https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

Monitoring, Reporting, and Verification for Ocean Alkalinity Enhancement

David T. Ho[1], Laurent Bopp[2], Jaime Palter[3], Matthew C. Long[4], Philip Boyd[5], Griet Neukermans[6], Lennart Bach[5]

[1]Department of Oceanography, University of Hawai‘i at Mānoa, Honolulu, HI, 96822, USA
[2]Département de Géosciences, Ecole normale supérieure, 75005 Paris, France
[3]Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA
[4]Oceanography Section, Climate and Global Dynamics Laboratory, National Center for Atmospheric Research, Boulder, CO
[5]Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tasmania, Australia
[6]Department of Biology Ghent University, 9000 Gent, Belgium

Correspondence to: David T. Ho (ho@hawaii.edu)

Abstract. Monitoring, Reporting, and Verification (MRV) refers to the multistep process of monitoring the amount of greenhouse gas removed by a Carbon Dioxide Removal (CDR) activity and reporting the results of the monitoring to a third party. The third party then verifies the reporting of the results. While MRV is usually conducted in pursuit of certification in a voluntary or regulated CDR market, this chapter focuses on key recommendations for MRV relevant to ocean alkalinity enhancement (OAE) research. Early-stage MRV for OAE research may become the foundation on which markets are built. Therefore, we argue that such research carries a special obligation toward comprehensiveness, reproducibility, and transparency. Observational approaches during field trials should aim to quantify the delivery of alkalinity to seawater and monitor for secondary precipitation, biotic calcification, and other ecosystem changes that can feed back on sources or sinks of greenhouse gases where alkalinity is measurably elevated. Observations of resultant shifts in ocean pCO_2 and pH can help determine the efficacy of OAE and are amenable to autonomous monitoring. However, because the ocean is turbulent and energetic and CO_2 equilibration between the ocean and atmosphere can take several months or longer, added alkalinity will be diluted to perturbation levels undetectable above background variability on timescales relevant for MRV. Therefore, comprehensive quantification of carbon removal via OAE will be impossible through observational methods alone and numerical simulations will be required. The development of fit-for-purpose models, carefully validated against observational data, will be a critical part of MRV research.

1 What is MRV?

Monitoring, reporting, and verification (MRV) for ocean-based CDR mainly entails determining the amount of additional CO_2 removed from the atmosphere and the durability of that removal. Investment in CDR is motivated by an interest

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

in mitigating climate change, and so the value of a CDR purchase stems from its correspondence to genuine removal. MRV must therefore provide accurate estimates of net carbon removal and the uncertainty of those estimates. Delivering uncertainty estimates will enable markets to value carbon removal projects appropriately through the application of discount factors scaled in accordance with uncertainty.

Assessment of OAE effects on ecosystems are covered in Subhas et al., (2023, this volume) and Fennel et al. (2023, this volume) and will not be considered MRV in this chapter, unless they directly impact radiative forcing such as the fluxes of other greenhouse gases (e.g., CH_4, N_2O) or other climatically important trace gases (e.g., DMS), or they impact the efficiency of OAE (e.g., biogenic calcification). In the same vein, side benefits (e.g., increase in pH due to OAE) should also not be considered MRV. Finally, for the purpose of this chapter, we do not consider life cycle assessment (LCA), which might entail accounting for, e.g., CO_2 emissions from manufacturing, transportation, and deployment. While LCA is extremely important to quantify the net carbon removed by a CDR strategy, the focus of this chapter is on MRV following OAE deployment in the ocean.

MRV must deliver an assessment of three interrelated metrics:

1. Additionality: The net quantity of CO_2 removal above a counterfactual baseline after OAE has been conducted in the ocean.
2. Leakage: The amount over time of CO_2 that escapes removal or is otherwise emitted due to the CDR intervention. In the context of this chapter, we do not consider economic leakage (e.g., emissions from rock crushing), but do consider leakage to include phenomena such as precipitation-induced loss of alkalinity or a response in biogenic calcification that reduces alkalinity impacts
3. Durability: The average length of time over which CO_2 is sequestered from the atmosphere by a given deployment. OAE presents few concerns in the context of durability and leakage. OAE increases the ocean's buffer capacity and hence its ability to store CO_2 as DIC on timescales associated with alkalinity cycling in the ocean—which are on the order of 10^5 years (Middelburg et al. 2020). Therefore, in our assessment, storage durability does not require an explicit methodology for quantification, but rather we can assume that CO_2 removed via OAE will be stored for >1000 years.

Further, as highlighted above, effective MRV systems must deliver estimates of the uncertainty in these metrics. To quantify these metrics, MRV for OAE must provide quantitative assessments in the context of the following questions:

1. How much alkalinity was effectively added to seawater? The difficulty of answering this question depends on the technology used for OAE. For example, understanding the dissolution kinetics of mineral particulates is a requirement to quantify alkalinity additions for crushed-rock feedstocks, but much less of a concern for electrochemical techniques.
2. Has there been precipitation or biogenic feedback mitigating the alkalinity addition? Seawater is mostly above saturation in the surface ocean with respect to calcium carbonate, thus the addition of alkalinity has the potential to

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

induce precipitation of carbonate, which would reduce the OAE efficiency (i.e., mole DIC sequestered per mole TA added) but increase the storage durability because CO_2 stored as $CaCO_3$ is potentially locked away from the atmosphere for even longer than CO_2 converted to bicarbonate. Abiotic $CaCO_3$ (or $MgCO_3$) precipitation is very slow but increases exponentially when the saturation state increases. Such high saturation states can occur near alkalinity release sites. Furthermore, calcifying organisms in the ocean, such as coccolithophores, have the potential to respond to OAE by modifying their rate of growth or the relative amount of carbonate production. Finally, enhanced saturation states could also reduce surface ocean carbonate dissolution and therefore more effectively transfer alkalinity (in particulate form) from the surface ocean, thereby enhancing a natural alkalinity sink. Understanding these feedbacks of OAE via the calcium (magnesium) carbonate cycle is important for OAE MRV.

3. What is the ensuing perturbation to the air-sea exchange of CO_2 resulting from the OAE deployment? Alkalinity shifts carbonate equilibrium reactions away from aqueous CO_2, thereby generating a reduction in pCO_2; CDR occurs when the atmosphere equilibrates with the altered surface ocean via air-sea CO_2 exchange. A primary goal for MRV is to quantify this flux; notably, however, in many envisioned circumstances, the alkalinity addition will be entrained in the ocean flow, causing the OAE signal to be transported away from the injection site and potentially away from the sea surface; coupled with the fact that CO_2 gas equilibration occurs slowly, the ensuing air-sea flux perturbation will occur over large regions in space and time.

Observations alone are unlikely to provide a sufficient basis for assessing the net carbon removal accomplished by OAE deployments. MRV for OAE requires the development of quantitative estimates of air-sea CO_2 exchange. Since the ocean is constantly moving and because CO_2 takes a long-time to equilibrate across the air-sea interface, robust MRV would require intensive observation over large regions in space and time. High-quality carbon markets will require uncertainty bounds for net carbon removal estimates that would be prohibitively expensive to obtain via investment in direct observing over such scales, except, perhaps in targeted intensive research arrays. A further complication with observations is that assessments of net carbon removals associated with OAE deployments require quantification of air-to-sea CO_2 transfer relative to a counterfactual scenario: The air-sea CO_2 exchange that would have occurred in the absence of OAE intervention. Observing a counterfactual scenario is impossible in a strict sense, but it could be possible to use observations to assess counterfactual scenarios by leveraging analogs, such as different regions, or other statistical constructions, such as long-term climatological means.

In practice, identifying such analogs is a challenging task due to the heterogeneous nature of the ocean air-sea flux field, as well as the potential for OAE effects to spread over very large spatial and temporal scales. Notably, the background air-sea CO_2 flux field is highly dynamic on local to global scales. The ocean both absorbs and releases a massive amount of CO_2 each year; the net flux amounts to an uptake of about 10 Pg CO_2 yr^{-1}—but this net flux is a small residual of large gross fluxes (about ±330 Pg CO_2 yr^{-1}). OAE can stimulate either an increase in ocean CO_2 uptake or a reduction in CO_2 outgassing—either will constitute a net carbon removal. Geographic patterns of CO_2 ingassing and outgassing are controlled by the ocean's large-scale overturning circulation, mesoscale and submesoscale motions, variations in winds, storms, upwelling dynamics,

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

local inputs from rivers, or exchanges with sediments. Outside of the tropics, there is pronounced seasonal variability in air-sea CO_2 fluxes induced by the annual cycles of heating accompanied by phytoplankton blooms that draw down CO_2 in the surface ocean. All these dynamics are subject to variations in the climate and ocean circulation caused by internally fluctuating modes of variability or external forcing associated with CO_2 emissions and other human activities.

Given the complex nature of the ocean biogeochemical system, robust MRV for high-quality carbon removal markets will presumably depend on model-based approaches when quantifying net CO_2 removals. Ocean biogeochemical models (OBMs) will be a critical tool in this context (see Fennel et al., 2023). These models represent the physical, chemical, and biological processes affecting the distribution of carbon, alkalinity, and nutrients in the ocean. OBMs represent inorganic and organic carbon pools, alkalinity, and nutrients as "tracers" that have units of mass per volume (or mass) of seawater. OBMs are based on ocean general circulation models (OGCM) that represent the movement of tracers mediated by ocean circulation and mixing. Biogeochemical tracers, including DIC and TA, have sources and sinks from processes such as biologically-mediated production and remineralization of organic matter. Boundary fluxes for OBM tracers include riverine inputs, aeolian deposition, sediment-water exchange, and air-sea gas exchange. Fennel et al. (2023, this volume) provides an overview of the most relevant modeling tools for OAE research with high-level background information, illustrative examples, and references to more in-depth methodological descriptions and further examples.

2. Specificities of Ocean CDR for MRV

The natural ocean carbon cycle is extremely dynamic on a wide range of temporal and spatial scales, typically spanning more than 10 orders of magnitude. These scales range from that of the ocean skin, a thin layer of less than a millimeter in contact with the atmosphere where air-sea CO_2 exchange is controlled by molecular diffusion, to that of the global ocean circulation that typically transports dissolved carbon over more than a thousand years and 10,000 km. As such, the ocean represents a very challenging environment to carry out MRV. Three specific time scales are to be considered when discussing challenges for MRV of mCDR, and in particular OAE.

The first relates to natural variability in carbonate chemistry, especially pCO_2 and total alkalinity due to biological, chemical, and physical processes in the ocean. For example, using in situ observations from 37 stations spanning diverse ocean environments, Torres et al. (2021) showed that in the open ocean stations, the average seasonal cycle of pCO_2 was 49 ± 23 µatm, and that diurnal variability could also be as high as 47 ± 18 µatm. Temporal variability at coastal stations where OAE is likely to be deployed is significantly higher with seasonal variability in pCO_2 being 210 ± 76 µatm, and diurnal variability reaching 178 ± 82 µatm. OAE-induced changes in pCO_2 are likely to be lower than the range in natural variability, complicating MRV.

The second of these time scales relates to air-sea CO_2 equilibrium. This time scale is of particular relevance for OAE as it determines the time required from an alkalinity-driven shift in surface seawater carbonate equilibrium to a new air-sea CO_2 equilibrium and the resulting atmospheric carbon uptake. It is well established that the characteristic timescale for air-sea

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

exchange of CO_2 is of the order of 6 months (Sarmiento and Gruber, 2006). But Jones et al. (2014) have shown that this time scale is highly variable at the regional scale, ranging from less than a month to almost 2 years, with especially long values in the northern North Atlantic, the Atlantic subtropical gyres, and the Southern Ocean. This regional variability is explained by the dependency of the air-sea CO_2 equilibrium time scale on the gas transfer velocity, the depth of the mixed layer, and the initial carbonate chemistry of seawater. More precisely, this time scale is negatively correlated with the gas transfer velocity and Revelle buffer factor but positively correlated with the depth of the mixed layer and the ionization fraction (i.e., the ratio between DIC and dissolved CO_2).

The third of these time scales relates to ocean physical processes and alkalinity transport away from the injection location. First, horizontal currents, ranging from a few centimeters to a few meters per second have the potential to transport the OAE signal away from the initial injection site, and thus complicate MRV. A simple calculation using a mean flow of 0.5 m/s shows a potential transport of the alkalinity signal over a typical 6-month time more than 100 km away from the initial site. Second, vertical entrainment and mixing and/or other subduction processes might also transport the OAE signal to depth, potentially hindering atmospheric CO_2 uptake and associated MRV.

Lessons learned during Ocean Iron Fertilization (OIF) mesoscale in situ studies are applicable to MRV for OAE. Ocean circulation and mixing will cause a range of effects that are scale dependent and will influence MRV across a range of approaches from pilot studies (of a few km^2) to larger deployments (100 km^2 scale). This presupposes that elements of MRV will be needed at all spatial scales during the development and testing of an mCDR method.

Pilot studies following or tracking the perturbed area are often done in a controlled volume (e.g., within an eddy; Smetacek et al. 2012) or using a tracer such as SF_6 (e.g., Coale et al. 1996). For example, in the context of M (Measurement), the use of SF_6 in an OIF perturbation revealed a dynamic upper ocean in which perturbed waters were subducted under less dense waters in a few days leading to the termination of the study (Coale et al. 1998).

At larger spatial scales (>100 km^2), ocean physics imposes a strain and concurrent rotation of a perturbed patch of ocean leading to the perturbed patch of waters to 'grow' in areal extent from 100 km^2 to > 1000 km^2 via the entrainment of the surrounding 'control' seawater (Law et al., 2006). Such entrainment sets up concentration gradients into (in the case of OIF nutrients are resupplied to the nutrient-deplete patch) and out of (in the case of OIF, chlorophyll which has accumulated and iron which has been added) the perturbed waters. In the case of OIF, these represent major artifacts since the patch is transformed into a chemostat due to loss of chlorophyll and concurrent nutrient enrichment. Chemostats are used in phytoplankton lab cultures to maintain a steady state of biomass for months. The accumulation of phytoplankton within the patch never reaches the biomass threshold that leads to the onset of algal aggregation (Jackson, 1990) and the sinking of algal carbon into the ocean's interior (modeling study by Jackson et al. 2005). Thus even 1000 km^2 pilot OIF studies are prone to experimental artifacts and so do not represent the ocean C cycle. It is likely that OAE, which is based on chemical sequestration, will be less impacted by some of these physical effects than OIF which is the biological sequestration of C.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

3. Observation-based techniques for MRV and limitations

OAE depends on (at least) a two-stage process to achieve mCDR: First, the intervention raises ocean total alkalinity (TA) in order to lower seawater pCO_2, and then atmospheric CO_2 must equilibrate with the altered waters. This two-stage process points to many of the variables that would ideally be observed in an OAE MRV scheme, namely TA and pCO_2 at the ocean's surface and DIC throughout the perturbed volume. With extensive measurements of these variables along the Lagrangian pathway of a perturbed water mass, a carbon budget could theoretically be closed and CDR quantified for a given OAE deployment. Though appealing in its comprehensiveness, the reality of observing all of the parameters needed to quantitatively close a perturbed carbon budget and compare it against an unperturbed counterfactual is likely impossible in the near to medium-term, even in the context of highly-monitored field trials. The difficulty is inherent in the fact that the patch of water perturbed by the addition of TA is likely to be turbulently dispersed in the ocean and its signal diluted below the limit of detectability by mixing over the time scale required for CO_2 equilibration (He and Tyka, 2023; Mu et al., 2023; Wang et al., 2022).

This leads to the conclusion that MRV via direct observational approaches should not be expected to completely follow every molecule of additional CO_2 resulting from an OAE deployment - as doing so would set an insurmountable barrier to MRV. Instead, we outline what can feasibly be observed, what questions these observations can answer, and which questions are left to be addressed in statistical and/or prognostic models with their attendant uncertainties.

A variety of autonomous sensors hold promise to inform the results of an OAE deployment, both in field trials and for sampling that might offer constraints on open water applications and data for model validation and/or assimilation.

The most direct measurement relevant to OAE experiments is TA, which would reveal if the initially planned perturbation were successful. Though autonomous sensors for TA have been in development for several years (Briggs et al., 2017), they are not commercially available at the time of writing, and the laboratory analysis of bottle samples cannot currently be replaced or even supplemented by sensor-based measurements (see Albright et al., 2023, this volume).

In contrast, to determine the ocean uptake of CO_2, there are effective sensors capable of measuring $p$$CO_2$ with a nominal accuracy of 2 μatm, although they are restricted to the upper ocean (~50 m). This is potentially important because while it is difficult to detect changes in the carbon inventory of the ocean with measurements of DIC, it can be done with measurements of $p$$CO_2$ (Wanninkhof et al. 2013). These can be deployed on moorings (MAPCO2, ProCV) and autonomous surface vehicles like Wave Glider (ASVCO2) (Chavez et al., 2018) and Saildrone (Sabine et al. 2020). These sensors have the advantage of being able to collect measurements continuously in harsh weather and sea state with little involvement of a skilled analyst. The MAPCO2 and ASVCO2 were designed at NOAA-PMEL and there are also SAMI and ProOceanus systems (see Albright et al., 2023, this volume, for more details).

Another MRV-relevant aspect of OAE that is well suited for sensor measurements is the reduction of OAE efficiency via OAE-induced precipitation of carbonates (see Schulz et al., 2023, this volume for further context). For example, marine calcifiers, such as coccolithophores, may proliferate under high alkalinity and pH conditions, thus reducing OAE efficiency

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

(Bach et al., 2019). Autonomous optical sensors for coccolithophore particulate inorganic carbon (PIC) based on the intrinsic birefringence of calcite have also been in development for several decades by Bishop et al. (2009, 2022). Since the deployment of the first prototype in 2003, the optical PIC sensor was re-engineered several times and the most recent versions require further re-engineering to correct for thermal and pressure effects, as well as misalignment effect of the linear polarizers (Bishop et al., 2022). A new autonomous PIC measurement concept was recently proposed by Neukermans and Fournier (2022) which is expected to overcome the aforementioned issues. PIC sensors are currently under development and are designed to operate on autonomous platforms operating in the epi- and mesopelagic ocean, such as profiling floats and buoys, in open ocean environments to cover a PIC concentration range of 0.5 to 500 μgC L^{-1} (Neukermans et al., 2023), enabling careful monitoring of coccolithophore PIC.

Wind speed is the most common correlate for air-sea gas exchange. Since gas transfer velocities as a function of wind speed differ between the open and coastal oceans, depending on the OAE deployment location, $^3He/SF_6$ tracer release experiments might have to be performed to determine this relationship (e.g., Wanninkhof et al., 1993). The tracer data will also be useful for calibrating and validating models that will most likely be used to determine the efficiency and efficacy of CO_2 equilibration.

4. Model-based techniques for MRV and limitations

OBMs can be used to explicitly represent the effects of OAE by conducting numerical experiments in which the model is provided with forcing data that represents alkalinity additions. Currently, fit-for-purpose models are not available, and developing such models in the region/scale of OAE deployment should be a priority to enable function frameworks for MRV.

A model integrated forward in time with the alkalinity additions will simulate the transport of the associated mass of alkalinity and its ensuing effect on biogeochemical processes, including gas exchange. These simulations can be used to evaluate net carbon removal by comparing integrations that include the OAE signal to others in which that forcing is not present — i.e., the baseline counterfactual condition or "control." If an ensemble of integrations is performed, the variation of net carbon removal across the ensemble can be used to assess uncertainty. Explicit simulation of OAE deployments can be compared to observations, including measurements from background observing systems, as well as bespoke data collection efforts associated with the OAE project. In some cases, explicit data assimilation procedures may be applied (see Fennel et al., 2023, this volume), thereby potentially improving confidence in the model simulations and providing a means of both reducing and quantifying uncertainty.

4.1 Adding alkalinity to models

In order for the effects of OAE to be properly simulated, models must be supplied with the correct amount of alkalinity applied as forcing. Alkalinity additions are likely to occur on scales that are much smaller than the ensuing anomaly generated

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

in air-sea CO_2 exchange. For this reason, MRV frameworks must invoke a separation of concerns, wherein near-field processes are treated differently than the broader regional effects. Explicit modeling of near-field dynamics is likely to require different modeling frameworks than those simulating the full expression of the OAE effects in the ocean—however, it is not necessarily a requirement to simulate near-field dynamics in the context of MRV. Near-field processes must be constrained by direct observations and/or their dynamics must be accurately captured in verified parameterizations applied to models too coarse to simulate the local effects explicitly. Notably, different OAE technologies and feedstocks present different challenges in this regard. Electrochemical techniques, which might produce, for instance, an alkalinity-enhanced stream from an outfall pipe, are different from crushed-rock particulates where dissolution kinetics come into play. Moreover, as discussed in Fennel et al. (2023, this volume), ancillary constituents associated with rock-derived feedstocks may induce biological responses with impacts on the total efficacy of the OAE process.

4.2 Representing OAE effects

In order to provide a suitable basis for MRV applied to OAE deployments, models must meet several requirements in addition to providing a sufficiently accurate representation of alkalinity additions. First, models must provide a reasonable representation of ocean circulation and mixing; these processes are critical to determining the residence time of added alkalinity in the surface mixed layer, where gas exchange with the atmosphere is possible. Given that the equilibration time scale for CO_2 via gas exchange is long, the residence time of alkalinity enhanced water parcels at the ocean surface is likely a primary control on the efficiency of uptake (He & Tyka, 2022). Second, the models must accurately capture the surface ocean $p\mathrm{CO_2}$ anomaly induced by alkalinity additions. This implies having a correct representation of the carbon system thermodynamics (see Fennel et al., 2023, this volume). Further, since the change in $p\mathrm{CO_2}$ depends on the background DIC:TA ratio (Hinrichs et al. 2023), it is important that the model has a good representation of the mean state prior to perturbation. Third, presuming an accurate representation of the change in $p\mathrm{CO_2}$ and the transport of alkalinity following injection, the model must be able to simulate the gas transfer of CO_2 with sufficient accuracy. Notably, the gas exchange velocity is highly uncertain, particularly in coastal environments where many OAE deployments are likely to occur. If surface water residence times are much longer than the gas equilibration timescale, uncertainty in the gas exchange velocity may not contribute substantially to the overall uncertainty—but in intermediate regimes where the two timescales are comparable, uncertainty in the gas exchange velocity may be an important consideration. Finally, a comprehensive assessment of OAE efficacy will depend on accurate characterization of feedback in the biological system. If there are changes in the natural distribution of calcification or organic carbon export, this "leakage" term should be quantified—or its potential magnitude and impact on overall carbon transfer assessed as a component of the uncertainty budget. At present, further empirical research is required to enable modeling systems to treat this aspect of OAE effects robustly.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

4.3 Defining the baseline counterfactual

Identifying an appropriate framework to define counterfactual scenarios involves somewhat nuanced judgment and depends on knowledge of the nature of OAE-induced feedback. In the simplest case, it may be possible to ignore feedback between OAE and the ocean's physical state, including patterns in circulation and mixing. In the absence of physical feedback, the control state would have identical circulation dynamics (at least in a statistical sense). It is important to understand, therefore, whether there is feedback between OAE and the ocean's physical state.

Some potential mechanisms for such feedback are easy to imagine. For example, if OAE changes the distribution of primary productivity and hence the amount of chlorophyll in the surface ocean, this may alter ocean temperatures owing to the role chlorophyll plays in absorbing heat from sunlight. If the resulting differences in ocean temperature are large, ocean circulation could be affected. The likelihood of a substantially altered circulation is probably low, in part based on the results of an idealized modeling study in which all chlorophyll was artificially removed to explore the impact of the resulting optical changes on the ocean's circulation (Oschlies, 2004; Anderson et al., 2007). The no-chlorophyll simulations showed fascinating dynamical changes (including a stronger El Niño) but not a radically different ocean circulation (Anderson et al., 2007). With the much smaller expected perturbation to ocean optics from calcifiers and PIC due to OAE influence on ocean ecosystems, we anticipate dynamical changes would be small enough to neglect when comparing OAE-perturbation to control simulations. A recommendation for future MRV research is to explore circulation feedbacks related to OAE optical changes in targeted modeling studies, across structurally-different ecosystem models and spatial scales, so we can either dispense with this concern or fold it into future uncertainty quantification.

5. The way forward on OAE MRV

Early-stage MRV research for OAE may become the foundation on which regulated markets are built. Therefore, such research carries a special obligation toward comprehensiveness, reproducibility, and transparency. To fulfill these obligations, best practices include the following:

- Field trials should be co-designed with modelers and observationalists to enable the iterative process of model validation and improvement and dynamically-informed data interpretation. In some scenarios, co-design may entail the development of formal Observing System Simulation Experiments and data-assimilating state estimates.
- MRV techniques and results should be well-documented and archived publicly and promptly, without restriction. Ideally, a central registry of OAE experiments would adhere to FAIR (Findable, Accessible, Interoperable, and Reproducible) data standards (Wilkinson et al. 2016). Researchers should eschew any practice that withholds MRV innovation from the community to "build a moat" in support of a commercial mCDR approach.
- Early field trials are recommended to be as comprehensive as possible, monitoring for both obvious, first-order risks like secondary precipitation and more remote tail risks like alterations to export production via shifts in phytoplankton community structure and mineral ballasting.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

- Model validation against observations should be tailored to the key processes in question. Fennel et al. (2023, this volume) argues that models may be used for a long list of purposes, including, for example, simulating ecosystem effects and sediment-water exchanges. Early MRV efforts can expose model skill and deficiencies in simulating these processes if the relevant observations are prioritized.
- An uncertainty budget should be quantified that includes both known uncertainties (e.g. measurement and mapping errors) and expert estimates of presently unmeasurable risks. An honest assessment of the poorly constrained uncertainties will point to key research areas in the future.

For MRV of OAE deployments, the initial increase in alkalinity should be monitored (i.e., both measured and modeled). If the enhancement is done via the dissolution of pulverized rocks, baseline alkalinity measurements should be made so that the range of concentration within its natural variability is known before the deployment of minerals. Furthermore, the dissolution rate needs to be known under in situ conditions. Knowledge of this rate includes the dependency on various factors such as temperature, salinity, etc. but also to what extent minerals become buried in sediments and how this change in exposure affects dissolution. If the enhancement is done via electrochemistry, the dosing rate of the solution (e.g., $Mg(OH)_2$, NaOH) and the precise amount of added alkalinity need to be determined.

Furthermore, any potential secondary precipitation caused by the alkalinity enhancement (e.g., if alkalinity is added too quickly, brucite precipitation could occur) should be monitored. Monitoring of secondary precipitation is particularly critical in the non-equilibrated state (i.e., before atmospheric CO_2 influx has occurred) and when the alkalinity-perturbed patch is in close contact with sediments since the risk for secondary precipitation is particularly high under these circumstances (see Chapter 2).

Finally, the drawdown of pCO_2 in the ocean due to alkalinity addition should be measured. Given the potential natural variability in pCO_2, especially in coastal regions, monitoring of pCO_2 should be done before the OAE deployment. Considering the spatial- and time-scales discussed above, these measurements will need to be complemented by modeling approaches.

MRV of CO_2 influx after the application of OAE will likely depend on fit-for-purpose modeling (see Fennel et al., 2023, this volume). Exceptions to this may apply if the deployment is made in an enclosed area where the water is confined, or the deployment is made in a heavily instrumented and surveyed area of the ocean. Models used to constrain atmospheric CO_2 influx will need to be calibrated and validated with observations. Since CO_2 influx is due to physical and chemical processes, the following observational data to improve the modeling framework includes (but is not restricted to): observations of ocean currents from ADCPs, Lagrangian floats or tracers, and remote sensing; observations of air-sea gas exchange from $^3He/SF_6$ tracer release experiments; temperature and salinity profile measurements; and measurements of carbonate chemistry parameters.

While it appears that OBMs will ultimately provide a critical foundation for robust ocean MRV frameworks, they are not currently ready to serve in this capacity. These models represent complicated systems; Ocean General Circulation Models (OGCMs) are based on fundamental governing equations, but solving these equations numerically requires approximations. Ocean ecosystems comprise diverse groups of organisms with differing physiological capacities and complex interactions.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

There are no generally-accepted governing equations for these systems; rather models are built on the basis of empirically-determined relationships and theory or hypothesis. For OBMs to provide a credible basis to support ocean MRV, they must be based on broadly accepted theory or well-constrained parameterizations and they must be explicitly validated relative to the quantification of gas exchange anomalies arising as a result of perturbations in alkalinity. Models have not yet been robustly validated in the context of these explicit requirements.

We note that at this point we have yet to develop the best modeling tools for OAE MRV (and likely MRV for mCDR in general). A rigorous research and development program to establish OBMs as fit-for-purpose, credible tools for MRV is needed. However, there is currently a major problem with basing MRV on models. OBMs are run on high-performance computing architectures and because they are big calculations, they are very computationally expensive. It is unlikely that technological innovation will dramatically reduce this computational cost in the next 5-10 years, during which time we are required to deliver a functional framework for MRV. Therefore, while models are required for MRV, we first need to establish that models can provide credible representations of key CDR processes. We can then leverage these models to generate datasets from which to derive robust statistical approximations, including through the application of techniques derived from AI and machine learning. For instance, well-calibrated models could be used to produce training data for machine learning algorithms to predict the CDR efficiency of OAE deployments in different locations at different times, i.e. as a function of initial environmental conditions such as water temperature, carbonate chemistry, mixed layer depth such as suggested in Bach et al. (2023).

Conducting explicit OAE modeling experiments coupled with field trials are important research milestones necessary to identify the long-term approach to robust MRV. It is likely that the models to effectively support field trials will use regional OGCMs that are capable of high-fidelity simulations of ocean flows at scales commensurate with those driving the initial dispersion of OAE signal on timescales of weeks to months. Beyond this initial period, the OAE signals are likely to be diluted and less easily tracked with observations. Critically, it is important to demonstrate that the models provide simulations that are consistent with the observations.

Models that compare well to observations can be deemed credible for assessing OAE effects. However, fully-explicit mechanistic calculations are computationally intensive and thus unlikely to provide a scalable framework for conducting MRV under the scenario of widespread OAE deployments. On this basis, it is important that research on OAE field trials aim toward building trust in models to develop approaches to MRV that can be accomplished at a reduced computational cost.

Competing interests

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

Acknowledgments

This is a contribution to the "Guide for Best Practices on Ocean Alkalinity Enhancement Research". We thank our funders the ClimateWorks Foundation and the Prince Albert II of Monaco Foundation. Thanks are also due to the Villefranche Oceanographic Laboratory for supporting the lead authors' meeting in January 2023.

References

Anderson, W. G., Gnanadesikan, A., Hallberg, R., Dunne, J., & Samuels, B. L. (2007). Impact of ocean color on the maintenance of the Pacific Cold Tongue. 34(11). https://doi.org/https://doi.org/10.1029/2007GL030100.

Bach, L. T., S. J. Gill, R. E. M. Rickaby, S. Gore, and P. Renforth (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), https://doi.org/10.3389/fclim.2019.00007.

Bach, L. T., D. T. Ho, P. W. Boyd, and M. D. Tyka (2023), Toward a consensus framework to evaluate air–sea CO_2 equilibration for marine CO_2 removal, https://doi.org/10.1002/lol2.10330.

Bishop, J., 2009. Autonomous Observations of the Ocean Biological Carbon Pump. Oceanography 22, 182–193. https://doi.org/10.5670/oceanog.2009.48.

Bishop, J. K. B., V. J. Amaral, P. J. Lam, T. J. Wood, J.-M. Lee, A. Laubach, A. Barnard, A. Derr, and C. Orrico (2022), Transmitted Cross-Polarized Light Detection of Particulate Inorganic Carbon Concentrations and Fluxes in the Ocean Water Column: Ships to ARGO Floats, Frontiers in Remote Sensing, 3, https://doi.org/10.3389/frsen.2022.837938.

Briggs, E. M., S. Sandoval, A. Erten, Y. Takeshita, A. C. Kummel, and T. R. Martz (2017), Solid State Sensor for Simultaneous Measurement of Total Alkalinity and pH of Seawater, ACS Sensors, 2(9), 1302-1309, https://doi.org/10.1021/acssensors.7b00305.

Coale, K. H., K. S. Johnson, S. E. Fitzwater, R. M. Gordon, S. Tanner, F. P. Chavez, L. Ferioli, C. Sakamoto, P. Rogers, F. Millero, P. Steinberg, P. Nightingale, D. Cooper, W. P. Cochlan, M. R. Landry, J. Constantinou, G. Rollwagen, A. Trasvina, and R. Kudela (1996), A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, Nature, 383(6600), 495-501, https://doi.org/10.1038/383495a0.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

Chavez, F. P., J. Sevadjian, C. Wahl, J. Friederich, and G. E. Friederich (2018), Measurements of pCO_2 and pH from an autonomous surface vehicle in a coastal upwelling system, Deep Sea Res. II, 151, 137-146, https://doi.org/10.1016/j.dsr2.2017.01.001.

Coale, K. H., K. S. Johnson, S. E. Fitzwater, S. P. G. Blain, T. P. Stanton, and T. L. Coley (1998), IronEx-I, an in situ iron-enrichment experiment: Experimental design, implementation and results, Deep Sea Res. II, 45(6), 919-945, https://doi.org/10.1016/S0967-0645(98)00019-8.

He, J., and M. D. Tyka (2023), Limits and CO_2 equilibration of near-coast alkalinity enhancement, Biogeosciences, 20(1), 27-43, https://doi.org/10.5194/bg-20-27-2023.

Hinrichs, C., Köhler, P., Völker, C., & Hauck, J. (2023). Alkalinity biases in CMIP6 Earth System Models and implications for simulated CO_2 drawdown via artificial alkalinity enhancement. Biogeosciences Discuss., 2023, 1-21. https://doi.org/10.5194/bg-2023-26.

Jackson, G. A. (1990), A model of the formation of marine algal flocs by physical coagulation processes, Deep Sea Research Part A. Oceanographic Research Papers, 37(8), 1197-1211, https://doi.org/10.1016/0198-0149(90)90038-W.

Jackson, G. A., A. M. Waite, and P. W. Boyd (2005), Role of algal aggregation in vertical carbon export during SOIREE and in other low biomass environments, Geophys. Res. Lett., 32(13), https://doi.org/10.1029/2005GL023180.

Jones, D. C., T. Ito, Y. Takano, and W.-C. Hsu (2014), Spatial and seasonal variability of the air-sea equilibration timescale of carbon dioxide, Glob. Biogeochem. Cycle, 28(11), 1163-1178, https://doi.org/10.1002/2014GB004813.

Law, C. S., W. R. Crawford, M. J. Smith, P. W. Boyd, C. S. Wong, Y. Nojiri, M. Robert, E. R. Abraham, W. K. Johnson, V. Forsland, and M. Arychuk (2006), Patch evolution and the biogeochemical impact of entrainment during an iron fertilisation experiment in the sub-Arctic Pacific, Deep Sea Res. II, 53(20), 2012-2033, https://doi.org/10.1016/j.dsr2.2006.05.028.

Middelburg, J. J., Soetaert, K., & Hagens, M. (2020). Ocean Alkalinity, Buffering and Biogeochemical Processes. 58(3), e2019RG000681. https://doi.org/10.1029/2019RG000681

Mu, L., J. B. Palter, and H. Wang (2023), Considerations for hypothetical carbon dioxide removal via alkalinity addition in the Amazon River watershed, Biogeosciences, 20(10), 1963-1977, https://doi.org/10.5194/bg-20-1963-2023.

Neukermans, G., L.T. Bach, A. Butterley, Q. Sun, H. Claustre, and G. R. Fournier (2023), Quantitative and mechanistic understanding of the open ocean carbonate pump - perspectives for remote sensing and autonomous in situ observation, Earth-Science Reviews, 239, 104359, https://doi.org/10.1016/j.earscirev.2023.104359.

Neukermans, G. and G. R. Fournier (2022), A method to produce a matched pair of polarizing filters and a method and apparatus to determine the concentration of birefringent particles using a pair of polarizing filters, International Patent WO/2022/002939.

Sabine, C., A. Sutton, K. McCabe, N. Lawrence-Slavas, S. Alin, R. Feely, R. Jenkins, S. Maenner, C. Meinig, J. Thomas, E. van Ooijen, A. Passmore, and B. Tilbrook (2020), Evaluation of a New Carbon Dioxide System for Autonomous Surface Vehicles, J. Atmos. Oceanic Tech., 37(8), 1305-1317, https://doi.org/10.1175/JTECH-D-20-0010.1.

Sarmiento, J. L., and N. Gruber (2006), Ocean Biogeochemical Dynamics, Princeton University Press, https://doi.org/10.2307/j.ctt3fgxqx.

Smetacek, V., C. Klaas, V. H. Strass, P. Assmy, M. Montresor, B. Cisewski, N. Savoye, A. Webb, F. d'Ovidio, J. M. Arrieta, U. Bathmann, R. Bellerby, G. M. Berg, P. Croot, S. Gonzalez, J. Henjes, G. J. Herndl, L. J. Hoffmann, H. Leach, M. Losch, M. M. Mills, C. Neill, I. Peeken, R. Röttgers, O. Sachs, E. Sauter, M. M. Schmidt, J. Schwarz, A. Terbrüggen, and D. Wolf-Gladrow (2012), Deep carbon export from a Southern Ocean iron-fertilized diatom bloom, Nature, 487(7407), 313-319, https://doi.org/10.1038/nature11229.

Torres, O., L. Kwiatkowski, A.J. Sutton, N. Dorey, and J.C. Orr (2021) Characterising mean and extreme diurnal variability of ocean CO_2 system variables across marine environments, Geophysical Research Letters, e2020GL090228, https://doi.org/10.1029/2020GL090228,

Wang, H., D. J. Pilcher, K. A. Kearney, J. N. Cross, O. M. Shugart, M. D. Eisaman, and B. R. Carter (2023), Simulated Impact of Ocean Alkalinity Enhancement on Atmospheric CO_2 Removal in the Bering Sea, Earth's Future, 11(1), e2022EF002816, https://doi.org/10.1029/2022EF002816.

Wanninkhof, R., W. Asher, R. Weppernig, H. Chen, P. Schlosser, C. Langdon, and R. Sambrotto (1993), Gas transfer experiment on Georges Bank using two volatile deliberate tracers, J. Geophys. Res., 98, 20237-20248, https://doi.org/10.1029/93JC01844.

https://doi.org/10.5194/sp-2023-2
Preprint. Discussion started: 14 June 2023

Wanninkhof, R., Park, G.-H., Takahashi, T., Feely, R. A., Bullister, J. L., & Doney, S. C. (2013). Changes in deep-water CO_2 concentrations over the last several decades determined from discrete pCO_2 measurements. Deep Sea Research Part I: Oceanographic Research Papers, 74, 48-63. https://doi.org/https://doi.org/10.1016/j.dsr.2012.12.005

Wilkinson, M. D., M. Dumontier, I. J. Aalbersberg, G. Appleton, M. Axton, A. Baak, N. Blomberg, J.-W. Boiten, L. B. da Silva Santos, P. E. Bourne, J. Bouwman, A. J. Brookes, T. Clark, M. Crosas, I. Dillo, O. Dumon, S. Edmunds, C. T. Evelo, R. Finkers, A. Gonzalez-Beltran, A. J. G. Gray, P. Groth, C. Goble, J. S. Grethe, J. Heringa, P. A. C. 't Hoen, R. Hooft, T. Kuhn, R. Kok, J. Kok, S. J. Lusher, M. E. Martone, A. Mons, A. L. Packer, B. Persson, P. Rocca-Serra, M. Roos, R. van Schaik, S.-A. Sansone, E. Schultes, T. Sengstag, T. Slater, G. Strawn, M. A. Swertz, M. Thompson, J. van der Lei, E. van Mulligen, J. Velterop, A. Waagmeester, P. Wittenburg, K. Wolstencroft, J. Zhao, and B. Mons (2016), The FAIR Guiding Principles for scientific data management and stewardship, Scientific Data, 3(1), 160018, https://doi.org/10.1038/sdata.2016.18.