Field experiments in ocean alkalinity enhancement research 1 2 Tyler Cyronak¹*, Rebecca Albright²*, Lennart <u>T.</u>Bach³ 3 4 ¹Georgia Southern University, Institute for Coastal Plain Science, Statesboro, GA 5 ²California Academy of Sciences, San Francisco, CA 7 ³Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tasmania, Australia 8 *These authors contributed equally to the writing of this manuscript. 9 10 Correspondence to: Tyler Cyronak (tcyronak@georgiasouthern.edu) and Rebecca Albright 11 (ralbright@calacademy.org) 12

Abstract

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This chapter focuses on considerations for conducting open-system field experiments in the 14 15 context of ocean alkalinity enhancement (OAE) research. By conducting experiments in realworld marine and coastal systems, researchers can gain valuable insights into ecological 16 dynamics, biogeochemical cycles, and the safety, efficacy, and scalability of OAE techniques 17 under natural conditions. However, logistical constraints and complex natural dynamics pose 18 challenges for successful field trials. To date, only a limited number of OAE field studies have 19 20 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, 21 knowledge, and lessons learned as quickly and efficiently as possible within the broader OAE 22 23 community and beyond. Considering the potential ecological and societal consequences of field experiments, active engagement with the public and other stakeholders is is essentialdesirable 24 25 while .- Ccollaboration, data sharing, and transdisciplinary scientific teams are vital for maximizing can maximize the return on investment during field trials. The outcomes s-of early 26 early field experiment deployments araree likely to shape the future of OAE research, 27 implementation, and public acceptance, -emphasizing the need for transparent and open 28 scientific practices. 29

1. Introduction

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33 This chapter addresses considerations for conducting open-system field experiments related to 34 ocean alkalinity enhancement (OAE). We define , where 'field experiment' or 'field studies' broadly as refers to the addition or manipulation of alkalinity into a natural system in ways that 35 simulatethat is relevant to planned OAE, independent of the spatial and temporal scale. We 36 intentionally exclude spatial and temporal scales from our definition to encompass the wide 37 spectrum of OAE methods and approaches. In fact, field experiments are likely to span spatial 38 scales of m² to 100s of km² and last from days to years. Field experiments and studies differ 39 from both 'field trials' and 'field deployments' in their motivation, as both trials and deployments 40 41 which denote the practical application and usage of a specific product, device, or technology. 42 deploymentsThe scientific focus during field trials is likely to be on the efficacy of Carbon Dioxide Removal (CDR) and fine-tuning operational deployment, while field experiments will 43 44 encompass a broader range of scientific goals and objectives. The nature, logistics, and objectives of field experiments are likely to make them smaller in scale than operational 45 deployments. This will be advantageous, as field experiments that emulate planned OAE trials 46 and deployments will help create the scientific framework needed to scale operational OAE 47 safely and responsibly. 48

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observing complex natural ecological dynamics and ecosystem dynamics/impacts at the 51 ecosystem level, understanding the role of natural-biogeochemical cycles and physical processes 52 that cannot be replicated in other settings, and and assessing scalability and CDR under real-53 54 world scenarios. The complexity and breadth of some field experiments willmay necessitate science that transcends disciplinary boundaries, making collaboration a priority. Conducting 55 56 successful field trials, however, Success in the field poses faces many challenges due to the 57 inherent complex physical and biogeochemical processes that occur incomplexity of natural 58 marinenatural systems in addition to along with limiting logistical constraints (e.g., permitting, access, social license, infrastructure, life cycle emissions). In light of these challenges, few OAE 59 60 field studies have been conducted to date and associated guidelines are, therefore, still evolving. Despite these challenges, tThe first OAE field experiments are already underway, many of which 61

. Advantage The benefits of conducting experiments in the real worldnatural systems -include

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62 are likely to be small-scale representations of scalable OAE approaches., but each experiment 63 will have different goals and objectives. There will be much to learn from the earliest 64 experiments, and any knowledge gained, and lessons learned should be shared as efficiently and openly as possible to the wider OAE community. There will be much to learn from these early 65 field experiments studies, and any knowledge or insights gained should be shared as efficiently 66 and openly as possible within the wider OAE community and beyond. 67 68 While some OAE field experiments have been completed or are already in progress, many more 69 are on the horizon. We suggest recommend that three overarching questions should be taken into 70 consideration, especially when planning an OAE field experiment in the planning stages: 71 72 What are the main goals of the experiment? Establishing the objectives of a field experiment early indeployment during the planning stage 73 will help guide all aspects of the scientific research plan, including site selection, measurement 74 75 techniques and approaches, data analysis, and measured outcomes. Potential overarching goals of 76 OAE field experiments include demonstrating functionality, efficacy, process, and/or scalability, 77 determining ecological and environmental impacts, developing measurement, reporting, and 78 verification (MRV) protocols, and assessing community engagement. Life cycle assessments 79 (LCA) may be a critical learning objective for some projects (e.g., Foteinis et al. 2023), especially those that are examining OAE at the scale of operational deployments. This list of 80 overarching goals is not comprehensive, and goals are not necessarily mutually exclusive. For 81 example, larger projects may wish to assess multiple components of an OAE 82 approachdeployment while smaller projects might be highly focused on one goal. 83 84 What is the type of alkalinity perturbation? 85 The type of alkalinity that is added (e.g., aqueous vs. solid, carbonates, hydroxides, oxides, or 86 naturally occurring (ultra-)mafic rocks) will ultimately determine many aspects of the scientific 87 research plan. For example, projects adding ground alkaline minerals (e.g., olivine) to the ocean 88 will-may require have different goals and timelines than projects that add aqueous alkalinity 89 (e.g., liquid NaOH) (see Eisaman et al., 2023, this volumeGuide). Priorities for projects adding 90 ground material might include tracking tracking both the dissolution of the alkaline material plus 91

monitoring plus tithe fate of the dissolved alkalinity and its dissolution co-products (e.g. trace

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93 metals), while projects adding aqueous alkalinity will likely only be more concern-mored with 94 the latterfate of alkalinitylatter. while projects that add aqueous alkalinity (e.g., NaOH) will not 95 have to track dissolution in situ (see Eisaman et al., 2023, this volume). Other important experimental considerations that will be driven by the type of alkalinity perturbation includee, 96 the concentration of added alkalinity, duration of additions, dilution and-advection at the field 97 siteadvection at the field site, residence time, controlled versus uncontrolled air-sea 98 equilibrationium, co-deployed tracers, sampling scheme, and environmental side-effects and 99 other aspects etc. These and other research considerations are discussed in more detail below. 100 101 What are the permitting constraints and wider social implications? 102 Addressing the the relevant the appropriate public concern and regulatory requirements is 103 essential before any field experiment deployments can move forward. Permitting requirements will be influenced by the studyfield experiment's location, type of alkalinity perturbation, spatial 104 scale, and duration. The field site will determine the permitting requirements. The use of existing 105 106 infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., beach renourishment) may offer ways to facilitate alkalinity perturbations under existing regulatory 107 108 frameworks. Community engagement and outreach areis an other areas that may will be important to address, during field experiments, especially when the alkalinity perturbation is 109 110 large and uncontained. and potential for community engagement. Ideally, lthe local 111 communitiesy should be engaged at the earliest possible stage as since social license to operateby local stakeholders will beis critical for the success of CDR projects (Nawaz et al., 2022). The use 112 113 of existing infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., 114 beach renourishment) may offer ways to facilitate deployments, although permitting will be 115 governed by existing regulations.). -For a more detailed discussion of legal and social issues see 116 Steenkamp et al. (2023, this Guidevolume) and Satterfield et al. (2023, this volumeGuide). 117 118 With these overarching questions in mind, we discuss considerations for OAE field deployments 119 experiments in more detail below.

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120 2. Research Methods

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2.1 Types of alkalinity addition

122	Field experiments of OAE present many challenges. One of the biggest obstacles to a successful
123	field deploymentsuccess is tracking-the-alkalinity added to an open system. Methods for adding
124	alkalinity can be divided into two general approaches: (1) in situ or coastal enhanced weathering
125	from, or the addition of ground alkaline minerals and rocks with the expectation they will
126	dissolve directly directly in seawaterseawater, and (2) aqueous alkalinity additions, or the
127	addition of 'pre-dissolved' alkalinity to seawater that can be generated in numerous ways
128	including through dissolution reactors and electrochemical techniques (Eisaman et al., 2023, this
129	volumeGuide). Tracking Tracking the added alkalinity added, and subsequent CDR, by under
130	each approach comes with its own unique set of challenges and considerations.
1,21	Adding ground minerals and rocks to an open system presents two distinct scientific challenges.
131 132	First, for alkalinity to be considered additional it needs to be any additional alkalinity that is
133	observed needs to be attributedable to the the dissolution of the (and subsequent alkalinity
134	addition) of the solidadded material inerals needs to be detected and confirmed. This can be
135	accomplished through a range of techniques including measuring the loss of mass of the added
136	mineral material or using geochemical tracers in the receiving waters. Determining dissolution
137	kinetics <i>in situ</i> will be particularly important and they are likely to vary between different Formatted: Font: Italic
138	deployment environments and strategies (e.g., coastal vs open ocean). For example, the
139	chemistry (e.g., salinity, pH, temperature) of the waters where the mineral is deployed added
140	could vary significantly depending on the environment (e.g., beach face, estuary, continental
141	shelf) Chemical (e.g., seawater conditions such as salinity, pCO ₂ , and silica concentrations) and
142	pPhysical (e.g., especially the grain size and surface area of the added material), and chemical Formatted: Subscript
143	eonditions-will be critical in determining_the dissolution rates of any added rocks and minerals
144	(Rimstidt et al., 2012; Montserrat et al., 2017; Fuhr et al. 2022). Physical abrasion through wave
145	action -and currents is also likely to be an important control on dissolution (Flipkens et al., 2023).
146	and initial fField deployments experiments will help translate dissolution kinetics results from
147	laboratory and mesocosm experiments experiments to natural systems, which is not often
148	straightforward due to complicated biogeochemical processes that are hard to replicate ex situ
149	(Morse et al., 2007).
150	The second major challenge is common to both solid and aqueous approaches and involves

tracking the added alkalinity, which and observing drawdown of atmospheric CO2. Tracking

152 additional alkalinity becomes a particularly difficult problem in open-system field experiments 153 where water is freely exchanged. Depending on the objectives of the field deployment, this is 154 likely to be the a main scientific concern. However, it is important to note that tracking the added 155 alkalinity does notsn't necessarily equate to observing CDR (i.e., an increase in seawater CO₂ stored as bicarbonate or carbonate). Observing an increase in atmospheric CO₂ stored as 156 Formatted: Subscript seawater dissolved inorganic carbon comes with its own set of challenges that are discussed in 157 158 depth by Ho et al. (2023, this Guide). 159 Whether or not the alkalinity is derived from in situ mineral dissolution or direct aqueous 160 additions, for OAE to be successful theatmospheric dissolved inorganic carbon (DIC) deficit 161 162 generated through an OAE deployment needs to be equilibrated with atmospheric CO2 needs to 163 be taken up by seawater or CO2 effluxes from seawater to the atmosphere need to be reduced... Formatted: Subscript Therefore, understanding the physical mixing and air-sea gas exchange dynamics of the 164 deployment site will be a factor of interest for many field studies. Incorporating physical mixing 165 models with biogeochemical processes will likely be the end goal of many field experiments 166 167 focused on MRV (Ho et al. a, and Fennel et al., 2023, this volumGuidee). Choosing sites that 168 minimizewith minimal mixing of different water masses or have with well defined well-defined diffusivities could facilitate tracing released alkalinity and subsequent air-sea CO2 influxes. 169 170 While minimal mixing of different ocean water masses may be desired, higher wind speeds and 171 wave action will increase the rate of air-sea gas exchange and may make CDR easier to measure. 172 Background seawater chemistry will also be important in controlling air-sea gas exchange. For 173 example, sites with naturally lower buffering capacities will see greater changes in CO₂ per unit Formatted: Subscript 174 of added alkalinity (Egleston et al., 2010; Hauck et al., 2016). The release of conservative tracers with alkalinity will likely be useful and is discussed in more detail below. Incorporating physical 175 mixing models with biogeochemical processes will likely be the end goal of many field 176 177 experiments focused on MRV (Ho et al., and Fennel et al., 2023, this volume). The release of 178 conservative tracers with alkalinity will likely be useful for field experiments that wish to track the added alkalinity and is discussed in more detail below (Section 2.5). 179 180 181 Other experimental considerations related to the type of alkalinity perturbation include the 182 duration and location of alkalinity addition, which will be important for environmental and

regulatory considerations... 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., 20223, Fuhr et al., 2022). Compared to experiments based on one-time additions of aqueous alkalinity or fast dissolving solid-phase materials (e.g., Ca(OH)2), Ffield experiments adding solid minerals with comparatively slow dissolution rates (e.g., olivine) will likely need to consider much longer experimental time frames to incorporate the monitoring of mineral dissolution than experiments based on one time additions of aqueous alkalinity. However, the timescale of each experiment will ultimately depend on the scientific objectives and could last from weeks to years and even decades. Location is another important factor that will influence logistics. For example, amending beach sand with alkaline minerals will present different challenges than compared to the addition of alkaline material to outfalls that discharge into the ocean. Based on these and other considerations, eEach plan-field experiment will require specific spatial and temporal sampling schemes to be developed. These sampling schemes which should be planned well in advance of any deployments perturbation and may require preliminary sampling campaigns to fine tune. 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 eOAE via coastal enhanced weathering can be accomplished using a 204 205 variety of naturally occurring and human-made rocks and minerals (Table 1). The addition of 206 these rocks and minerals is done after they have been ground to a desired grain size with many 207

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unique application techniques proposed after the initial grinding step (see Eisaman et al., 2023, this volumeGuide). 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 (Koehler et al., 2013; Fakharee et al., 2023) and has not gained widespread support as a viable OAE option, although deployment in boat wakes may be viable

(Renforth et al., 2017; He and Tyka, 2023). Other application techniques include spreading 213 material in coastal ecosystems including on such as on beach faceses, marshes, riverbeds, and Formatted: Subscript

214 estuaries, which riverbeds, have etc. This has the potential to enhance dissolution through 215 processes such as physical wave action and favorable water chemistry (cite new olivine paper). 216 However, the complex physical and biogeochemical processes that promote enhanced 217 weathering in coastal ecosystems can make field experimentation more complicated by creating 218 strong spatiotemporal modes of variability in water chemistry. To make results more broadly applicable, field experiments should attempt to mimic real world alkalinity application scenarios 219 such as those described above. 220 221 Any field experiments that add ground material to marine ecosystems may consider tracking the 222 223 fate of that material from the addition site. Experiments could also artificially contain the 224 material using barriers to avoid rapid loss of the ground material via ocean-currents, however, 225 this could make the experiment less applicable comparable to real world OAE deployments. Sampling should extend from the water column into areas where the material is added including 226 227 sediments and pore waters. 228 Likely environmental impacts associated with coastal enhanced weathering come from the 229 physical impacts of adding finely ground material and or the chemical release of trace elements 230 231 and other contaminants. Both processes could have associated risks and/or co-benefits for a 232 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, 233 234 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 235 primary production or cause harm to biological systems. The bioaccumulation of toxic metals in 236 237 higher trophic level organisms, especially those of commercial importance, is a widespread 238 particularly important concern. 239 240 Safety criteria should be put in place that can create a pause in the field experiment or prevent 241 future experiments of the same type from taking place. These guardrails should be developed by the broader OAE community but may include things like obvious damage or health impacts to 242 243 ecologically important organisms such as primary producers and keystone species, large and 244 unexpected changes in biogeochemical cycles, and the general deterioration of environmental

245	conditions. Risk-benefit analysis may be particularly useful in determining whether projects can
246	or should move forward and may already be included in regulatory requirements through
247	existing frameworks such as Eenvironmental iImpact aAssessments.
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249	Aqueous and slurry-based additions of alkalinity provide different benefits and challenges
250	compared to solid forms of alkalinity feedstock. One of the primary benefits of aqueous
251	additions is that the alkalinity has been pre-dissolved, avoiding the often slow dissolution
252	kinetics of minerals and rocks in seawater. Aqueous alkalinity can be generated by two main
253	mechanisms (1) the dissolution of alkaline rocks and minerals in reactors, and (2)
254	electrochemical processes that generate alkalinity by splitting seawater or other brine streams
255	into an acid and base (Eisaman et al., 2023, this Guidevelume). For some materials, such as
256	Ca(OH) ₂ lime_aand Mg(OH) ₂ , dissolution slurries are formed and a combination of particulate
257	and aqueous alkalinity can be dosed into seawater. Any particulates that are dosed from the
258	slurry need to dissolve, meaning dissolution kinetics in seawater will be critical. However, the
259	dissolution of these materials tends to be much quicker than with rocks and minerals (Table 1).
260	There are important processes that need to be considered when adding aqueous alkalinity,
261	including the unintended precipitation of calcium carbonates due to locally elevated saturation
262	states (Hartmann et al., 2023; Moras et al., 2023).
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264	Field experiments that use aqueous or slurry-based alkalinity additions will need to assess the
265	impacts on seawater chemistry at the source of addition and across a dilution radius. Depending
266	on the type of experiment and magnitude of additions this dilution radius could extend upwards
267	of kilometers, but the magnitude of the perturbation to carbonate chemistry would become
268	smaller the further away from the alkalinity source -(He & Tyka, 2023). The potential
269	environmental impacts from aqueous type alkalinity additions will be similar to those discussed
270	for coastal enhanced weathering, but also include extreme localized changes in carbonate
271	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 redissolves relatively quickly in most cases.	Alkalinity, Na ⁺
Manufactured and natural Mg derived alkalinity sources (e.g., Mg(OH)2, brucite)2	Solid or aqueous slurry	Relatively fast but a combination of dissolution rates both in the receiving and dosing waters.	Alkalinity, limited amounts of nutrients and trace metals (generally less than silicates), Mg ²⁺ .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 limederived alkalinity sources (e.g. quicklimeCaO, ikaite))	Solid or aqueous slurry	Relatively fast but different kinetics between lime products.	Alkalinity, limited amounts of nutrients and trace metals (generally less than silicates), Ca ²⁺ . 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.
Natural and synthetic carbonates (e.g. calcite, aragonite)	Solid	They don't dissolve under common surface ocean carbonate chemistry conditions.	Alkalinity, phosphate in some mined sources, dissolved inorganic carbon.

Dissolution rates can
be higher in microenvironments such as corrosive
sediment porewaters where saturation is
low due to respiratory CO ₂ .

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2.3 Considerations for site selection

Careful consideration should be given to site the site selection and experimental design to make sure the study adequately address the specific research questions and goals. Some aspects of the field site that will be important include, account for ecosystem- and site-specific characteristics, the prevailing meteorological and oceanographic conditions, and natural spatiotemporalas 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 experiments and will likely be first-order determinants of where field trials experiments take place, For example, proximity to a marine institute (for land-based approaches) or access to a research cruise (for open ocean approaches) may be desirable. Logistics will ultimately determine where operational OAE deployments take place and early field experiments will help to elucidate important issues including the impacts of life cycle emissions on CDR. OAE field experimentation requires eareful 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. OAE field experimentation requires careful assessment of the field site prior to alkalinity additions to provide foundational knowledge of the site characteristics. Scientific considerations of for 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,

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some of the listed parameters may be more applicable to specific OAE approaches. Preliminary
knowledge of the field site will inform both the experimental design as well as interpretation of
data and experimental outcomes. Due to the large investments in cost and time required to collect
baseline data, locations with a wealth of pre-existing scientific data may be considered. This
baseline data could be available in the peer-reviewed literature and/or from publicly available
coastal and open ocean time-series (e.g., Sutton et al., 2019).

Physics:

- What are the expecteded dilution rates of the additional added alkalinity?
- 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 increase ind turbidity have on this?
- What is the residence time of water in the surface ocean or mixed layer and how does this
 relate to the estimated air-sea equilibration time?
- What is driving the natural air-sea gas exchange?
- Will changes in turbidity impact the albedo of the experimental site? and is there any risk of water mass subduction before air-sea CO₂-flux happens?

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- What are risks associated withis the potential for the lateral export and exchange of alkalinity and other materials?
- Is there the potential <u>for of physical</u> 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? What modes of variability (e.g., daily, seasonal, interannual) impact seawater chemistry?
- —How will variations in seawater chemistry this impact signal to noise?

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- How will seawater chemistry impact mineral dissolution rates?
- Is there potential to disturb the natural concentrations of macro- or micronutrients or toxic metals through dissolution by-products?
- How do anthropogenic sources of alkalinity interact with (and potentially -modify)
 natural modify) natural sources and sinks of alkalinity?

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 culturally or commercially important species present?
- 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.
- Are there times of the day or seasons with elevated species or ecosystem sensitivities?

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Box 1. Scientific considerations for field experiments.

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 timelong 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. May be useful for residence time as well.	 Tracer release experiment Virtual Lagrangian particle tracking. Utilizing natural tracers observable via remote sensing (e.g., CDOM or Gelbstoff). Mixed layer depth.
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 how 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. Schulz et al., (2023, thisthis gGuide)

Macronutrients	- Assessment of whether the designated system is prone to macronutrient fertilization via OAE. (NPlease note that not all OAE approaches would introduce macronutrients into the ocean system).	Standard photometric approaches (Hansen and Koroleff, 1999). Experimental assessment of limiting elements.
Micronutrients	- Assessment of whether the designated system is prone to micronutrient fertilization via OAE. (Please noteNote that not all OAE approaches would introduce micronutrients into the ocean system).	GEOTRACES cookbook. (https://www.geotraces.org/m ethods-cookbook/) Experimental assessment of limiting elements.
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.

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.
	organisms.	

2.4. Measurement considerations

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What to measure and the type of instrumentation needed will ultimately depend on the site, 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 the dilution of the alkalinity and ultimately CO₂ signal will make MRV more challenging (Ho et al., 2023, this volumeGuide). 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; Ho et al., this Guide). Bushinsky et al. (Figure 1; 2019) provides a comprehensive overview of the spatiotemporal capabilities of existing carbonate chemistry sensors and platforms, and care should be taken to make sure sensors are appropriate for measurements in seawater. The appropriate methods and protocols for sampling and analysis are outlined in other chapters in this guide (Schulz et al., 2023, this Guidevolume) and in the Guide to Best Practices (Dickson et al., 2007). Some general considerations for field experiments include appropriately characterizing categorizing the natural variability that occurs at the field site through space and time. While

344 total alkalinity titrations should remain a priority, at least two ideally measurements of two 345 carbonate chemistry parameters (e.g., total alkalinity, dissolved inorganic carbon, pH, or pCO₂) 346 should be measured ade-for each sample. It is important to note that the combination of pCO₂ 347 and pH is not ideal when calculating CO₂ chemistry (e.g., using CO2SYS) due to the elevated errors when combining those parameters in determining the rest of the carbonate chemistry 348 system in seawater (Lee and Millero, 1995). Currently, commercially available autonomous 349 sensors exist for pH and pCO₂, with sensors in development for both TA and DIC (Fassbender et 350 al., 2015; Briggs et al., 2020; Qiu et al., 2023). While autonomous sensors generally have greater 351 uncertainty than bottle samples coupled with laboratory analysis, they will likely play an 352 important role in sampling schemes to help cover adequate spatial and temporal resolution in 353 354 naturally variable marine systems. While monitoring the background variability and subsequent additions of alkalinity will be 355 356 critical, scientists may also wish attempt wish to directly measure fluxes of carbon within theat 357 the field study site (Ho et al., this Guide). The direct measurement of carbon fluxes can be 358 accomplished via different methods including benthic and floating chambers, eddy covariance 359 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 360 361 enclose the natural system (e.g., chambers) and elevated uncertainty that could be outside of the expected changes due to the perturbation (e.g., eddy covariance). Benthic chamber 362 363 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 364 need to be coupled with numerical modeling to estimate the overall drawdown of atmospheric 365 366 CO₂ (Fennel et al., 2023, this volumeGuide). Field experiments should be informed by other scientific studies as much as possible (e.g., 367 368 studies based on laboratory experiments, mesocosm studies, natural analogs, and numerical 369 modelling). While not necessarily directly translatable to natural systems (Edmunds et al., 2016; 370 Page et al., 2021), smaller scalethese types of -studiesexperiments can provide first order 371 assessments on safety and efficacy, helping to prevent unintended harmful ecological side effects 372 when conducting large scale deployments perturbations.

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 added alkalinity will be 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 net ecosystem production 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.



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.

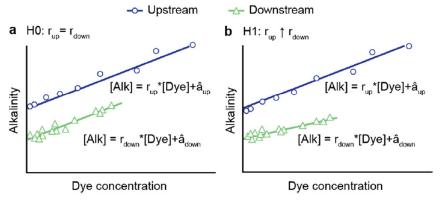


Figure 2. Theoretical representations of the null (H0) and alternative (H1) hypotheses for a dual tracer regression experiment where NaOH was used as a source of alkalinity and rhodamine dye

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, $r_{up} > r_{down}$).

Tracer	Туре	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. High global warming potential.		years
Trifluorom ethyl sulfur	Artificial gas	Good for large- scale ocean	Difficult to obtain, lower frequency detection and	years

pentafluori	experiments.	less flexibility with	
de		autonomous platforms,	
(CF ₃ SF ₅)		requires discrete	
		measurement. High global	
		warming potential.	

2.6 Detecting change and the importance of controlled experiments

Distinguishing between Separating an experimental the-'signal' from and the 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 essentialshould be a priority., a process which can take years. There is often considerable natural variability in marine systems, and especially in coastal systems, due to fluctuations in biological activity, hydrodynamics, seasonal and/or interannual influences, and others (Bates et al., 1998; Bates 2002; Hagens and Middelburg, 2016; Landschützer et al., 2018; Sutton et al., 2019; Kapsenberg and Cyronak, 2019; Torres et al., 2021 Kapsenberg and Cyronak, 2019). Fully characterizing this variability could take many years, which may create significant barriers to experimental progress in the field. Therefore, we recommend that any potential modes of spatiotemporal variability be recognized and evaluated while planning field experiments. For

Where possible, conducting controlled experiments <u>will</u> 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 <u>Guidevolume</u>), sample size will <u>inherently bebe inherently</u> 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

instance, in coastal systems with river and groundwater inputs it will be important to know the

impact that freshwater has on carbonate chemistry.

(Carpenter, 1990). Numerical simulations and machine learning based network design are

452 potentially valuable tools to optimize observational networks to detect experimental 453 change. However, good baseline knowledge of the natural variability in the study area is 454 essential, which may require baseline measurements over long time periods (e.g., seasonal and/or 455 interannual). 456 3. Additional considerations 457 458 **Permitting.** Addressing regulatory requirements is critical prior to conducting field 459 deployments, experiments. 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 460 requirements. Engaging with this process early is advised - for example, understanding who the 461 permit-granting authorities are for a given area and timelines for associated regulatory processes. 462 In some cases, the use of existing infrastructure (e.g., wastewater discharge sites) and 463 environmental projects (e.g., beach renourishment) may offer ways to streamline 464 deployments experiments, although permitting will be governed by existing regulations. For a 465 466 detailed discussion on legal considerations, see Steenkamp and Webb (2023, this volumeGuide). Community engagement and social considerations of field experiments. The likelihood of 467 harmful ecological consequences from OAE field experiments remains unclear and will 468 469 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 470 471 over vast-large spatial scales, so appropriate scaling (e.g., starting small) is necessary (NASEM, 472 2022). In response to these unknowns, researchers should follow the key components for a code 473 of conduct for marine CDR research, e.g., as outlined by Loomis et al. (2022), which details best 474 practices that encourage responsible research amongst both the public and private sectors. 475 476 Social license to operate is critical for the success of CDR projects; and researchers have an 477 obligation to involve the full community of people (public and stakeholders) who may be 478 impacted by the research (Nawaz et al., 2022; Cooley et al., 2023). Therefore, addressing public 479 concernpublic outreach is important both before and during field deployments experimentation. 480 The deployment study site will determine the potential for community engagement. Coordinating 481 with local and/or regional organizations who are connected to relevant stakeholders (for

482 example, your local SeaGrant office if in the United States) will be helpful. For additional 483 discussion on social considerations of OAE field trials, see Satterfield et al. (2023, this 484 Guidevolume). 485 Collaboration and data/information sharing. Considering that the initial number of OAE field experiments will likely be small due to the inherent challenges to OAE field experiments (cost, 486 487 permitting, access, logistics, environmental safety), fostering interdisciplinary and collaborative 488 teams around field campaigns may will help ensure the greatest return on investment. Examples 489 of ways to foster collaboration include, For example, developing test-bedthe early announcement of field sites that are campaigns to open to open participation to external groups and foster 490 collaboration from diverse groups; making efforts to include groups who may not traditionally 491 492 have access to and/or the capacity for field campaigns, and ; including travel support in grant 493 applications to support external collaborators. Making concerted efforts to share information, 494 resources, and ideas will allows researchers to combine knowledge and resources in ways that 495 might not have been possible when working alone, thereby advancing OAE technology and 496 science at a faster pace. When publishing in peer-reviewed literature, uploading data to publicly 497 available data repositories and publishing in open access journals following best practices should be prioritized (JLiang et al., 2023, this Guide). 498 499 Inclusivity and transparency during OAE field trials are crucial to ensure that knowledge gained 500 is fed back into scientific and other communities efficiently, iteratively informing and refining 501 the next generation of experiments. Some f Field experiments will presumably mimic plans for 502 real world OAE deployments and therefore should should therefore be done in collaboration with relevant stakeholders across science, industry, policy, and society communities. To foster 503 504 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, 505 freely accessible platform for early and/or 'real-time' information sharing (i.e., before 506 507 publication) that can facilitate faster information exchange within the research community (e.g., 508 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 509 community (https://community.oceanvisions.org/dashboard). It may prove useful to designate 510 core working groups of experts in various aspects of CDR that investigate specific needs and 511

514	priority, rapidly evolving, and highly collaborative fields, greatly benefiting the scientific			
515	community at large (e.g., the Coral Restoration Consortium, https://www.crc.world/ - and			
516	associated working groups). Coordinating field trials with research groupcommunities			
517	conducting laboratory and mesocosm experiments, studying natural analogs, and undertaking			
518	modeling efforts will help strengthen the interpretation and extrapolation of results.			
519	4.1 Conclusion and /Recommendations			
520	Given that few OAE field studies have been conducted to date, there is much to learn from the			
521	earliest experiments with respect to experimental design, measurement and monitoring,			
522	deployment considerations, environmental impact, and more. Early experiments will only engage			
523	with a fraction of the temporal and spatial scales involved in full-scale operational OAE, and			
524	longer-term and larger-scale studies will become increasingly important to reveal scale-			
525	dependencies as the field develops. It is important that marine CDR research is hypothesis-			
526	driven, structured, deliberate, and well-planned to best inform future decision-making about			
527	OAE techniques and deployments. Careful consideration of the physical, chemical, and			
528	biological components of the study area will help inform the experimental approach. The use of			
529	baseline studies (both previous and contemporary to the OAE deployment) and controls will help			
530	to maximize signal-to-noise ratios and identify experimental effects. The timescale of OAE field			
531	experiments should not be underestimated, especially when considering permitting and the data			
532	needed to capture the baseline variability of in natural systems.			
533	Considering the urgent timeline required for humanity to meet our climate goals, field			
534	experiments need to move forward swiftly yet deliberately. To ensure the success of OAE,			
535	diverse perspectives from research, industry, policy, and society must converge, demanding			
536	transdisciplinary thinking and a commitment to open and transparent science. Central to this			
537	ambitious undertaking are the early field deployments experiments, results from which will			
538	ultimately determine the successes and failures of OAE projects and technologies.	/	Formatted: Font: Bold	
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539	4.2 Key recommendations for field experiments relevant to the research of ocean alkalinity	// / 	Formatted: Font: Bold	
540	<u>enhancement</u>		Formatted: Font: Bold	
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priorities and work to synthesize and share existing knowledge in the context of field

deployments experiments. This approach has been adopted by other scientific disciplines in high

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541 1. Ensure inclusivity and transparency (community engagement, data sharing, etc) for Formatted: List Paragraph, Numbered + Level: 1 + Numbering Style: 1, 2, 3, ... + Start at: 1 + Alignment: 542 all OAE trials field experiments —to both advance the field as quickly as possible, Left + Aligned at: 0.5" + Indent at: 0.75" 543 and to ensure the field progresses in a socially responsible manner. Formatted: Font: (Default) Times New Roman, 12 pt 544 —Assess the potential risks and benefits for any perturbation Formatted: Font: (Default) Times New Roman, 12 pt 2. . P—proceed according to the code of conduct and precautionary principles. 545 Formatted: Font: (Default) Times New Roman, 12 pt 3. Develop methods to track signal versus noise in highly variable environments, 546 Formatted: Font: (Default) Times New Roman, 12 pt Formatted: Font: (Default) Times New Roman, 12 pt 547 including robust baseline studies to characterize underlying variability (biological, chemical, physical), and the inclusion of controlled experiments such as chamber 548 incubations to isolate treatment effects. 549 Formatted: Font: Not Bold ?Consider logistical constraints and opportunities. 550 Formatted: Font: Not Bold 551 Formatted: List Paragraph, Numbered + Level: 1 + Numbering Style: 1, 2, 3, ... + Start at: 1 + Alignment: Left + Aligned at: 0.5" + Indent at: 0.75" 552 553 **Competing Interests** 554 The contact author has declared that none of the authors has any competing interests. 555 **Disclosure Statement** 556 LTB is scientific advisor to Submarine, a start-up service provider for monitoring, reporting, and \leftarrow Formatted: Line spacing: 1.5 lines 557 verification of marine CDR. TC is an advisor on the Carbon-to-Sea Initiative OAE Field Site 558 Steering Committee. 559 560 561 Acknowledgements This is a contribution to the "Guide for Best Practices on Ocean Alkalinity Enhancement 562 Research". We thank our funders the ClimateWorks Foundation and the Prince Albert II of 563 Monaco Foundation. Thanks are also due to the Villefranche Oceanographic Laboratory for 564 565 supporting the lead authors' meeting in January 2023. LTB was supported by the Australian Research Council through Future Fellowship (FT200100846) and by the Carbon-to-Sea 566 567 Initiative. 568 569 28 570

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