110
$\Omega_{\text{aragonite},i}$	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
$\Omega_{\text{aragonite},\text{peak}}$	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
$\Omega_{\text{aragonite},f}$	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 assuming equilibrium with pCO_2 (atm,avg)	E	-	0.69	0.67	0.64	0.77	0.80	0.80	0.80	0.81	-	-	-	-
Estimated % equilibration at end of experiment	E	-	130	126	116	111	104	106	104	62	-	-	-	-
$CaCO_3$ precipitation?	M	-	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes

63 S4: Time-series results for all experiments

64 The results of one representative experiment were shown in Figure 3, for the case where pH_T of the bulk experiment
65 tank was raised to 8.5 without the addition of surface air forcing or bubbling. Time-series plots for the other tank-
66 scale experiments follow in Figures SM2 – 6.

Figure SM2 shows results for a case where pH_T of the bulk experiment tank was raised to 8.5 with the addition of surface air forcing (4-5 km/hr) but without air bubbling. This experiment was conducted identically to that shown in the main text in Figure 3, where pH_T was raised to 8.5 without surface air forcing or bubbling, in that seawater filtration, bleaching, crosspumping, and NaOH dosing steps were repeated as in the main text.

A particularly interesting feature is seen in the nTA and nDIC signals for both control and experiment tanks in panels g and h. There was an anomalous increase in nDIC in the control tank from $\sim 1978 \pm 5 \mu\text{mol kg}^{-1}$ (day 1 - 20) to $\sim 2085 \pm 5 \mu\text{mol kg}^{-1}$ (day 40 - 63). There was an increase in nTA in the control tank from $\sim 2090 \pm 10 \mu\text{mol kg}^{-1}$ (day 10 - 20) to $\sim 2225 \pm 10 \mu\text{mol kg}^{-1}$ (day 40 - 63). This $\sim 90 - 135 \mu\text{mol kg}^{-1}$ increase in both nDIC and nTA was also observed in the experiment tank on a different timeline, with an increase in nDIC from 2317 to $2426 \pm 10 \mu\text{mol kg}^{-1}$ that occurred more rapidly from days 34-42 than before and after this event, and an increase in nTA from 2587 to $2679 \pm 10 \mu\text{mol kg}^{-1}$ (days 34-42). 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.

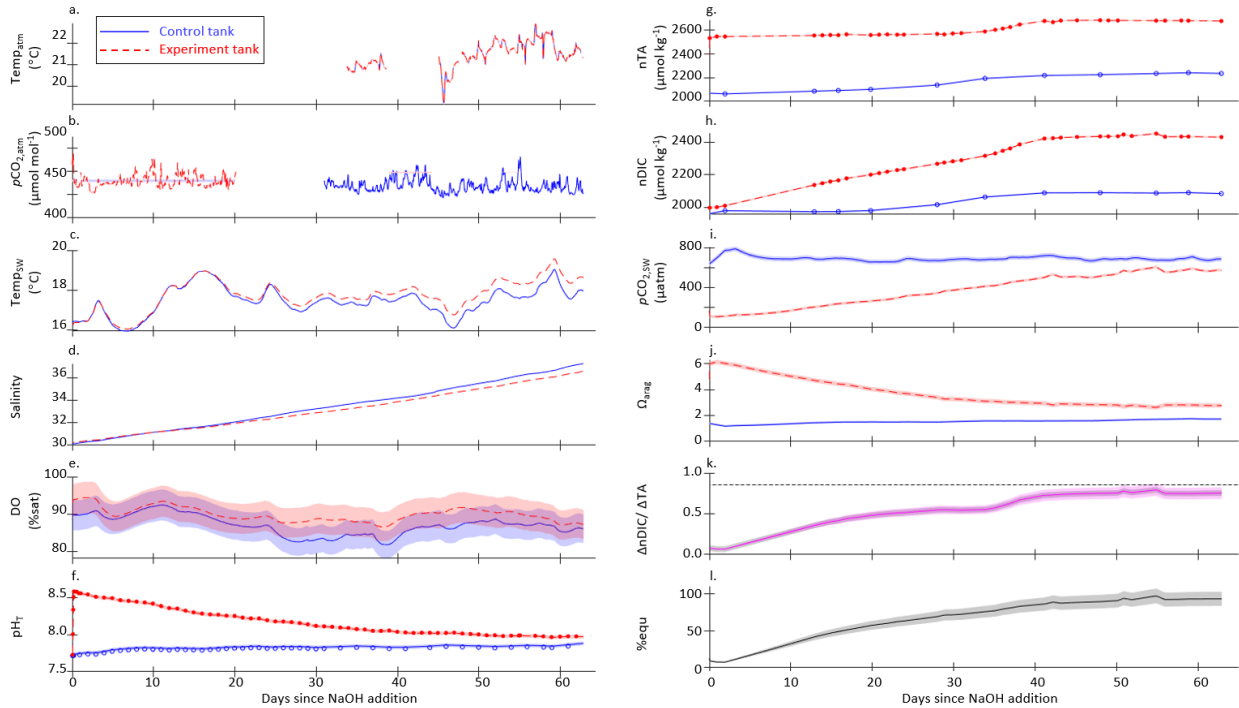


Figure S2: Time-series data for the case where pH_T of the bulk experiment tank was raised to 8.5 with forced air flow but no bubbling for control (blue, solid) and experiment (red, dashed) tanks: (a) continuously measured air temperature, (b) atmospheric $p\text{CO}_2$, (c) seawater temperature, (d) 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 $p\text{CO}_2$ 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 $(n\text{DIC}_{\text{exp}} - n\text{DIC}_{\text{control}}) / \Delta\text{TA}_{\text{NaOH addition}}$ (solid) and the theoretical CAR (dashed) from a CO2SYS calculation using measured TA and the average $p\text{CO}_{2\text{atm}}$ to estimate the equilibrium change in DIC (dashed); (l) the percent equilibration estimated between the observed and theoretical CAR. Data gaps in panel a are due to connectivity issues during sensor data offtake. The gap in panel b is due to a sensor connectivity issue after moving the LiCOR inlet from the experiment to control tank partway through the experiment.

Figure SM3 shows results for a case where pH_T of the bulk experiment tank was raised to 8.5 with both surface air forcing (4-5 km/hr) and air bubbling. This experiment was conducted identically to that shown in the main text in Figure 3, where pH_T was raised to 8.5 without surface air forcing or bubbling, in that seawater filtration, bleaching, crosspumping, and NaOH dosing steps were repeated as in the main text.

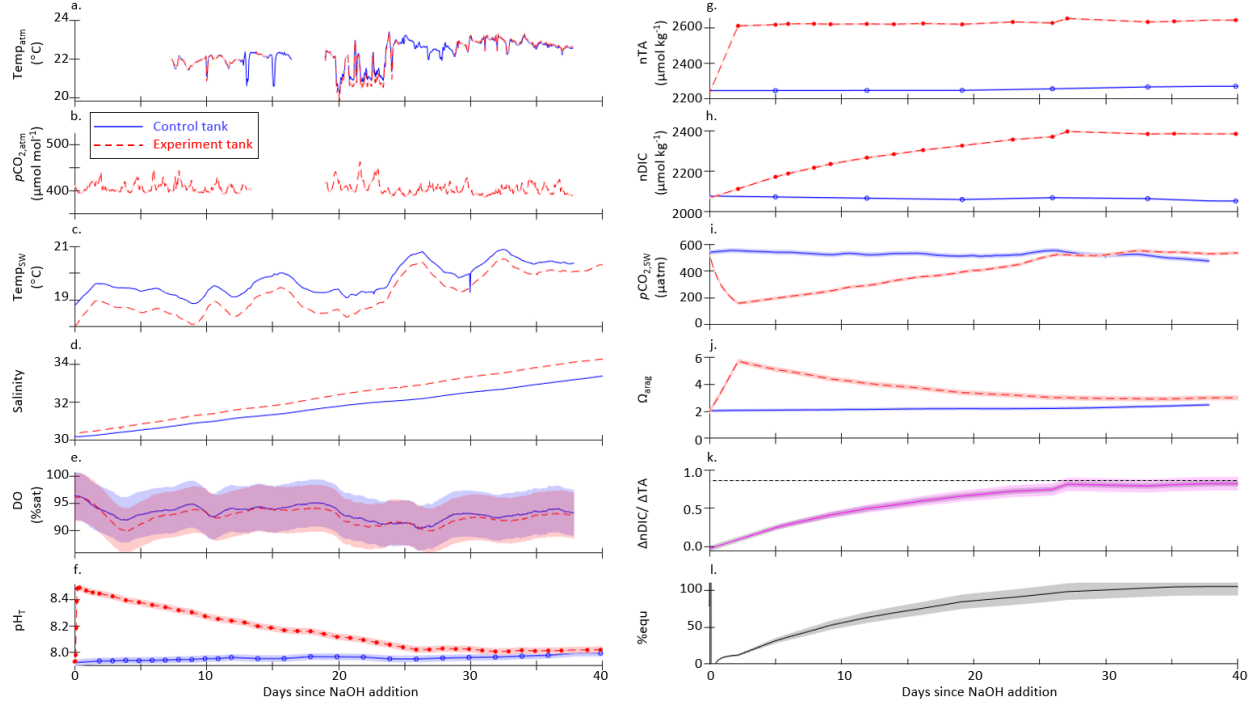


Figure S3: Time-series data for the case where pH_T of the bulk experiment tank was raised to 8.5 with both forced air flow and bubbling for control (blue, solid) and experiment (red, dashed) tanks: (a) continuously measured air temperature, (b) atmospheric $p\text{CO}_2$, (c) seawater temperature, (d) 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 $p\text{CO}_2$ 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 $(n\text{DIC}_{\text{exp}} - n\text{DIC}_{\text{control}}) / \Delta\text{TA}_{\text{NaOH addition}}$ (solid) and the theoretical CAR (dashed) from a CO2SYS calculation using measured TA and the average $p\text{CO}_{2\text{atm}}$ to estimate the equilibrium change in DIC (dashed); (l) the percent equilibration estimated between the observed and theoretical CAR. Data gaps in panels a and b were due to connectivity issues during sensor data offtake.

Figure SM4 shows results for a case where pH_T of the bulk experiment tank was raised to 8.7 without either forced air or bubbling (still surface). As the earliest experiment presented, this case was not conducted identically to that shown in the main text in Figure 3, where pH_T was raised to 8.5 without surface air forcing or bubbling. Seawater was filtered, bleached, and dosed with NaOH as in other experiments, but there was no crosspumping to homogenize the two tanks before dosing the experiment tank with NaOH. Because of this, the initial bulk seawater in the control tank was pH_T 0.17 units higher and $78 \mu\text{mol kg}^{-1}$ DIC lower than that of the experiment tank. The initial TA values were identical. The crosspumping step was added after this experiment to ensure that the starting seawater condition was as similar as possible between the two tanks.

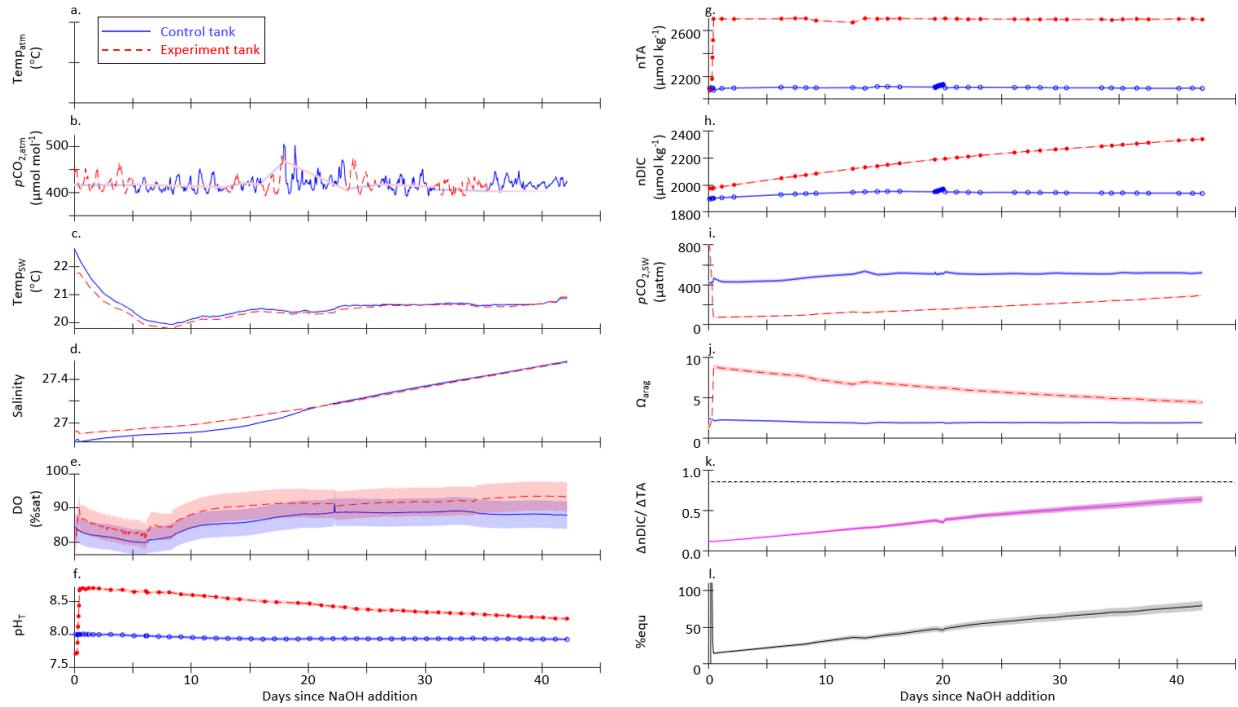


Figure S4: Time-series data for the case where pH_T of the bulk experiment tank was raised to 8.7 without forced air flow and bubbling (still surface) for control (blue, solid) and experiment (red, dashed) tanks: (a) air temperature, (b) atmospheric $p\text{CO}_2$, (c) seawater temperature, (d) salinity, 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 $p\text{CO}_2$ 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 $(n\text{DIC}_{\text{exp}} - n\text{DIC}_{\text{control}}) / \Delta\text{TA}_{\text{NaOH addition}}$ (solid) and the theoretical CAR (dashed) from a CO2SYS calculation using measured TA and the average $p\text{CO}_{2\text{atm}}$ to estimate the equilibrium change in DIC (dashed); (l) the percent equilibration estimated between the observed and theoretical CAR. No air temperature sensor was available for this early experiment, resulting in the lack of data in panel a. The inlet to the LiCOR atmospheric $p\text{CO}_2$ sensor was alternated above the control and experiment tanks every few days throughout the experiment, with no observable differences above the two tanks. The small uptick in DO ~day 22 in panel e was due to a brief displacement of the sensor in the tank to check for biofouling.

Figure SM5 shows results for a case where pH_T of the bulk experiment tank was raised to 9.5 with both surface air forcing (4-5 km/hr) and air bubbling. This experiment was conducted identically to that shown in the main text in Figure 3, where pH_T was raised to 8.5 without surface air forcing or bubbling, in that seawater filtration, bleaching, crosspumping, and NaOH dosing steps were repeated as in the main text.

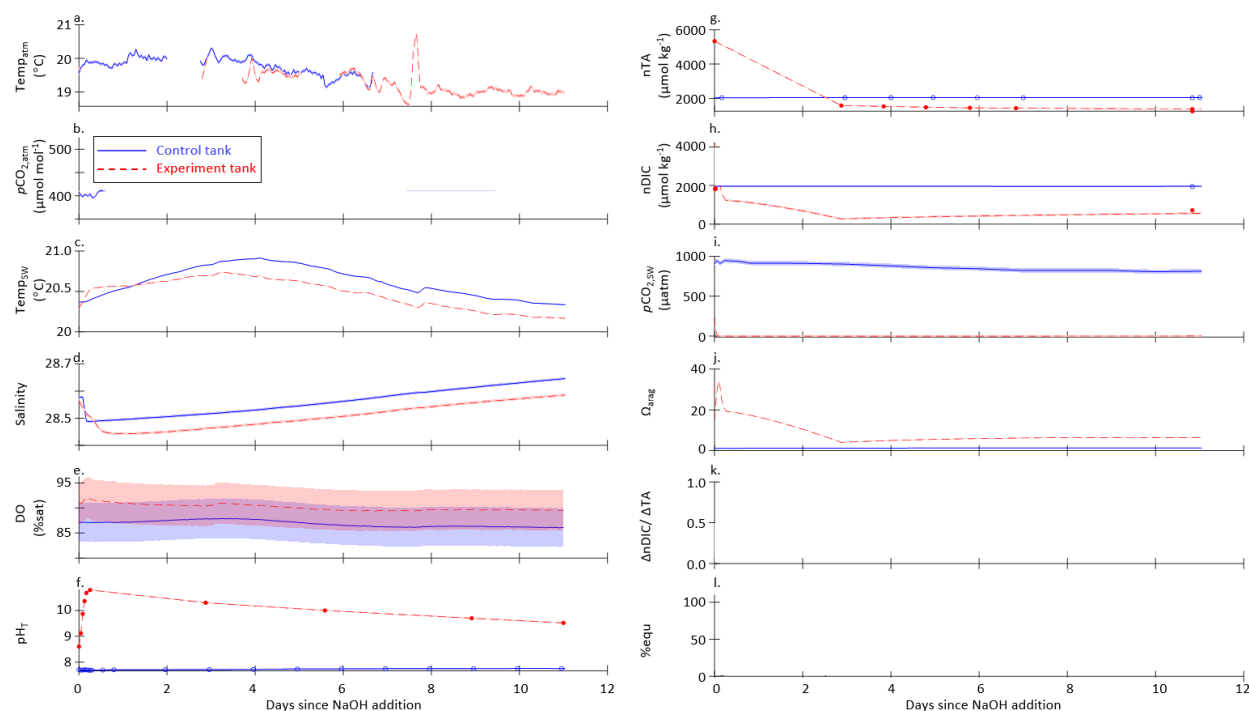


Figure S5: Time-series data for the case where pH_T of the bulk experiment tank was raised to 9.5 with both forced air flow and bubbling for control (blue, solid) and experiment (red, dashed) tanks: (a) continuously measured air temperature, (b) atmospheric $p\text{CO}_2$, (c) seawater temperature, (d) 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 $p\text{CO}_2$ 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 $(n\text{DIC}_{\text{exp}} - n\text{DIC}_{\text{control}}) / \Delta\text{TA}_{\text{NaOH addition}}$ (*solid*) and the theoretical CAR (*dashed*) from a CO2SYS calculation using measured TA and the average $p\text{CO}_{2\text{atm}}$ to estimate the equilibrium change in DIC (*dashed*); (l) the percent equilibration estimated between the observed and theoretical CAR. Data gaps in panels a and b were due to connectivity issues during sensor data offtake.

Figure SM6 shows results for a case where pH_T of the bulk experiment tank was raised to 10.3 without surface air forcing or air bubbling. As the second experiment presented, this case was not conducted identically to that shown in the main text in Figure 3, where pH_T was raised to 8.5 without surface air forcing or bubbling. Seawater was filtered, bleached, and dosed with NaOH as in other experiments, and a crosspumping step was used to homogenize the two tanks before dosing the experiment tank with NaOH, however, not enough water was exchanged between to completely homogenize them. Because of this, the initial bulk seawater in the control tank was pH_T 0.05 units and $10 \mu\text{mol kg}^{-1}$ DIC lower than that of the experiment tank. The initial TA values were identical. The crosspumping step was successfully lengthened after this experiment to ensure that the starting seawater condition was as similar as possible between the two tanks.

As described in the main text, samples of the bulk seawater were collected and filtered for mineral precipitation analysis, which began immediately after the NaOH addition. Limited DIC data is available for this experiment due to this precipitation of CaCO_3 – even after seawater was filtered and poisoned for DIC and TA analysis, precipitation occurred in the sealed bottles that were shipped to NOAA PMEL analysis, and most of these samples had too much solid precipitate to safely analyze. More TA data is available because these samples were filtered and immediately titrated on site at Stony Brook University, reducing the time for potential mineral precipitation. pH_T data is similarly

limited by analytical issues—because the dye used in both the SAMI and spec-pH systems is best used in the pH_T 7-9 range, a glass electrode was used at the surface of the tank for discrete sampling and corrections of pH data.

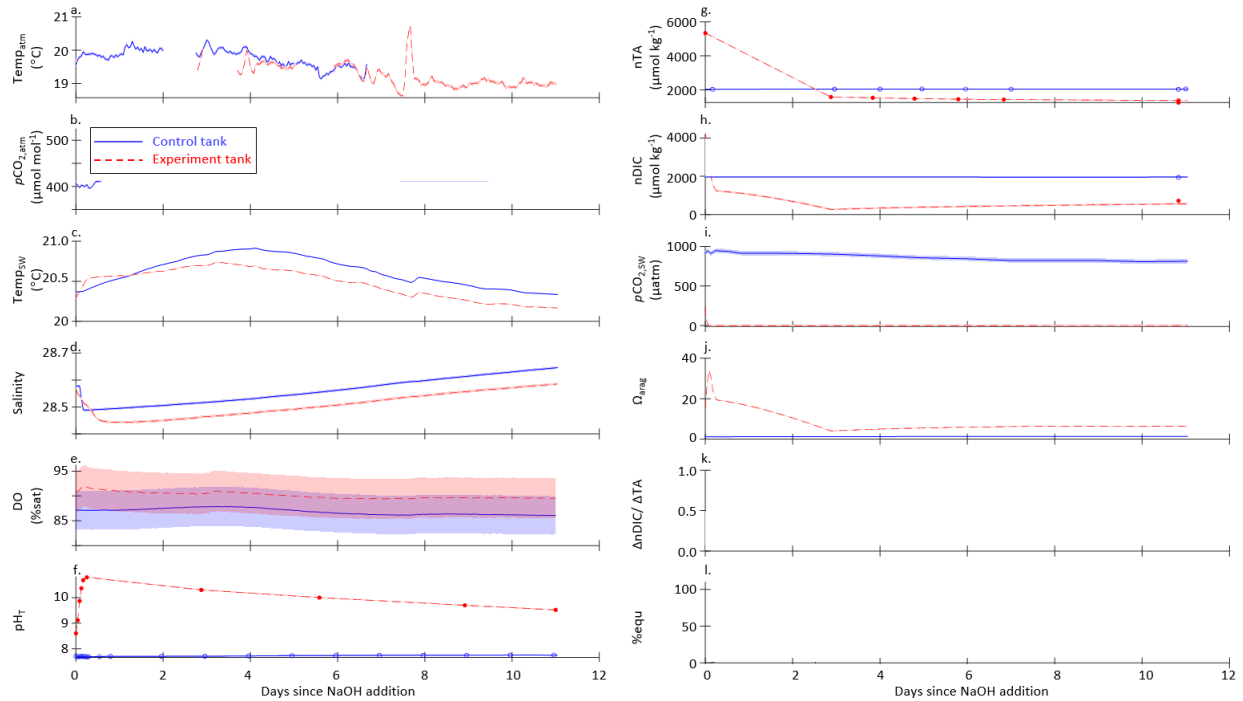


Figure S6: Time-series data for the case where pH_T of the bulk experiment tank was raised to 10.3 without forced air flow or bubbling for control (blue, solid) and experiment (red, dashed) tanks: (a) continuously measured air temperature, (b) atmospheric pCO_2 , (c) seawater temperature, (d) salinity, 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 $(\text{nDIC}_{\text{exp}} - \text{nDIC}_{\text{control}}) / \Delta\text{TA}_{\text{NaOH addition}}$ (solid) and the theoretical CAR (dashed) from a CO2SYS calculation using measured TA and the average $\text{pCO}_{2,\text{atm}}$ to estimate the equilibrium change in DIC (dashed); (l) the percent equilibration estimated between the observed and theoretical CAR. Data gaps in panels a and b were due to connectivity issues during sensor data offtake. No data was calculated for panels k or l.

S5: Processed Tank and Aquaria data

Hourly processed tank and aquaria data is available in the file, 'RinghamBiogeosciencesupplementarydata.xlsx'.