

# 1 **Monitoring, Reporting, and Verification for Ocean Alkalinity**

## 2 **Enhancement**

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14 **Abstract.** Monitoring, reporting, and verification (MRV) refers to the multistep process of monitoring the amount of  
15 greenhouse gas removed by a carbon dioxide removal (CDR) activity and reporting the results of the monitoring to a third  
16 party. The third party then verifies the reporting of the results. While MRV is usually conducted in pursuit of certification in a  
17 voluntary or regulated CDR market, this chapter focuses on key recommendations for MRV relevant to ocean alkalinity  
18 enhancement (OAE) research. Early-stage MRV for OAE research may become the foundation on which markets are built.  
19 Therefore, such research carries a special obligation toward comprehensiveness, reproducibility, and transparency.  
20 Observational approaches during field trials should aim to quantify the delivery of alkalinity to seawater and monitor for  
21 secondary precipitation, biotic calcification, and other ecosystem changes that can feed back on sources or sinks of greenhouse  
22 gases where alkalinity is measurably elevated. Observations of resultant shifts in the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) and ocean  
23 pH can help determine the efficacy of OAE and are amenable to autonomous monitoring. However, because the ocean is  
24 turbulent and energetic and CO<sub>2</sub> equilibration between the ocean and atmosphere can take several months or longer, added  
25 alkalinity will be diluted to perturbation levels undetectable above background variability on timescales relevant for MRV.  
26 Therefore, comprehensive quantification of carbon removal via OAE will be impossible through observational methods alone,  
27 and numerical simulations will be required. The development of fit-for-purpose models, carefully validated against  
28 observational data, will be a critical part of MRV for OAE.

## 29 **1 What is MRV?**

30 In this chapter, we consider monitoring, reporting, and verification (MRV) for marine CDR (mCDR), confining our  
31 focus to determining the amount of additional CO<sub>2</sub> removed from the atmosphere and the durability of that removal. Investment  
32 in CDR is motivated by an interest in mitigating climate change, so the value of a CDR purchase stems from its correspondence  
33 to genuine removal (Smith et al., 2023). MRV must, therefore, provide estimates of net carbon removal and the uncertainty of  
34 those estimates (Palter et al., 2023). Delivering uncertainty estimates will enable markets to value carbon removal projects  
35 appropriately by applying discount factors scaled in accordance with uncertainty (Carbon Direct and Microsoft, 2023).

36 While we recognize the importance of determining ecosystem impacts of OAE deployments, assessment of OAE  
37 effects on ecosystems are covered in Eisaman et al. (2023, this Guide), Iglesias-Rodríguez et al. (2023, this Guide), Riebesell  
38 et al. (2023, this Guide), and Fennel et al. (2023, this Guide) and will not be considered MRV in this guide, unless they impact  
39 the efficiency of OAE (e.g., biogenic calcification). In addition to monitoring carbonate chemistry parameters for MRV  
40 (discussed below), assessing ecosystem impacts would require monitoring other biogeochemical, environmental, or ecological  
41 changes that may arise from OAE application, such as changes in nutrient fluxes, particulate loading, and phytoplankton  
42 community structure. In the same vein, side benefits (e.g., an increase in pH due to OAE) are also not considered MRV for  
43 this contribution. Finally, for this guide, we do not consider life cycle assessment (LCA), which might entail accounting for,  
44 e.g., CO<sub>2</sub> emissions from manufacturing, transportation, and deployment. While LCA is extremely important for quantifying  
45 the net carbon removed by a CDR strategy, this contribution focuses on MRV following OAE deployment in the ocean.

46 To determine the amount and duration of CO<sub>2</sub> removal, MRV must deliver an assessment of two interrelated metrics:

- 47 1. **Additionality:** The net quantity of CO<sub>2</sub> removal above a counterfactual baseline after OAE has been conducted in the  
48 ocean. Additionality should include assessments of phenomena such as precipitation-induced loss of alkalinity or a  
49 response in biogenic calcification that could reduce the ability of alkalinity addition to induce CDR.
- 50 2. **Durability:** The average time over which CO<sub>2</sub> is sequestered from the atmosphere by a given deployment. In our  
51 assessment, OAE minimizes concerns in the context of durability as OAE increases the ocean's buffer capacity and  
52 hence its ability to store CO<sub>2</sub> as dissolved inorganic carbon (DIC) on timescales associated with alkalinity cycling in  
53 the ocean— with residence time far exceeding 10<sup>3</sup> years (Middelburg et al., 2020). Therefore, in our assessment,  
54 storage durability does not require an explicit methodology for quantification, but rather, we can assume that CO<sub>2</sub>  
55 removed via OAE will be stored mainly as bicarbonate (HCO<sub>3</sub><sup>-</sup>) for > 10<sup>3</sup> years. For CDR, the depth of where  
56 atmospheric CO<sub>2</sub> is stored in the oceans matters when it is stored as dissolved CO<sub>2</sub> (as is the case for macroalgae  
57 cultivation or iron fertilization). However, in the case of OAE, CO<sub>2</sub> is stored mainly as HCO<sub>3</sub><sup>-</sup>, which cannot be  
58 exchanged with the atmosphere, so surface ocean storage is chemically safe. Keeping alkalinity (and thus HCO<sub>3</sub><sup>-</sup>) in  
59 the surface ocean has benefits for ocean acidification, although these are very minor and heavily depend on whether  
60 alkalinity-enhanced seawater has been equilibrated with atmospheric CO<sub>2</sub> (see Fig. 3 in Bach et al., 2019).

61 Furthermore, retaining alkalinity ( $\text{HCO}_3^-$ ) in the surface ocean can enhance durability by limiting interactions with  
62 sediments and thus avoiding substantial loss terms to OAE, such as the risk of inducing secondary  $\text{CaCO}_3$   
63 precipitation in sediments and the reduction of natural alkalinity release (Fuhr et al., 2022; Moras et al., 2022; Bach,  
64 2023; Hartmann et al., 2023). We acknowledge that there are also loss terms to alkalinity ( $\text{HCO}_3^-$ ) in the surface  
65 ocean, such as the induction of biotic calcification. However, there is currently no reason to assume the deep ocean  
66 is a much safer place to store atmospheric  $\text{CO}_2$  as  $\text{HCO}_3^-$ .

67  
68 Further, as highlighted above, effective MRV systems must deliver estimates of the uncertainty in these metrics. To  
69 quantify these metrics, MRV for OAE must provide quantitative assessments in the context of the following questions:

- 70 1. How much alkalinity was effectively added to seawater? The difficulty of answering this question depends on the  
71 technology used for OAE. For example, understanding the dissolution kinetics of mineral particulates is a requirement  
72 to quantify alkalinity additions for crushed-rock feedstocks, but much less of a concern for electrochemical techniques  
73 and alkalinity added in dissolved form.
- 74 2. Has there been precipitation or biogenic feedback changing the efficacy of the alkalinity addition? Seawater is mostly  
75 above saturation in the surface ocean with respect to calcium carbonate; thus, the addition of alkalinity has the  
76 potential to induce precipitation of carbonate minerals (Moras et al., 2022), which would reduce the OAE efficiency  
77 (i.e., mole of DIC sequestered per mole of TA added). Abiotic  $\text{CaCO}_3$  (or  $\text{MgCO}_3$ ) precipitation is very slow but  
78 increases when the saturation state increases. Such high saturation states can occur near alkalinity release sites.  
79 Furthermore, calcifying organisms in the ocean, such as coccolithophores, can respond to OAE by modifying their  
80 growth rate or the relative amount of carbonate mineral production (Bach et al., 2019). Finally, enhanced saturation  
81 states could also reduce natural carbonate dissolution; this may have the effect of more effectively transferring  
82 alkalinity (in particulate form) from the surface ocean to depth or changing natural alkalinity sources from sediments  
83 or coastlines (Bach, 2023). Understanding these feedbacks of OAE via the calcium (magnesium) carbonate cycle is  
84 important for OAE MRV.
- 85 3. What is the ensuing perturbation to the air-sea exchange of  $\text{CO}_2$  resulting from the OAE deployment? Alkalinity shifts  
86 carbonate equilibrium reactions away from aqueous  $\text{CO}_2$ , thereby reducing seawater  $p\text{CO}_2$ ; CDR occurs when the  
87 atmosphere equilibrates with the altered surface ocean via air-sea  $\text{CO}_2$  exchange. A primary goal for MRV is to  
88 quantify this perturbation flux; notably, however, in many envisioned circumstances, the alkalinity addition will be  
89 entrained in the ocean flow, causing the OAE signal to be transported away from the injection site and potentially  
90 away from the sea surface; coupled with the fact that  $\text{CO}_2$  gas equilibration occurs slowly (Jones et al., 2014), the  
91 ensuing air-sea flux perturbation will occur over large regions in space and time.

92  
93 In our assessment, observations alone are unlikely to provide a sufficient basis for quantifying the net carbon removal  
94 accomplished by OAE deployments. MRV for OAE requires the development of quantitative estimates of air-sea  $\text{CO}_2$

95 exchange. Since the ocean is constantly moving and because CO<sub>2</sub> takes a long time to equilibrate across the air-sea interface,  
96 robust MRV would require intensive observations over large regions in space and time. High-quality carbon markets will  
97 require uncertainty bounds for net carbon removal estimates that would be prohibitively expensive to obtain via investment in  
98 direct observing over such scales, except, perhaps in targeted intensive observational arrays. A further complication with  
99 observations is that assessments of net carbon removals associated with OAE deployments require quantifying air-sea CO<sub>2</sub>  
00 flux relative to a counterfactual scenario: The air-sea CO<sub>2</sub> exchange that would have occurred without OAE intervention.  
01 Observing a counterfactual scenario is impossible in a strict sense, but it could be possible to use observations to assess  
02 counterfactual scenarios by leveraging analogs, such as nearby unperturbed regions, or statistical constructions, such as  
03 predicted seawater *p*CO<sub>2</sub> from empirical models built from historical observations of the carbon system and predictor variables  
04 like temperature, mixed layer depth, and chlorophyll (e.g., Landschützer et al., 2020; Rödenbeck et al., 2022; Sharp et al.,  
05 2022).

06 In practice, comparison with such analogs is a challenging task due to the heterogeneous nature of the ocean air-sea  
07 flux field, as well as the potential for OAE effects to spread over very large spatial and temporal scales. Notably, the  
08 background air-sea CO<sub>2</sub> flux field is highly dynamic on local to global scales. The ocean both absorbs and releases a massive  
09 amount of CO<sub>2</sub> each year; the net flux amounts to an uptake of about 10 Pg CO<sub>2</sub> yr<sup>-1</sup>—but this net flux is a small residual of  
10 large gross fluxes (about ±330 Pg CO<sub>2</sub> yr<sup>-1</sup>) (Friedlingstein et al., 2022). OAE can increase CO<sub>2</sub> flux into the ocean when the  
11 alkalinity enhancement reduces seawater *p*CO<sub>2</sub> below atmospheric CO<sub>2</sub>. However, OAE can also decrease CO<sub>2</sub> flux into the  
12 atmosphere when alkalinity enhancement reduces seawater *p*CO<sub>2</sub> closer to atmospheric *p*CO<sub>2</sub>. Both cases will constitute CDR  
13 as it leads to a net increase of DIC in the ocean reservoir (Bach et al., 2023). Geographic patterns of CO<sub>2</sub> ingassing and  
14 outgassing are controlled by the ocean’s large-scale and subtropical overturning circulations (e.g., Iudicone et al., 2016),  
15 mesoscale and submesoscale motions (e.g., Nakano et al., 2011; Ford et al., 2023), variations in winds (e.g., Andersson et al.,  
16 2013; Nickford et al., 2022), storms (e.g., Nicholson et al., 2022), upwelling dynamics, local inputs from rivers (e.g., Mu et  
17 al., 2023), exchanges with sediments, and biology (e.g., Huang et al., 2023). Outside the tropics, there is pronounced seasonal  
18 variability in air-sea CO<sub>2</sub> fluxes mostly driven by phytoplankton blooms that draw down CO<sub>2</sub> in the surface ocean during  
19 spring and summer (e.g., Fassbender et al., 2022), and winter mixing that brings carbon-rich waters to the surface. All these  
20 dynamics are subject to variations in the climate and ocean circulation caused by internally fluctuating modes of variability or  
21 external forcing associated with CO<sub>2</sub> emissions and other human activities.

22 Given the complex nature of the ocean biogeochemical system, robust MRV for high-quality carbon removal markets  
23 will presumably depend on model-based approaches when quantifying net CO<sub>2</sub> removals. Ocean biogeochemical models  
24 (OBMs) will be a critical tool in this context (see Fennel et al., 2023, this Guide). These models represent the physical,  
25 chemical, and biological processes affecting the distribution of carbon, alkalinity, and nutrients in the ocean. OBMs represent  
26 inorganic and organic carbon pools, alkalinity, and nutrients as tracers with units of mass per volume (or mass) of seawater.  
27 OBMs are based on ocean general circulation models (OGCMs) that represent the movement of tracers mediated by ocean  
28 circulation and mixing. Biogeochemical tracers, including DIC and TA, have sources and sinks from processes such as

29 biologically mediated production and remineralization of organic matter. Boundary fluxes for OBM tracers include riverine  
30 inputs, aeolian deposition, sediment-water exchange, and air-sea gas exchange. Fennel et al. (2023, this Guide) provide an  
31 overview of the most relevant modeling tools for OAE research with high-level background information, illustrative examples,  
32 and references to more in-depth methodological descriptions and further examples.

## 33 **2. Specificities of MRV for marine CDR**

34 The natural ocean carbon cycle is extremely dynamic on a wide range of temporal and spatial scales, typically  
35 spanning more than ten orders of magnitude (Sarmiento and Gruber, 2006). These scales range from that of the ocean skin, a  
36 thin layer of less than a millimeter in contact with the atmosphere where air-sea CO<sub>2</sub> exchange is controlled by molecular  
37 diffusion, to that of the global ocean circulation that typically transports dissolved carbon over more than a thousand years and  
38 10,000 km. As such, the ocean represents a challenging environment for MRV, especially compared to MRV of land-based  
39 CDR techniques. Three specific time scales are to be considered when discussing challenges for MRV of mCDR, and in  
40 particular OAE.

41 The first time scale relates to natural variability in carbonate chemistry, especially *p*CO<sub>2</sub> and alkalinity, due to  
42 biological, chemical, and physical processes in the ocean. Such variability can be substantial on daily and seasonal time scales.  
43 For example, using in situ observations from 37 stations spanning diverse ocean environments, Torres et al. (2021) showed  
44 that in the open ocean stations, the average seasonal cycle of *p*CO<sub>2</sub> was  $49 \pm 23 \mu\text{atm}$  (inter-station mean and standard  
45 deviation), and that diurnal variability could also be as high as  $47 \pm 18 \mu\text{atm}$ . Temporal variability at coastal stations where  
46 OAE is likely to be deployed — due to proximity to existing infrastructure, energy supply, and human resources — is  
47 significantly higher, with seasonal variability in *p*CO<sub>2</sub> being  $210 \pm 76 \mu\text{atm}$  and diurnal variability reaching  $178 \pm 82 \mu\text{atm}$   
48 (Torres et al., 2021). OAE-induced changes in *p*CO<sub>2</sub> are likely to be lower than the range in natural variability, complicating  
49 MRV. For example, an increase in alkalinity of  $10 \mu\text{mol kg}^{-1}$  would result in a decrease in *p*CO<sub>2</sub> of around  $20 \mu\text{atm}$  (given  
50 temp =20°C; salinity = 35; initial TA =  $2200 \mu\text{mol kg}^{-1}$ ; DIC =  $1965 \mu\text{mol kg}^{-1}$  and no secondary precipitation or biotic  
51 calcification). Historical carbonate system variability, like the examples given here, can be used in sensitivity studies to assess  
52 the detectability of a given OAE perturbation for different observing systems (Mu et al., 2023).

53 The second of these time scales relates to air-sea CO<sub>2</sub> equilibrium. This time scale is particularly relevant for OAE as  
54 it determines the time required from an alkalinity-driven shift in surface seawater carbonate equilibria to a new air-sea CO<sub>2</sub>  
55 equilibrium and the resulting atmospheric carbon uptake. It is well established that the characteristic timescale for air-sea  
56 exchange of CO<sub>2</sub> is of the order of 6 months (Sarmiento and Gruber, 2006). But Jones et al. (2014) have shown that the time  
57 to reach air-sea CO<sub>2</sub> equilibrium is highly variable at the regional scale, ranging from less than a month to several years, with  
58 especially long values in the northern North Atlantic, the Atlantic subtropical gyres, and the Southern Ocean. This regional  
59 variability is explained by the dependency of the air-sea CO<sub>2</sub> equilibrium time scale on the gas transfer velocity, the depth of  
60 the mixed layer, and the baseline carbonate chemistry of seawater. More precisely, this time scale shortens with higher gas

61 transfer velocities and Revelle factors, but lengthens with deeper mixed layers and larger ionization fractions (i.e., the ratio  
62 between DIC and dissolved CO<sub>2</sub>).

63 The third of these time scales relates to ocean physical processes and alkalinity and carbon transport away from the  
64 injection location. First, horizontal currents, ranging from a few centimeters to a few meters per second, can potentially  
65 transport the OAE signal away from the initial injection site, thus complicating MRV. A simple calculation shows that a mean  
66 flow of 0.5 m s<sup>-1</sup> could transport the alkalinity signal more than 100 km from the initial site in six months. Second, vertical  
67 entrainment, mixing, and/or other subduction processes might also transport the OAE signal to depths below the seasonal  
68 mixed layer, potentially hindering atmospheric CO<sub>2</sub> uptake and associated MRV.

69 Lessons learned from mesoscale in situ ocean iron fertilization (OIF) studies can be applied to MRV for OAE,  
70 especially during pilot studies of unenclosed OAE-perturbed patches of surface waters that are upscaled beyond a few km<sup>2</sup>.  
71 Ocean circulation and mixing will cause a range of effects that are scale-dependent and will influence MRV strategies as it is  
72 used to target pilot studies and, eventually, larger deployments (100 km<sup>2</sup> scale). This presupposes that elements of MRV will  
73 be needed at all spatial scales during the development and testing of an mCDR method.

74 The success of OIF in tracking and the repeated sampling of a coherent patch of perturbed waters over a timescale of  
75 weeks was due to the use of SF<sub>6</sub> as an ocean tracer (e.g., Coale et al., 1996), and, in one instance, using a quasi-controlled  
76 volume (e.g., within a mesoscale eddy; Smetacek et al., 2012). For example, the use of SF<sub>6</sub> allowed dynamic upper ocean  
77 behavior to be observed during an OIF perturbation, in which the perturbed water was subducted under less dense water in a  
78 few days, leading to the termination of the study (Coale et al., 1998). Subduction is a risk for the MRV of OAE trials being  
79 conducted in nearshore waters, and the use of tracers such as SF<sub>6</sub> would be crucial for observing this behavior.

80 At larger spatial scales (i.e., for perturbations done in waters not bounded by eddies >100 km<sup>2</sup>), ocean physics imposes  
81 a strain and concurrent rotation of a perturbed patch of ocean; as such, OIF studies revealed the perturbed patch of waters can  
82 ‘grow’ in areal extent from 100 km<sup>2</sup> to > 1000 km<sup>2</sup> via the entrainment of the surrounding ‘control’ seawater (Law et al., 2006).  
83 Such entrainment sets up concentration gradients that lead to fluxes into (in the case of OIF, nutrients are resupplied to the  
84 nutrient-depleted patch) and out of (in the case of OIF, chlorophyll which has accumulated due to OIF, and iron that has been  
85 added) the perturbed waters. Such artifacts may dilute the more alkaline waters in the patch of unenclosed OAE perturbed  
86 waters, which may hinder aspects of MRV such as detection of the OAE signal above a background level, or biological side-  
87 effects resulting from OAE.

### 88 **3. Observation-based techniques for MRV and limitations**

89 OAE depends on multi-step processes to achieve mCDR: First, the intervention raises ocean alkalinity in order to  
90 lower seawater *p*CO<sub>2</sub>, and then atmospheric CO<sub>2</sub> must equilibrate with the altered waters. These processes point to many of  
91 the variables that would ideally be observed in an OAE MRV scheme. Measurements of total alkalinity (TA) and DIC are  
92 important to quantify the background state of the carbon system, which determines the *p*CO<sub>2</sub> response per unit change in

93 alkalinity. Further, measurements of TA might help verify that alkalinity has been added effectively, although signal-to-noise  
94 ratios may be insufficiently strong to enable robust detection and attribution of TA anomalies (Mu et al., 2023). pH is an  
95 important measurement to ensure that the OAE deployment conforms with water quality limits (usually  $\text{pH} < 9$ ) and that the  
96 deployment does not create conditions that induce precipitation. Finally,  $p\text{CO}_2$  at the ocean's surface is a key control on gas  
97 exchange and is thus an important measurement target. With extensive measurements of these variables along the Lagrangian  
98 pathway of a perturbed water mass, a carbon budget could theoretically be closed by constraining the time-rate of change and  
99 making inferences about important driving processes such as air-sea gas exchange; such a budget could, in theory, be used to  
00 support quantification of CDR for a given OAE deployment. Though appealing in its comprehensiveness, the reality of  
01 observing all of the parameters needed to quantitatively close a perturbed carbon budget and compare it against an unperturbed  
02 counterfactual is likely impossible in the near to medium-term, even in the context of highly-monitored field trials. The  
03 difficulty is inherent in the fact that the patch of water perturbed by the addition of TA is likely to be turbulently dispersed in  
04 the ocean, and its signal diluted below the limit of detectability by mixing over the time scale required for  $\text{CO}_2$  equilibration  
05 (He and Tyka, 2023; Mu et al., 2023; Wang et al., 2023).

06 This leads to the conclusion that MRV via direct observational approaches should not be expected to completely  
07 follow every molecule of additional  $\text{CO}_2$  resulting from an OAE deployment - as doing so would set an insurmountable barrier  
08 to MRV. Instead, we outline what can feasibly be observed, what questions these observations can answer, and which questions  
09 are left to be addressed in statistical and/or prognostic models with their attendant uncertainties.

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

12 The most direct measurement relevant to OAE experiments is TA, which would reveal if the initially planned  
13 perturbation was successful. Though autonomous sensors for TA have been in development for several years (Briggs et al.,  
14 2017), they are not commercially available at the time of writing, and the laboratory analysis of bottle samples cannot currently  
15 be replaced or even supplemented by sensor-based measurements (see Cyronak et al., 2023, this Guide). Nevertheless,  
16 laboratory analysis of TA in bottle samples can be compared to “baseline” measurements taken before the alkalinity is added  
17 or outside the expected patch area. It is worth noting that measuring a TA increase near the OAE deployment point may be  
18 possible, but once the OAE-perturbed water has dispersed in the ocean flow, the signal-to-noise ratio will likely be too low to  
19 make any accurate quantification. This is also the case for attempting to quantify CDR using DIC, as discussed below. The  
20 TA in the OAE-influenced patch may also be compared to a predicted counterfactual TA constructed from regression methods  
21 built with historical salinity (and other available) data, like the Locally Interpolated Alkalinity Regression (LIAR) method  
22 (Carter et al., 2018).

23 In contrast to TA, to determine the ocean uptake of  $\text{CO}_2$ , there are effective equilibrators-based autonomous  $p\text{CO}_2$   
24 systems (e.g., ASVCO<sub>2</sub><sup>TM</sup>, MAPCO<sub>2</sub>) capable of measuring  $p\text{CO}_2$  with a nominal accuracy of  $2 \mu\text{atm}$  (R. Wanninkhof,  
25 Personal Communication), although they are restricted to the top few meters of the surface ocean due to the fact that  
26 equilibrators cannot be submerged. There are also in situ  $p\text{CO}_2$  sensors that rely on equilibrating seawater  $p\text{CO}_2$  with air

27 through a membrane (e.g., Pro-Oceanus CO2-Pro™ CV, CONTROS HydroC® CO<sub>2</sub>) or a pH-sensitive dye (e.g., SAMI-pH),  
28 followed by infrared detection or colorimetric spectroscopy. Due to fluctuations in the pressure of equilibration and calibration  
29 issues, the real-world accuracy of these instruments is ~5 μatm (R. Wanninkhof, Personal Communication). The existence of  
30 autonomous *p*CO<sub>2</sub> sensors is potentially important because while it is difficult to detect changes in the carbon inventory of the  
31 ocean with measurements of DIC, it can be done with measurements of *p*CO<sub>2</sub> (Wanninkhof et al., 2013). These *p*CO<sub>2</sub> sensors  
32 can be deployed on moorings (MAPCO2, ProCV) and autonomous surface vehicles like Wave Glider (ASVCO2) (Chavez et  
33 al., 2018) and Sailandrone (Sabine et al., 2020; Sutton et al., 2021; Nickford et al., 2022). These sensors have the advantage of  
34 being able to collect measurements continuously in harsh weather and with much reduced involvement from skilled analysts  
35 relative to field surveys with bottle collection. Most analysis focuses on collecting and analyzing calibration samples and  
36 performing quality control on data.

37 Sensors that measure pH on autonomous profiling floats, gliders, or moored platforms could provide additional data  
38 useful for MRV. Unfortunately, as demonstrated by Wimart-Rousseau et al. (2023), pH sensors on profiling floats have  
39 relatively large uncertainties that may compromise their usefulness for MRV. Moreover, these uncertainties are largest near  
40 the ocean's surface, where they would be most useful in the MRV context, as knowledge of the surface ocean disequilibrium  
41 is needed for CDR. Uncertainties in pH of 0.01 roughly translate to a *p*CO<sub>2</sub> uncertainty of 10 μatm (Wimart-Rousseau et al.,  
42 2023), but even achieving such accurate pH measurements will require significant advances in sensor accuracy and/or post-  
43 processing data analysis tools to correct surface pH data.

44 Another MRV-relevant aspect of OAE that is well suited for sensor measurements is the reduction of OAE efficiency  
45 via OAE-induced precipitation of carbonates (see Schulz et al., 2023 for further context). For example, marine calcifiers, such  
46 as coccolithophores, may benefit from high alkalinity and pH conditions, thus reducing OAE efficiency (Bach et al., 2019),  
47 but this effect is still uncertain (Gately et al., 2023). Autonomous optical sensors for particulate inorganic carbon (PIC) based  
48 on the birefringence of calcite and aragonite have been in development for several decades (James, 2009; Bishop et al., 2022).  
49 Since the deployment of the first prototype on a profiling float in 2003, this optical PIC sensor has been re-engineered several  
50 times, and the most recent versions require further re-engineering to correct for thermal and pressure effects, as well as  
51 misalignment effects of the linear polarizers (Bishop et al., 2022). A new autonomous PIC measurement concept was recently  
52 proposed by Neukermans and Fournier (2022), which may overcome the aforementioned issues. Such PIC sensors are currently  
53 under development and are expected to cover a PIC concentration range of 0.5 to 500 μgC L<sup>-1</sup> (Neukermans et al., 2023).  
54 These PIC sensors are intended for use on autonomous platforms such as floats profiling up to 2000 m deep, autonomous  
55 moorings, tethered buoys, or Sailandrones. Such PIC sensors would thus enable careful autonomous monitoring of PIC  
56 concentration in the epi- and mesopelagic ocean, as well as in shallow shelf seas. In addition, ocean color satellites can be used  
57 to obtain global maps of coccolithophore PIC concentration in the surface ocean at daily frequency using a variety of remote  
58 sensing algorithms (see Balch and Mitchell, 2023 for a review of remote sensing PIC algorithms and limitations). Both remote  
59 sensing and in situ observations of PIC concentration can contribute to assessing secondary precipitation and OAE efficiency.

60 Other more remote tail risks of OAE include alterations to carbon production and flux, for example, via shifts in  
61 phytoplankton community structure (Ferderer et al., 2022) or alterations in the availability of high-density biominerals such as  
62 opal or calcite, which may ballast POC flux to the deep ocean (Armstrong et al., 2001; Klaas and Archer, 2002). Ballasting of  
63 POC flux by coccolithophore calcite and the resulting increase in the sinking velocity of POC aggregates has been confirmed  
64 in many experimental studies and may be an important mechanism in some ocean regions. This potential secondary effect of  
65 OAE on POC flux could be monitored from autonomous profiling floats equipped with a PIC sensor (Neukermans et al., 2023).

66 Wind speed should be measured since it is the most common correlate for air-sea gas exchange, and there are wind  
67 speed/gas exchange parameterizations that predict gas transfer velocities well in the open ocean (e.g., Ho et al., 2006).  
68 Therefore, in these settings, measurements of wind speeds are sufficient to characterize air-sea gas exchange. However, since  
69 gas transfer velocities as a function of wind speed differ between the open and coastal oceans (e.g., Dobashi and Ho, 2023),  
70 depending on the OAE deployment location,  $^3\text{He}/\text{SF}_6$  tracer release experiments might have to be performed to determine this  
71 relationship (see Wanninkhof et al., 1993). While it is likely unfeasible to couple every individual OAE operation with a  
72  $^3\text{He}/\text{SF}_6$  dual tracer release during the deployment phase, during the testing phase, such experiments will be useful for  
73 calibrating and evaluating models that will most likely be used to determine the efficiency and efficacy of  $\text{CO}_2$  equilibration.

#### 74 **4. Model-based techniques for MRV and limitations**

75 OBMs can be used to explicitly represent the effects of OAE by conducting numerical experiments in which the  
76 model is provided with forcing data that represents alkalinity additions. Developing and validating models in the region/scale  
77 of OAE deployment should be a priority to enable functional frameworks for MRV (see Fennel et al., 2023, this Guide).

78 A model integrated forward in time with the alkalinity additions will simulate the transport of the associated mass of  
79 alkalinity and its ensuing effect on biogeochemical processes, including air-sea gas exchange. These simulations can be used  
80 to evaluate net carbon removal by comparing integrations that include the OAE signal to others in which that forcing is not  
81 present — i.e., the baseline counterfactual condition or “control.” If an ensemble of integrations is performed, the variation of  
82 net carbon removal across the ensemble can be used to assess uncertainty. Notably, there are different potential sources of  
83 uncertainty: If intrinsic variability in ocean dynamics is considered the dominant source of uncertainty, an initial condition  
84 ensemble could provide an appropriate representation of uncertainty. If model structure, in contrast, is the dominant source of  
85 uncertainty, alternative approaches to ensemble construction could be employed, including perturbing parameters or using  
86 multiple models (see Fennel et al., 2023, this Guide for further discussion). Explicit simulation of OAE deployments can be  
87 compared to observations, including measurements from background observing systems, as well as bespoke data collection  
88 efforts associated with the OAE project. In some cases, explicit data assimilation (DA) procedures may be applied (see Fennel  
89 et al., 2023, this Guide), potentially reducing model-data misfits and improving confidence in the model simulations. One  
90 challenge of applying DA to MRV is estimating additionality, which requires information about both the actual temporal  
91 evolution of the system and the counterfactual condition, i.e., the state of the system that would have occurred in the absence

92 of the CDR intervention. The counterfactual condition is impossible to observe directly, and to the extent that observations  
93 contain an imprint of the CDR, DA cannot be used to generate explicit estimates of the baseline state. This raises conceptual  
94 issues because simulations conducted with and without DA are not directly comparable; thus, a difference between DA-  
95 constrained and free-running models cannot provide a valid estimate of additionality. Further research is needed to understand  
96 and address these problems. Potential solutions may rely on the assumption that CDR signals are very small relative to the  
97 background variability and, thus, essentially negligible in the context of the constraints on model solutions imposed by DA.  
98 Further, if the CDR interventions can be assumed to have negligible impact on physical variables (e.g., temperature, salinity,  
99 currents, etc.), it may be possible to use DA selectively on just these variables.

#### 00 **4.1 Modelling alkalinity addition**

01 For the effects of OAE to be properly simulated, models must be supplied with the correct amount of alkalinity applied  
02 as forcing. Alkalinity additions, if performed over hours to days, are likely to occur on scales much smaller than the ensuing  
03 anomaly generated in air-sea CO<sub>2</sub> exchange, typically occurring over months to years (see Section 2). For this reason, MRV  
04 frameworks must invoke a separation of concerns, wherein near-field (i.e., within a few km of the source) processes are treated  
05 differently than the broader regional effects. Explicit modeling of near-field dynamics is likely to require different modeling  
06 frameworks (e.g., McGillicuddy, 2016) than those simulating the full expression of the OAE effects in the ocean—however,  
07 it is not necessarily a requirement to simulate near-field dynamics in the context of MRV. Near-field processes must be  
08 constrained by direct observations, and/or their dynamics must be accurately captured in verified parameterizations applied to  
09 models too coarse to simulate the local effects explicitly (e.g., Fox-Kemper et al., 2019). Notably, different OAE technologies  
10 and feedstocks present different challenges in this regard (see Eisaman et al., 2023, this Guide). Electrochemical techniques,  
11 which might produce, for instance, an alkalinity-enhanced stream from an outfall pipe, are different from crushed-rock  
12 particulates where dissolution kinetics come into play. Moreover, as discussed in Fennel et al. (2023, this Guide), ancillary  
13 constituents (e.g., iron or nickel) associated with rock-derived feedstocks may induce biological responses with impacts on the  
14 total efficacy of the OAE process.

#### 15 **4.2 Representing OAE effects**

16 To provide a suitable basis for MRV applied to OAE deployments, models must meet several requirements and  
17 provide a sufficiently accurate representation of alkalinity additions. First, models must provide a reasonable representation of  
18 ocean circulation and mixing; these processes are critical to determining the residence time of added alkalinity in the surface  
19 mixed layer, where gas exchange with the atmosphere is possible. Given that the equilibration time scale for CO<sub>2</sub> via gas  
20 exchange is long, the residence time of alkalinity-enhanced water parcels at the ocean surface is likely a primary control on  
21 the efficiency of uptake (He and Tyka, 2023). Second, the models must accurately capture the surface ocean *p*CO<sub>2</sub> anomaly  
22 induced by alkalinity additions. This implies having a correct representation of the carbon system thermodynamics (see Fennel  
23 et al., 2023, this Guide). Further, since the change in *p*CO<sub>2</sub> depends on the background DIC:TA ratio (Hinrichs et al., 2023), it

24 is important that the model has a good representation of the mean state prior to perturbation (Planchat et al., 2023). Third,  
25 presuming an accurate representation of the change in  $p\text{CO}_2$  and the transport of alkalinity following injection, the model must  
26 be able to simulate the gas transfer of  $\text{CO}_2$  with sufficient accuracy. Notably, the gas transfer velocity is highly uncertain,  
27 particularly in coastal environments where many OAE deployments are likely to occur (e.g., Dobashi and Ho, 2023). If surface  
28 water residence times are much longer than the gas equilibration timescale, uncertainty in the gas transfer velocity may not  
29 contribute substantially to the overall uncertainty—but in intermediate regimes where the two timescales are comparable,  
30 uncertainty in the gas transfer velocity may be an important consideration. Finally, a comprehensive assessment of OAE  
31 efficacy will depend on accurate characterization of feedbacks in the biological system. If there are changes in the natural  
32 distribution of calcification or organic carbon export, this term should be quantified—or its potential magnitude and impact on  
33 overall carbon transfer should be assessed as a component of the uncertainty budget. At present, further empirical research is  
34 required to enable modeling systems to treat this aspect of OAE effects robustly (Fennel et al., 2023, this Guide).

## 35 **5. The way forward for MRV of OAE**

36 There is much work to be done to establish how to optimize monitoring OAE with respect to which observations are  
37 needed and at what spatial and temporal resolution and duration. Nevertheless, early field trials should all monitor the initial  
38 increase in alkalinity (i.e., both measured and modeled). Baseline alkalinity measurements should be made so that the range  
39 of concentration within its natural variability is known before the deployment of alkalinity. Furthermore, if the enhancement  
40 is done via the dissolution of pulverized rocks, the dissolution rate needs to be known under in situ conditions. Knowledge of  
41 this rate includes the dependency on various factors such as temperature, salinity, etc. but also to what extent minerals become  
42 buried in sediments and how this change in exposure affects dissolution. If the enhancement is done via electrochemistry, the  
43 dosing rate of the solution (e.g.,  $\text{Mg}(\text{OH})_2$ ,  $\text{NaOH}$ ) should be quantified and reported with complete information about the  
44 measurement methods and a thorough accounting of their uncertainties.

45 Furthermore, any potential secondary precipitation caused by the alkalinity enhancement (e.g., if alkalinity is added  
46 too quickly, brucite precipitation could occur) should be monitored. Monitoring of secondary precipitation is particularly  
47 critical in the non-equilibrated state (i.e., before atmospheric  $\text{CO}_2$  influx has occurred) and when the alkalinity-perturbed patch  
48 is in close contact with sediments since the risk for secondary precipitation is particularly high under these circumstances (see  
49 Eisaman et al., 2023, this Guide; Schulz et al., 2023, this Guide).

50 Finally, the drawdown of  $\text{CO}_2$  in the ocean due to alkalinity addition should be measured. Given the potential natural  
51 variability in  $p\text{CO}_2$ , especially in coastal regions, monitoring of  $p\text{CO}_2$  should also be done before the OAE deployment.  
52 Considering the spatial and time scales discussed above, these measurements will need to be complemented by modeling  
53 approaches.

54 MRV of  $\text{CO}_2$  influx after the application of OAE will likely depend on fit-for-purpose modeling (see Fennel et al.,  
55 2023, this Guide). Exceptions to this may apply if the deployment is made in an enclosed area where the water is confined, or

56 the deployment is made in a heavily instrumented and surveyed area of the ocean. Models used to constrain atmospheric CO<sub>2</sub>  
57 influx must be calibrated and evaluated with observations. Since CO<sub>2</sub> influx is due to physical and chemical processes, the  
58 following observational data to improve the modeling framework includes (but is not restricted to):

- 59 • Observations of ocean currents from acoustic Doppler current profilers (ADCPs), Lagrangian floats or tracers like  
60 SF<sub>6</sub>, and remote sensing;
- 61 • Observations of air-sea gas exchange from <sup>3</sup>He/SF<sub>6</sub> tracer release experiments;
- 62 • Temperature and salinity profile measurements;
- 63 • Measurements of carbonate chemistry parameters (i.e., TA, pH, *p*CO<sub>2</sub>, and DIC).

64 While it appears that OBMs will ultimately provide a critical foundation for robust ocean MRV frameworks, they are  
65 not currently ready to serve in this capacity (Fennel et al., 2023, this Guide). These models represent complicated systems;  
66 Ocean General Circulation Models (OGCMs) are based on fundamental governing equations, but solving these equations  
67 numerically requires approximations (e.g., Fox-Kemper et al. 2019). Ocean ecosystems comprise diverse groups of organisms  
68 with differing physiological capacities and complex interactions. There are no generally accepted governing equations for  
69 these systems; rather, models are built on the basis of empirically determined relationships and theory or hypothesis (e.g.,  
70 Planchat et al., 2023). For OBMs to provide a credible basis to support ocean MRV, they must be based on broadly accepted  
71 theory or well-constrained parameterizations, and they must be explicitly validated relative to the quantification of gas  
72 exchange anomalies arising as a result of perturbations in alkalinity. Models have not yet been robustly validated in the context  
73 of these explicit requirements.

74 We note that at this point, we have yet to develop the best modeling tools for OAE MRV (and likely MRV for mCDR  
75 in general). A rigorous research and development program to establish OBMs as fit-for-purpose, credible tools for MRV are  
76 needed. However, there is currently a major problem with basing MRV on models. OBMs are run on high-performance  
77 computing architectures, and because they are big calculations, they are very computationally expensive (and therefore  
78 financially expensive). It is unlikely that technological innovation will dramatically reduce this computational cost in the next  
79 5-10 years, during which time we will be required to deliver a functional framework for MRV. Therefore, we suggest  
80 combining direct model simulations with advanced statistical approaches to overcome the computational challenges. First, we  
81 must establish that models can provide credible representations of key CDR processes by ensuring that model output agrees  
82 with available observations. Then, we can leverage these models to generate datasets from which to derive robust statistical  
83 approximations, including through the application of techniques derived from artificial intelligence and machine learning. For  
84 instance, well-calibrated models could be used to produce training data for machine learning algorithms to predict the CDR  
85 efficiency of OAE deployments in different locations at different times, i.e., as a function of initial environmental conditions  
86 such as water temperature, carbonate chemistry, mixed layer depth such as suggested in Bach et al. (2023).

87 Conducting explicit OAE modeling experiments coupled with field trials are important research milestones necessary  
88 to identify the long-term approach to robust MRV. It is likely that the models that can effectively support field trials will use  
89 regional OGCMs that are capable of high-fidelity simulations of ocean flows at scales commensurate with those driving the

90 initial dispersion of OAE signal on timescales of weeks to months. Unless alkalinity is continuously applied at a level  
91 measurable by long-duration observing platforms, the OAE signals are likely to be diluted and less easily tracked with  
92 observations. Critically, it is important to demonstrate that the models provide simulations consistent with the carbonate  
93 chemistry and deliberate tracer observations.

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

## 98 **6. Key recommendations for MRV of OAE**

99 Early-stage MRV research for OAE may become the foundation on which regulated markets are built. Therefore,  
00 such research carries a special obligation toward comprehensiveness, reproducibility, and transparency. To fulfill these  
01 obligations, we suggest the following overarching best practice guidelines:

- 02 ● Field trials should be co-designed with modelers and observationalists to enable the iterative process of model  
03 validation and improvement and dynamically informed data interpretation. In some scenarios, co-design may entail  
04 the development of formal Observing System Simulation Experiments, and data-assimilating state estimates (Fennel  
05 et al., 2023, this Guide).
- 06 ● MRV techniques and results should be well-documented and archived publicly and promptly, without restriction (e.g.,  
07 Planetary Technologies, 2023). Ideally, a central registry of OAE experiments would adhere to FAIR (Findable,  
08 Accessible, Interoperable, and Reproducible) data standards (Wilkinson et al., 2016). Researchers should eschew any  
09 practice that withholds MRV innovation from the community to “build a moat” in support of a commercial mCDR  
10 approach.
- 11 ● Early field trials are recommended to be as comprehensive as possible, monitoring for obvious, first-order risks like  
12 secondary precipitation and more remote tail risks like alterations to export production via shifts in phytoplankton  
13 community structure and mineral ballasting.
- 14 ● Model evaluation against observations should be tailored to the key processes in question. Fennel et al. (2023, this  
15 Guide) argue that models may be used for a long list of purposes, including, for example, simulating ecosystem effects  
16 and sediment-water exchanges. Early MRV efforts can expose model skill and deficiencies in simulating these  
17 processes if the relevant observations are prioritized.
- 18 ● An uncertainty budget should be quantified that includes both known uncertainties (e.g., measurement and mapping  
19 errors) and expert estimates of presently unmeasurable risks. A comprehensive assessment of the poorly constrained  
20 uncertainties will point to key research areas in the future.

21

22 **Competing interests**

23 DTH and MCL are Co-Founders as well as Director of Science and Executive Director, respectively, of [C]Worthy, LLC, a  
24 non-profit research organization focused on building open-source tools to support MRV for marine CDR. DTH is also a  
25 Science Advisor at Carbon Direct, Inc., an end-to-end carbon management company. LTB is a scientific advisor to Submarine,  
26 a start-up service provider for MRV of marine CDR.

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