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Field experiments in ocean alkalinity enhancement research

Tyler Cyronak[1]*, Rebecca Albright[2]*, Lennart Bach[3]

[1]Georgia Southern University, Institute for Coastal Plain Science, Statesboro, GA
[2]California Academy of Sciences, San Francisco, CA
[3]Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tasmania, Australia

*These authors contributed equally to the writing of this manuscript.

Correspondence to: Tyler Cyronak (tcyronak@georgiasouthern.edu) and Rebecca Albright (ralbright@calacademy.org)

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Abstract

This chapter focuses on considerations for conducting open-system field experiments in the context of ocean alkalinity enhancement (OAE) research. By conducting experiments in real-world marine systems, researchers can gain valuable insights into ecological dynamics, biogeochemical cycles, and the safety, efficacy, and scalability of OAE techniques under natural conditions. However, logistical constraints and complex natural dynamics pose challenges for successful field trials. To date, only a limited number of OAE field studies have been conducted, and guidelines for such experiments are still evolving. Due to the fast pace of carbon dioxide removal (CDR) research and development, we advocate for openly sharing data, knowledge, and lessons learned as quickly and efficiently as possible within the broader OAE community and beyond. Considering the potential ecological and societal consequences of field experiments, active engagement with the public and other stakeholders is essential. Collaboration, data sharing, and transdisciplinary teams are vital for maximizing the return on investment during field trials. The outcomes of early field deployments are likely to shape the future of OAE, emphasizing the need for transparent and open scientific practices.

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1. Introduction

This chapter addresses considerations for conducting open-system field experiments related to ocean alkalinity enhancement (OAE), where 'field experiment' refers to the addition of alkalinity to a natural system in ways that simulate planned OAE deployments. Advantages of conducting experiments in the real world include observing natural ecological and ecosystem dynamics/impacts, understanding the role of natural biogeochemical cycles and physical processes, and assessing scalability. Conducting successful field trials, however, poses many challenges due to the complex physical and biogeochemical processes that occur in natural marine systems in addition to logistical constraints (e.g., permitting, access, social license). In light of these challenges, few OAE field studies have been conducted to date and associated guidelines are, therefore, still evolving. The first field experiments are likely to be small-scale representations of scalable OAE approaches, but each experiment will have different goals and objectives. There will be much to learn from the earliest experiments, and any knowledge gained, and lessons learned should be shared as efficiently and openly as possible to the wider OAE community.

We suggest that three overarching questions should be taken into consideration when planning an OAE field experiment:

What are the main goals of the experiment?

Establishing the objectives of a field deployment during the planning stage will help guide all aspects of the scientific research plan, including site selection, measurement techniques and approaches, data analysis, and measured outcomes. Potential overarching goals of OAE field experiments include demonstrating functionality, process, and/or scalability, determining ecological and environmental impacts, developing measurement, reporting, and verification (MRV) protocols, and assessing community engagement. This list of overarching goals is not comprehensive, and goals are not necessarily mutually exclusive. For example, larger projects may wish to assess multiple components of an OAE deployment while smaller projects might be highly focused on one goal.

What is the type of alkalinity perturbation?

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The type of alkalinity that is added (e.g., aqueous vs solid, carbonates, hydroxides, oxides, naturally occurring (ultra-)mafic rocks) will ultimately determine many aspects of the scientific research plan. For example, projects adding ground alkaline minerals (e.g., olivine) to the ocean will require tracking both the dissolution of alkaline material plus the fate of the dissolved alkalinity, while projects that add aqueous alkalinity (e.g., NaOH) will not have to track dissolution *in situ* (see Eisaman et al., 2023, this volume). Other important considerations include, the concentration of added alkalinity, duration of additions, dilution and advection at the field site, controlled versus uncontrolled air-sea equilibrium, co-deployed tracers, sampling scheme, etc. These and other research considerations are discussed in more detail below.

What are the permitting and wider social implications?

Addressing public concern and regulatory requirements is essential before field deployments can move forward. The field site will determine the permitting requirements and potential for community engagement. Ideally, the local community should be engaged at the earliest possible stage as social license by local stakeholders will be critical for the success of CDR projects (Nawaz et al., 2022). The use of existing infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., beach renourishment) may offer ways to facilitate deployments, although permitting will be governed by existing regulations. For a more detailed discussion of legal and social issues see Steenkamp et al. (2023, this volume) and Satterfield et al. (2023, this volume).

With these overarching questions in mind, we discuss considerations for OAE field deployments in more detail below.

2. Research Methods

2.1 Types of alkalinity addition

Field experiments of OAE present many challenges. One of the biggest obstacles to a successful field deployment is tracking the alkalinity added to an open system. Methods for adding alkalinity can be divided into two general approaches: (1) *in situ* enhanced weathering, or the addition of ground alkaline minerals and rocks with the expectation they will dissolve directly in seawater, and (2) aqueous alkalinity additions, or the addition of ‘pre-dissolved’ alkalinity to

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seawater that can be generated in numerous ways including through dissolution reactors and electrochemical techniques (Eisaman et al., 2023, this volume). Tracking the alkalinity added by each approach comes with its own unique set of challenges and considerations.

Adding ground minerals and rock to an open system presents two distinct scientific challenges. First, the dissolution (and subsequent alkalinity addition) of the added minerals needs to be detected and confirmed. This can be accomplished through a range of techniques including measuring the loss of mass of the added mineral or using geochemical tracers in the receiving waters. Determining dissolution kinetics will be particularly important and they are likely to vary between different deployment environments and strategies (e.g., coastal vs open ocean). For example, the chemistry (e.g., salinity, pH, temperature) of the waters where the mineral is deployed could vary significantly depending on the environment (e.g., beach face, estuary, shelf). Physical, especially the grain size of the added material, and chemical conditions will be critical in determining the dissolution rate of any added rocks and minerals and initial field deployments will help translate laboratory experiments to natural systems.

The second major challenge is common to both solid and aqueous approaches and involves tracking the added alkalinity and observing drawdown of atmospheric CO_2. Tracking additional alkalinity becomes a particularly difficult problem in open-system field experiments where water is freely exchanged. Depending on the objectives of the field deployment, this is likely to be the main scientific concern. Whether or not the alkalinity is derived from in situ mineral dissolution or direct aqueous additions, for OAE to be successful the dissolved inorganic carbon (DIC) deficit generated through an OAE deployment needs to be equilibrated with atmospheric CO_2. Therefore, understanding the physical mixing and air-sea gas exchange dynamics of the deployment site will be a factor of interest for field studies. Choosing sites that minimize mixing or have well defined diffusivities could facilitate tracing released alkalinity and subsequent air-sea CO_2 influx. The release of conservative tracers with alkalinity will likely be useful and is discussed in more detail below. Incorporating physical mixing models with biogeochemical processes will likely be the end goal of many field experiments focused on MRV (Ho et al, and Fennel et al., 2023, this volume).

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Other experimental considerations related to the type of alkalinity perturbation include the duration and location of alkalinity addition. Alkalinity can be added once, in timed doses, or continuously. Aqueous alkalinity could be added directly to seawater, but the rate of this addition will likely be important, especially for avoiding secondary precipitation (Hartmann et al., 2023; Moras et al., 2023). Location is another important factor. For example, amending beach sand with alkaline minerals will present different challenges than the addition of alkaline material to outfalls that discharge into the ocean. Each plan will require specific spatial and temporal sampling schemes to be developed which should be planned well in advance of any deployments. Field experiments adding solid minerals will likely need to consider much longer experimental time frames than experiments based on one-time additions of aqueous alkalinity.

2.2 Alkalinity sources

Alkalinity additions from coastal enhanced weathering can be accomplished using a variety of naturally occurring and human-made rocks and minerals (Table 1). The addition of these rocks and minerals is done after they have been ground to a desired grain size with many unique application techniques proposed after the initial grinding step (see Eisaman et al., 2023, this volume). The simplest application is done via sprinkling the ground material on the ocean surface, although this has many disadvantages including sinking and advection of the material before it dissolves and has not gained widespread support as a viable option. Other application techniques include spreading material in coastal ecosystems including on beach faces, marshes, riverbeds, etc. This has the potential to enhance dissolution through processes such as physical wave action and favorable water chemistry. To make results more broadly applicable, field experiments should attempt to mimic real world alkalinity application scenarios such as those described above.

Any field experiments that add ground material to marine ecosystems may consider tracking the fate of that material from the addition site. Experiments could also artificially contain the material using barriers to avoid rapid loss of the ground material via ocean currents. Sampling should extend from the water column into areas where the material is added including sediments and pore waters.

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Likely environmental impacts associated with coastal enhanced weathering come from the physical impacts of adding finely ground material and the chemical release of trace elements and other contaminants. Both processes could have associated risks and/or co-benefits for a range of ecological processes and biogeochemical cycles (Bach et al., 2019). For example, the addition of finely ground material could lead to increased turbidity from the initial addition, subsequent resuspension, or secondary precipitation of particulates in the water column. Additionally, any release of nutrients or heavy metals from the dissolving material could alter primary production or cause harm to biological systems.

Aqueous and slurry-based additions of alkalinity provide different benefits and challenges compared to solid forms of alkalinity feedstock. One of the primary benefits of aqueous additions is that the alkalinity has been pre-dissolved, avoiding the often slow dissolution kinetics of minerals and rocks in seawater. Aqueous alkalinity can be generated by two main mechanisms (1) the dissolution of alkaline rocks and minerals in reactors, and (2) electrochemical processes that generate alkalinity by splitting seawater or other brine streams into an acid and base (Eisaman et al., 2023, this volume). For some materials, such as lime and $Mg(OH)_2$, dissolution slurries are formed and a combination of particulate and aqueous alkalinity can be dosed into seawater. Any particulates that are dosed from the slurry need to dissolve, meaning dissolution kinetics in seawater will be critical. However, the dissolution of these materials tends to be much quicker than with rocks and minerals (Table 1). There are important processes that need to be considered when adding aqueous alkalinity, including the unintended precipitation of calcium carbonates due to locally elevated saturation states (Hartmann et al., 2023; Moras et al., 2023).

Field experiments that use aqueous or slurry-based alkalinity additions will need to assess the impacts on seawater chemistry at the source of addition and across a dilution radius. Depending on the type of experiment and magnitude of additions this dilution radius could extend upwards of kilometers (He & Tyka, 2023). The potential environmental impacts from aqueous type alkalinity additions will be similar to those discussed for coastal enhanced weathering, but also include extreme localized changes in carbonate chemistry.

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Table 1. Types of alkalinity sources and considerations for each.

Alkalinity Source	**Solid/Aqueous**	**Dissolution kinetics**	**Dissolution co-products**
NaOH	Aqueous	Instantaneous but can induce brucite ($Mg(OH)_2$) precipitation when NaOH elevates pH >9. Brucite re-dissolves relatively quickly in most cases.	Alkalinity, Na^+
$Mg(OH)_2$	Solid or aqueous slurry	Relatively fast but a combination of dissolution rates both in the receiving and dosing waters.	Alkalinity, Mg^{2+}
Silicates (e.g. olivine, basalt, wollastonite)	Solid	Relatively slow dissolution kinetics, but rates are different between silicates.	Alkalinity, silicate, phosphate, trace metals. Materials need to be individually assessed prior to their use.
Manufactured lime-derived alkalinity sources (e.g. CaO)	Solid or aqueous slurry	Relatively fast but different kinetics between lime products.	Alkalinity, limited amounts of nutrients and trace metals (generally less than silicates). Materials need to be individually assessed prior to their use.
Iron and steel slag	Solid	Components within steel slag that provide alkalinity (e.g. CaO) dissolve relatively fast but different iron and steel slag contain different amounts.	Alkalinity, Ca^{2+}, Mg^{2+}, silicate, phosphate, and trace metals. Materials need to be individually assessed prior to their use.

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Natural and synthetic carbonates (e.g. calcite, aragonite)	Solid	They don't dissolve under common surface ocean carbonate chemistry conditions. Dissolution rates can be higher in microenvironments such as corrosive sediment porewaters where saturation is low due to respiratory CO_2.	Alkalinity, phosphate, dissolved inorganic carbon.

2.3 Considerations for site selection

Careful consideration should be given to the site selection and experimental design to adequately address the specific research questions, account for ecosystem- and site-specific characteristics, as well as temporal and spatial variability. Logistical considerations for site selection include physical access, permitting, availability of electricity, ship time, and consideration of the local community. These considerations will grow with the scale of field trials and will likely be first-order determinants of where field trials take place. OAE field experimentation requires careful assessment of the field site prior to alkalinity additions to provide foundational knowledge of the site characteristics. Foundational knowledge of the field site will inform both the experimental design as well as interpretation of data and experimental outcomes.

Scientific considerations of site selection can be broken down into three categories, the (1) physical, (2) chemical, and (3) biological properties of each site. Important considerations for each category are provided in Box 1. To facilitate baseline assessments and site selection we propose Table 2 as guidance for relevant parameters to measure. We note that this list is broad, however it is not exhaustive and specific field sites may require the monitoring of different or additional parameters. Furthermore, some of the listed parameters may be more applicable to specific OAE approaches.

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Box 1. Scientific considerations for field experiments.

Physics:

- What are the expected dilution rates?
- What is the site turbulence and how will this impact alkalinity additions (e.g., keeping particles in suspension)?
- What is the natural light penetration (e.g., turbidity) and what impacts could increased turbidity have on this?
- What is the natural air-sea gas exchange and is there any risk of water mass subduction before air-sea CO_2 flux happens?
- What are risks associated with lateral export and exchange of alkalinity and other materials?
- Is there the potential of physical disturbance (e.g. impacts of alkalinity additions on physical water mass parameters such as density or the physical impacts of adding undissolved minerals to the benthos)?
- Where will the alkalinity signal be most observable (e.g., pore water vs. water column)?

Chemistry:

- What are the natural carbonate chemistry conditions? How will this impact signal to noise?
- Is there potential to disturb the natural concentrations of macro- or micronutrients through dissolution by-products?

Biology:

- What organisms (benthic and pelagic) are present in the study area and what are their relative sensitivities to fluctuations in seawater carbonate chemistry (if known)?
- Are there endangered or rare species present? Is the site a nursery and/or nesting ground? Are there keystone species and/or important primary producers present? These considerations will likely be part of the permitting process.
- What are the trophic dynamics in the environment, and how might the food web be impacted (e.g., shifts in predator/prey relationships)? What are the cascading implications for the ecosystem as a whole? Might effects be transferred beyond the study site via migratory species?
- Could particulates (e.g., ground rock) cause physical damage prior to dissolution?

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Table 2. Parameters that could be considered in assessing sites for OAE field experiments. Importantly, some parameters summarized below may require a baseline assessment over sufficiently long time frames to cover the intrinsic variability of physical, chemical, and biological parameters in the studied system. For example, baseline assessment of marine food web structure will likely require a prolonged monitoring effort before (and after) the OAE deployment to have a higher chance of detecting OAE-induced effects on marine biota.

Parameter	Rationale	Potential pathway for assessment
Dilution rate	- Exposure risk to alkalinity and mineral dissolution products. - Detectability of OAE-induced chemical changes.	Tracer release experiment (section 2.5).
Turbulence	- Physical energy input to keep ground particles near the sea surface during dissolution.	Microstructure profiler.
Residence time of perturbed patch in surface ocean	- Determination of residence time of an OAE-perturbed patch in the surface to assess whether there is enough time for air-sea equilibration with the atmosphere.	Risk assessment for incomplete air-sea CO_2 exchange (He and Tyka, 2023; Bach et al., 2023).
Transboundary transport	- Determination of whether there is a high risk for OAE-derived chemicals to be transported into sensitive areas (e.g. marine protected areas, other state territories) in high concentrations.	- Tracer release experiment - Virtual Lagrangian particle tracking. - Utilizing natural tracers observable via remote sensing (e.g., CDOM or Gelbstoff).
Light penetration	- Determination of light environment to assess to what extent the addition of particulate alkalinity source could impact turbidity.	Light loggers, turbidity, CTD casts.
Carbonate chemistry conditions	- Baseline of mean conditions and variability to assess high much change OAE must induce to become detectable. - Determination if OAE-related changes are likely to affect marine organisms.	Dickson et al. (2007) and ocean acidification literature.

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Macronutrients	- Assessment of whether the designated system is prone to macronutrient fertilization via OAE. (Please note that not all OAE approaches would introduce macronutrients into the ocean system).	Standard photometric approaches (Hansen and Koroleff, 1999).
Micronutrients	- Assessment of whether the designated system is prone to micronutrient fertilization via OAE. (Please note that not all OAE approaches would introduce micronutrients into the ocean system).	GEOTRACES cookbook. (https://www.geotraces.org/methods-cookbook/)
Marine food web structure	- Assessment of the planktonic and/or benthic food web structure prior to testing an OAE deployment.	There is a whole range of surveying tools that could be applied depending on the size and abundance of organisms. Applied methods could range from OMICS (including eDNA), optical observations, acoustics, and flow cytometry.
Risk of damaging organisms by adding ground minerals	- Providing knowledge of whether organisms could be physically harmed, for example through covering them with mineral powder.	Same range of methods as for the food web assessment.
Endangered species	- Clarification if endangered species could be present at the designated field site.	Same range of methods as for the food web assessment. Plane or drone surveys can help to confirm sightings of larger organisms and there may be online resources to be utilized (e.g., WhaleMap). Furthermore, local knowledge should be sought after from the diverse range of stakeholder groups. For example, consultation with indigenous communities, fishermen, local authorities, and environmental agencies.

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Foraging/breeding ground	- Clarification if the designated field site is an important breeding/foraging area for migratory organisms.	Same range as for endangered species assessments.

2.4. Measurement considerations

What to measure and the type of instrumentation needed will ultimately depend on the scale and goals of each individual experiment and should be considered on a case-by-case basis. For example, depending on the alkalinity source utilized (Table 1), it may (e.g., in the case of olivine) or may not (e.g., in the case of NaOH) be a priority to measure trace metal or nutrient concentrations. In addition to alkalinity type, the experimental scale will also dictate measurement considerations. For example, if the scale of the perturbation is small or the signal is very dilute, environmental impacts will not likely be measurable far from where the perturbation takes place. If there is a large addition of alkalinity, especially in a semi-enclosed system, both environmental impacts and changes in chemistry will be easier to detect. Ultimately, when OAE is done at a larger scale (e.g., millions of moles alkalinity) it is likely that large changes in seawater chemistry will wish to be avoided to reduce environmental impacts and avoid secondary precipitation. This presents an interesting challenge to conducting field experiments, as dilution of the alkalinity and ultimately CO_2 signal will make MRV more challenging (Ho et al., 2023, this volume).

Seawater carbonate chemistry measurements will be central to most sampling schemes for OAE. To cover the appropriate spatial and temporal scales, traditional bottle sampling will likely have to be combined with state of the art *in situ* sensors (Bushinsky et al., 2019; Briggs et al., 2020). The appropriate methods and protocols for sampling and analysis are outlined in other chapters in this guide (Schulz et al., 2023, this volume) and in the Guide to Best Practices (Dickson et al., 2007). Some general considerations for field experiments include appropriately categorizing the natural variability that occurs at the field site through space and time. While total alkalinity titrations should remain a priority, ideally measurements of two carbonate chemistry parameters (e.g., total alkalinity, dissolved inorganic carbon, pH, or pCO_2) should be made for each sample. It is important to note that the combination of pCO_2 and pH is not ideal when calculating CO_2

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chemistry (e.g., using CO2SYS) due to the elevated errors when combining those parameters in determining the rest of the carbonate chemistry system in seawater (Lee and Millero, 1995). Currently, commercially available autonomous sensors exist for pH and pCO_2, with sensors in development for both TA and DIC (Fassbender et al., 2015; Briggs et al., 2020). While autonomous sensors generally have greater uncertainty than bottle samples coupled with laboratory analysis, they will likely play an important role in sampling schemes to help cover adequate spatial and temporal resolution in naturally variable marine systems.

While monitoring the background variability and subsequent additions of alkalinity will be critical, scientists may also wish to directly measure fluxes of carbon within the field study site. The direct measurement of carbon fluxes can be accomplished via different methods including benthic and floating chambers, eddy covariance and other benthic boundary layer techniques, and mass balances (Subhas et al. and Riebesell et al., 2023, this volume). These techniques have benefits and drawbacks, including having to enclose the natural system (chambers) and elevated uncertainty that could be outside of the expected changes due to the perturbation (eddy covariance). Benthic chamber measurements may be particularly important to quantify the dissolution of minerals and rocks added to sediments. Ultimately, any measurements of fluxes due to OAE activities will likely need to be coupled with numerical modeling to estimate the overall drawdown of atmospheric CO_2 (Fennel et al., 2023, this volume).

Field experiments should be informed by other scientific studies as much as possible (e.g., studies based on laboratory experiments, mesocosm studies, natural analogs, and numerical modelling). While not necessarily directly translatable to natural systems (Edmunds et al., 2016; Page et al., 2021), smaller scale experiments can provide first order assessments on safety and efficacy, helping to prevent unintended harmful ecological side effects when conducting large scale deployments.

Other measurements that may be useful during OAE field experiments are outlined in Table 2. It is important to note that this list is not meant to be exhaustive, and measurement selection will have to be made on a case-by-case basis. Considering the difficulties of tracking water masses in an open system, the next section is a more detailed discussion on tracers for monitoring mixing and dilution of water within the OAE field experiment site. Tracking additional alkalinity will be

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critical to determine the impacts and efficacy of alkalinity enrichments and may be one of the biggest challenges facing OAE field experiments.

2.5 Dual tracer regression technique

If the goal is to track alkalinity additions and measure their effects on community carbon fluxes (i.e., a biological response or air-sea exchange), a dual tracer regression method can be used (e.g., Albright et al. 2016 & 2018). This approach uses the change in ratios between an active tracer (alkalinity) and a passive tracer (dye, artificial gas tracer, Table 3) to assess the fraction of added alkalinity taken up or released by biogeochemical processes in the system. Passive tracers do not affect fluid dynamics and are passively advected by the surrounding flow field. The use of passive tracers, such as dye tracers (e.g., rhodamine, fluorescein) or artificial gas tracers (e.g., SF6, CF3SF5) that do not occur in nature, helps eliminate background noise. Additional considerations include how many tracers to use and what information each tracer provides (Table 3).

During a dual tracer experiment, changes in the active tracer (alkalinity) result from mixing, dilution, and biogeochemical activity, whereas changes in the passive tracer are due solely to mixing and dilution. By comparing the alkalinity to dye ratios before (e.g., upstream) and after (e.g., downstream) the water mass interacts with a study area, it is possible to isolate the change in alkalinity that is due to biogeochemical processes such as calcium carbonate precipitation and dissolution (Figures 1 & 2). This technique is an extension of Friedlander et al. (1986) and may have applications in other areas of research pertinent to marine CDR, such as nutrient or pollution assessments and the uptake of industrial or agricultural waste. The primary experimental criteria for the dual tracer technique are that the active and passive tracers are added in a fixed ratio and at a fixed rate, in areas where there is a dominant flow direction, dispersion or dilution.

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Figure 1. Rhodamine dye flowing over a coral reef flat study site during a study in One Tree Island, Australia (Albright et al. 2016). NaOH was used as an active tracer to raise alkalinity, and rhodamine was used as a passive tracer to account for mixing and dilution. Changes in the alkalinity-dye ratios were used to isolate the change in alkalinity flux that was associated with an increase in net community calcification on the reef flat.

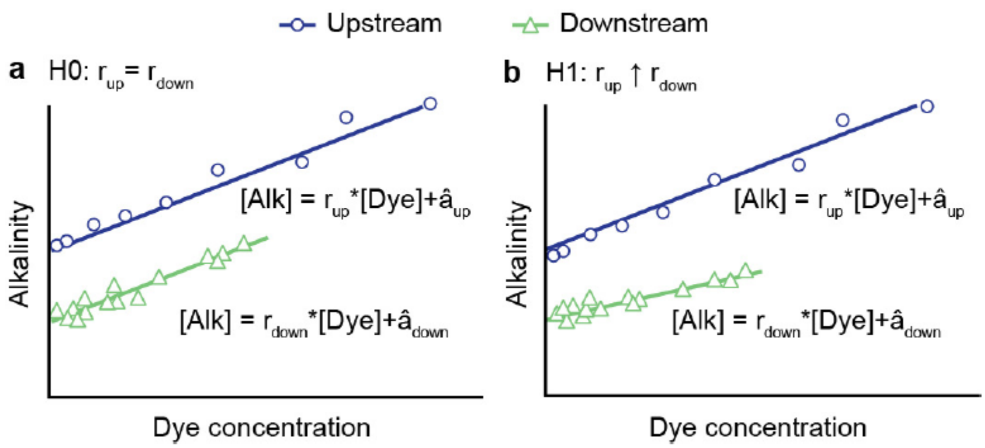

Figure 2. Theoretical representations of the null (H0) and alternative (H1) hypotheses for a dual tracer regression experiment where NaOH was used as a source of alkalinity and rhodamine dye

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was used as a passive tracer (from Albright et al. 2016). (a). In H0, the benthic community does not take up added alkalinity. Here, the change in alkalinity between the upstream and downstream transects would not be systematically related to the dye concentration, and the ratio of the alkalinity–dye relationship, r, would not be expected to change between the upstream and downstream locations (that is, $r_{up} = r_{down}$). (b). In H1, an uptake of added alkalinity occurs by the benthic community. Here, areas with more alkalinity (and more dye) change at a different rate than areas with less alkalinity (and less dye), resulting in a change in the alkalinity–dye slope (that is, $r_{up} > r_{down}$).

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Table 3. Passive tracers that are available for use in field experiments and considerations for each. Additional tracers may be useful that are not listed in this table, including Helium 3 and Tritium.

Tracer	**Type**	**Pros**	**Limitations**	**Lifespan**
Rhodamine	Fluorescent dye	Sensor-based, high frequency (>4 Hz) detection, platform flexibility, detection from space and/or the sky for surface releases	Optically degrades and absorbs to particles, not good for longer-term studies, not as good signal to noise/detection limits as inert gas tracers	Several days to weeks
Fluorescein	Fluorescent dye	Sensor-based, high frequency (>4 Hz) detection, platform flexibility, detection from space and/or the sky for surface releases	Degrades optically - not good for longer-term studies (>24h)	<24 h
SF6	Artificial gas	Inert; capable of being measured at very low concentrations; able to quantify mixing and residence time; good for large-scale ocean tracer release experiments	Lower frequency detection and less flexibility with platforms, requires discrete measurement	years
Trifluoromethyl sulfur	Artificial gas	Good for large-scale ocean	Difficult to obtain, lower frequency detection and	years

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pentafluoride (CF_3SF_5)		experiments	less flexibility with autonomous platforms, requires discrete measurement	

2.6 Detecting change and the importance of controlled experiments

Distinguishing between the ‘signal’ and the background ‘noise’ that is inherent in natural systems can be challenging, especially in large-scale field experiments where replication may not be practical (Carpenter, 1990). Gaining baseline knowledge on the physical, chemical, and biological components of the study site is essential, a process which can take years. There is often considerable natural variability in marine systems due to fluctuations in biological activity, hydrodynamics, seasonal and/or interannual influences, and others (Kapsenberg and Cyronak, 2019). Where possible, conducting controlled experiments helps to maximize the ratio of signal to noise, thereby improving statistical power to detect experimental effects. The pros and cons of replicating experimental controls in space versus time should be taken into consideration. For many field experiments (and natural analogs; see Subhas et al., 2023, this volume), sample size will inherently be limited (e.g., one, or few study site(s)); therefore, conducting controls in time (e.g., every third day) may be the best option. For studies with limited (or no) replication, there are statistical methods that can be used to isolate effects pre- and post-treatment (Carpenter, 1990). However, good baseline knowledge of the natural variability in the study area is essential, which may require baseline measurements over long time periods (e.g., seasonal and/or interannual).

3. Additional considerations

Permitting**.** Addressing regulatory requirements is critical prior to conducting field deployments. The spatial and temporal scale of the field trial, as well as the specific considerations of the deployment site (e.g., protection status) will determine permitting requirements. Engaging with this process early is advised - for example, understanding who the permit-granting authorities are for a given area and timelines for associated regulatory processes. In some cases, the use of existing infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., beach

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renourishment) may offer ways to streamline deployments, although permitting will be governed by existing regulations. For a detailed discussion on legal considerations, see Steenkamp and Webb (2023, this volume).

Community engagement and social considerations of field experiments. The likelihood of harmful ecological consequences from OAE field experiments remains unclear and will ultimately depend on the technology and temporal and spatial scale of the experiment. Field experiments evaluating CDR approaches carry the risk of unintended consequences and impacts over vast spatial scales, so appropriate scaling (e.g., starting small) is necessary (NASEM, 2022). In response to these unknowns, researchers should follow the key components for a code of conduct for marine CDR research, as outlined by Loomis et al. (2022), which details best practices that encourage responsible research amongst both the public and private sectors.

Social license is critical for the success of CDR projects; researchers have an obligation to involve the full community of people (public and stakeholders) who may be impacted by the research (Nawaz et al., 2022; Cooley et al., 2023). Therefore, addressing public concern is important both before and during field deployments. The deployment site will determine the potential for community engagement. Coordinating with local and/or regional organizations who are connected to relevant stakeholders (for example, your local SeaGrant office if in the United States). For additional discussion on social considerations of OAE field trials, see Satterfield et al. (2023, this volume).

Collaboration and data/information sharing. Considering that the initial number of OAE field experiments will likely be small due to inherent challenges (cost, permitting, access, logistics, environmental safety), fostering interdisciplinary and collaborative teams around field campaigns may ensure the greatest return on investment. For example, the early announcement of field campaigns to open participation to external groups and foster collaboration; making efforts to include groups who may not traditionally have access to and/or capacity for field campaigns; including travel support in grant applications to support external collaborators. Making concerted efforts to share information, resources, and ideas allows researchers to combine knowledge and resources in ways that might not have been possible when working alone, thereby advancing OAE technology and science at a faster pace.

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Inclusivity and transparency during OAE field trials are crucial to ensure that knowledge gained is fed back into scientific and other communities efficiently, iteratively informing and refining the next generation of experiments. Field experiments will presumably mimic plans for real world OAE deployments and therefore should be done in collaboration with relevant stakeholders across science, industry, policy, and society. To foster collaboration and technology transfer, we advocate for a centralized platform and/or organization to share data and information in this rapidly evolving field. This might look like a centralized, freely accessible platform for early and/or 'real-time' information sharing (i.e., before publication) that can facilitate faster information exchange within the research community (e.g., data sharing, permitting issues). Two existing options that could help fill this gap are the OA information exchange (https://www.oainfoexchange.org/index.html) and the Ocean Visions community (https://community.oceanvisions.org/dashboard). It may prove useful to designate core working groups of experts in various aspects of CDR that investigate specific needs and priorities and work to synthesize and share existing knowledge in the context of field deployments. This approach has been adopted by other scientific disciplines in high priority, rapidly evolving, and highly collaborative fields, greatly benefiting the scientific community at large (e.g., the Coral Restoration Consortium, https://www.crc.world/ - and associated working groups). Coordinating field trials with research communities conducting laboratory and mesocosm experiments, studying natural analogs, and undertaking modeling efforts will help strengthen the interpretation and extrapolation of results.

4. Conclusion/Recommendations

Given that few OAE field studies have been conducted to date, there is much to learn from the earliest experiments with respect to experimental design, measurement and monitoring, deployment considerations, environmental impact, and more. Early experiments will only engage with a fraction of the temporal and spatial scales involved in full-scale OAE, and longer-term and larger-scale studies will become increasingly important as the field develops. It is important that marine CDR research is hypothesis-driven, structured, deliberate, and well-planned to best inform future decision-making about OAE techniques and deployments. Careful consideration of the physical, chemical, and biological components of the study area will help inform the experimental approach. The use of baseline studies (both previous and contemporary to the OAE

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deployment) and controls will help to maximize signal-to-noise ratios and identify experimental effects. The timescale of OAE field experiments should not be underestimated, especially when considering permitting and the data needed to capture the baseline variability of natural systems. Considering the urgent timeline required for humanity to meet our climate goals, field experiments need to move forward swiftly yet deliberately. To ensure the success of OAE, diverse perspectives from research, industry, policy, and society must converge, demanding transdisciplinary thinking and a commitment to open and transparent science. Central to this ambitious undertaking are the early field deployments, results from which will ultimately determine the successes and failures of OAE projects.

Competing Interests

The contact author has declared that none of the authors has any competing interests.

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References

Albright, R., Caldeira, L., Hosfelt, J., Kwiatkowski, L., Maclaren, J. K., Mason, B. M., ... & Caldeira, K. (2016), Reversal of ocean acidification enhances net coral reef calcification. Nature, 531(7594), 362-365.

Albright, R., Takeshita, Y., Koweek, D. A., Ninokawa, A., Wolfe, K., Rivlin, T., ... & Caldeira, K. (2018), Carbon dioxide addition to coral reef waters suppresses net community calcification. Nature, 555(7697), 516-519.

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

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

Briggs, E. M., De Carlo, E. H., Sabine, C. L., Howins, N. M., & Martz, T. R. (2020), Autonomous ion-sensitive field effect transistor-based total alkalinity and pH measurements on a barrier reef of Kane'ohe Bay. ACS Earth and Space Chemistry, 4(3), 355-362.

Bushinsky, S. M., Takeshita, Y., & Williams, N. L. (2019), Observing changes in ocean carbonate chemistry: our autonomous future. Current climate change reports, 5, 207-220.

Carpenter, S. R. (1990), Large-scale perturbations: opportunities for innovation. Ecology, 71(6), 2038-2043.

Cooley, S. R., Klinsky, S., Morrow, D. R., & Satterfield, T. (2023), Sociotechnical considerations about ocean carbon dioxide removal. Annual Review of Marine Science, 15, 41-66.

Dickson, A. G., Sabine, C. L., & Christian, J. R. (2007), Guide to best practices for ocean CO2 measurements. North Pacific Marine Science Organization.

Edmunds, P. J., Comeau, S., Lantz, C., Andersson, A., Briggs, C., Cohen, A., ... & Carpenter, R.

https://doi.org/10.5194/sp-2023-9
Preprint. Discussion started: 27 June 2023

C. (2016), Integrating the effects of ocean acidification across functional scales on tropical coral reefs. Bioscience, 66(5), 350-362.

Fassbender, A. J., Sabine, C. L., Lawrence-Slavas, N., De Carlo, E. H., Meinig, C., & Maenner Jones, S. (2015), Robust sensor for extended autonomous measurements of surface ocean dissolved inorganic carbon. Environmental science & technology, 49(6), 3628-3635.

Friedlander, S.K., Turner, J.R. & Hering, S.V. (1986), A new method for estimating dry deposition velocities for atmospheric aerosols. J. Aerosol Sci. 17, 240–244.

Hansen, H. P., & Koroleff, F. (1999), Determination of nutrients. Methods of seawater analysis, 159-228.

Hartmann, J., Suitner, N., Lim, C., Schneider, J., Marín-Samper, L., Arístegui, J., ... & Riebesell, U. (2022), Stability of alkalinity in Ocean Alkalinity Enhancement (OAE) approaches–consequences for durability of CO_2 storage. Biogeosciences, 1-29.

He, J., & Tyka, M. D. (2023), Limits and CO2 equilibration of near-coast alkalinity enhancement. Biogeosciences, 20(1), 1726-4189.

Kapsenberg, L., & Cyronak, T. (2019), Ocean acidification refugia in variable environments. Global Change Biology, 25(10), 3201-3214.

Lee, K., & Millero, F. J. (1995), Thermodynamic studies of the carbonate system in seawater. Deep Sea Research Part I: Oceanographic Research Papers, 42(11-12), 2035-2061.

Loomis, R., Cooley, S. R., Collins, J. R., Engler, S., & Suatoni, L. (2022), A Code of Conduct Is Imperative for Ocean Carbon Dioxide Removal Research. Frontiers in Marine Science, 9.

Moras, C. A., Bach, L. T., Cyronak, T., Joannes-Boyau, R., & Schulz, K. G. (2022), Ocean alkalinity enhancement–avoiding runaway $CaCO_3$ precipitation during quick and hydrated lime dissolution. Biogeosciences, 19(15), 3537-3557.

Nawaz, S., Peterson St-Laurent, G., & Satterfield, T. (2023), Public evaluations of four approaches to ocean-based carbon dioxide removal. Climate Policy, 23(3), 379-394.

https://doi.org/10.5194/sp-2023-9
Preprint. Discussion started: 27 June 2023

National Academies of Sciences, Engineering, and Medicine. (2022), A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration. Washington, DC: The National Academies Press. doi.org/10.17226/26278.

Page, H. N., Bahr, K. D., Cyronak, T., Jewett, E. B., Johnson, M. D., & McCoy, S. J. (2022), Responses of benthic calcifying algae to ocean acidification differ between laboratory and field settings. ICES Journal of Marine Science, 79(1), 1-11.