Cascade Climate

Foundations for Carbon Dioxide Removal Quantification in Enhanced Rock Weathering Deployments

October 2024

Contents

1 Scope and Purpose of this Document

1.1 Document Scope

This document represents an assessment of the science and practice of carbon dioxide removal (CDR) quantification for enhanced rock weathering (ERW) deployments, undertaken through a multi-stakeholder process from October 2023 through August 2024. The focus of the assessment is scoped to ERW practices that involve the spreading of alkaline feedstocks (e.g., silicates, carbonates, or other alkaline materials) on agricultural soils. It excludes ERW conducted in other terrestrial ecosystems (e.g., forests or non-managed soils), and excludes CDR practices that add alkalinity directly to surface water or ocean systems.

At this stage of the ERW field, agricultural soil systems are more operationally accessible for practitioners—routine monitoring and infrastructure for transporting, spreading, and incorporation of feedstock materials to a large extent already exist. In addition, the quantification considerations for managed agricultural systems and other terrestrial ecosystems are different in noticeable ways (e.g., forests have deeper root networks than agricultural soils, and non-managed ecosystems can be more exposed to fire and mass wasting events in ways that managed agricultural systems are not).

The primary focus of this document is the quantification of additional CDR generated by ERW deployments, articulating in detail the relevant biogeochemical fluxes that can impact the net carbon balance, including the current state of scientific understanding and considerations for constraining the impact of relevant fluxes in practice. In select sections, the document also provides high-level guidance on safety considerations for early-stage deployments (e.g., Section 6 on feedstock characterization), but does not attempt to generate comprehensive guidelines. More detailed considerations of ecological and human health safety, along with best practices for community engagement and equity concerns, are critical for ERW as a pathway, but are outside the scope of this current work.

In addition, this document is focused on project-level quantification, in which CDR is quantified for a single deployment, at field-scale, attributing CO_2 removal to individual feedstock spreading events. A detailed exploration of what jurisdiction- or landscape-level quantification could entail is left for future work (Khan, 2024).

The scope covered by each section of the document is as follows:

- **Section 2**
  Establishes an overarching framework for netCDR quantification, including the consideration of two independent conformance zones—the Near-Field Zone (NFZ) and the Far-Field Zone (FFZ)—and the fluxes/components of the term balance that should be considered within each zone.
- **Section 3**
  Provides high-level guidance on site characterization to inform project design and interpretation of monitoring results.
- **Section 4**
  Provides guidance and considerations for determining the spatial extent of the NFZ in a site-specific manner.
- **Section 5**
  Establishes a term balance for overall netCDR and calculating the carbon balance in the NFZ, FFZ, and for project life cycle emissions, and provides guidance on defining and quantifying counterfactual baseline CDR, navigating the complexities of time accounting for ERW projects, and uncertainty quantification.
- **Sections 6 and 7**
  Provide additional guidance on feedstock characterization, sampling design, and considerations for taking solid, aqueous, and gas-phase measurements as part of netCDR quantification.
- **Sections 8 and 9**
  Provide a detailed consideration of each of the fluxes/components of the term balance in the NFZ and FFZ. Context on the underlying science and state of understanding is combined with considerations and recommendations for capturing that flux in project-level quantification for early-stage deployments. For many components of the term balance, priority areas for further research and development are flagged and discussed.
- **Section 10**
  Covers high-level recommendations for quantifying life cycle emissions for ERW projects.

1.2 Document Use

This document represents an assessment of the state of ERW quantification at a specific moment in time, in the relatively early stages of the development of ERW as a CDR pathway. We do not intend for this to be a static assessment with fixed recommendations; instead, we intend to regularly publish follow-on case studies, analyses, assessment reports, and updates that reflect progress in the fundamental science underpinning CDR quantification for ERW deployments, improvements in measurement and modeling methods, and learnings from ongoing field trials and early-stage commercial deployments.

Please note that this document is not intended as an articulation of generalizable standard requirements for quantifying netCDR of ERW deployments. It is the Cascade team's assessment that the ERW pathway is in a pre-standardization phase, where more real-world deployments are needed before coalescing around a fixed set of requirements governing deployment practices. The key rationale for this assessment is that the heterogeneity of deployment environments calls for quantification approaches that are tailored to the site-specific context of a given deployment, and at this stage of the pathway, transparently reporting site characterizations, measurement approaches, and quantification outcomes is likely to drive higher impact than coalescing around a single approach. Additional data from deployments across a range of environments and agronomic settings are required before we can more reliably characterize the optimal implementation of quantification in different deployment settings. It is our view that putting out a standard could create premature lock-in around an overly narrow set of measurement approaches. At this stage, we believe it is better for practitioners to preserve diversity and flexibility in approaches taken across different cropping systems, soil systems, topography, and operational constraints to maximize learning.

In short, we don't intend for this document to be used as a standard or as "generalized rules" for netCDR quantification in crediting activities. Instead, we intend for this document to be a foundation and 'jumping off point' for the ERW community to systematically discover what approaches work in what situations, which will lay the groundwork for robust, site-specific quantification of carbon removal outcomes across deployment contexts over time.

We invite all ERW stakeholders to use this document–in particular:

- **Project developers** and **credit issuers** can integrate the scientific context, considerations, and recommendations outlined in this document into new and refined methodologies, protocols and project design documents for ERW deployments.

- **Carbon removal buyers** can build the considerations and recommendations provided into measurement, reporting, and verification (MRV) due-diligence requirements and contractual expectations for project developers' quantification approaches.

- **Policymakers** can use this document to gain a more nuanced understanding of the R&D priorities and open system-level questions in ERW quantification, which can then inform the design of targeted public funding and innovation support programs.

- **The broader research community** can use the multi-stakeholder assessment and key R&D priorities highlighted in the document to inform CDR quantification for field, mesocosm, and laboratory experiments, as well as inspire near-term research efforts.

All stakeholders are enthusiastically encouraged to provide feedback on, and contribute data and insights to, the improvement of this document and Cascade's follow-on work on ERW quantification.

1.3 Process Architecture and Acknowledgements

This document is the primary output of a multi-stakeholder community process undertaken from October 2023 through August 2024. The process spanned 14 technical Working Group discussions and 19 collaborative Working Group-industry targeted problem solving sessions. Iterative periods of drafting, reading, and constructive feedback were interlaced throughout the process.

The initial detailed assessment of the science and practice of CDR quantification for ERW deployments was developed through facilitated discussions of **five technical Working Groups**. The focus areas of each Working Group were designed to (as much as possible) comprehensively address the core components of CDR quantification and target known challenges and open questions. Each Working Group met for three, 2-hour sessions from November 2023-January 2024. Following each session, a synthesis of discussions from the session was circulated to all process participants for feedback; this feedback was presented to Working Group members during the next session, and is publicly available as an appendix to this document.

In constructing the technical Working Groups, all participants confirmed in writing that they do not own any equity stake in a for-profit company working in ERW, do not have any revenue-linked compensation agreement with any for-profit company working in ERW, do not work for a carbon removal buyer nor are involved in ERW purchasing decisions of any kind, and are not full-time employees of ERW suppliers, credit issuers, or MRV services providers.

Working Group 1
Focused on methods for measuring initial feedstock dissolution and alkalinity dynamics in the soil column, with a particular focus on sampling design and uncertainty characterization. The Working Group was composed of Thorben Amann, Antonio Carlos de Azevedo, Jelle Bilma, James Campbell, Rachael James, Mike Kelland, Frank McDermott, Isabel Montañez, Ian Power, Tom Reershemius, Radomir Schmidt, Jesper Suhrhoff, and Noah Planavsky, who chaired the group. Discussions from Working Group 1 sessions directly contributed to Sections 4, 5, 6, 7, and 8.1-8.2 of this document.

Working Group 2
Focused on the details of the carbon cycle fluxes / biogeochemical processes in the soil column that need to be considered in a holistic accounting of netCDR, including interactions between ERW interventions and soil organic carbon cycling and the non-CO_2 greenhouse gas fluxes. The Working Group was composed of Christiana Dietzen, Mathilde Hagens, Isabel Montañez, Noah Planavsky, Chris Reinhard, Rafael Santos, Radomir Schmidt, Eric Slessarev, Noah Sokol, Sara Vicca, Arthur Vienne, Bonnie Waring, and Kate Maher, who chaired the group. Discussions from Working Group 2 sessions directly contributed to Sections 4, 5, 7, and 8.

Working Group 3
Focused on downstream systems and the biogeochemical fluxes that should be considered as weathering products are transported from the application site to the durable storage reservoir–discussing in detail how to constrain net changes to the carbon balance in the lower vadose zone and along groundwater flow paths, in surface water systems, and the ocean as a result of an ERW deployment. The Working Group was composed of Yoshiki Kanzaki, Becca Neumann, Kirsty Harrington, Pete Raymond, Jim Saiers, Tao Wen, Chris Reinhard, and Shuang Zhang, who chaired the Group. Discussions from Working Group 3 sessions are primarily reflected in Section 9.

Working Group 4
Focused on soil biogeochemistry models, with a particular emphasis on the current role of modeling in netCDR quantification and the infrastructure needed for evaluating, intercomparing and validating models moving forward. The Working Group was composed of Salvatore Calabrese, Yoshiki Kanzaki, Maria Val Martin, Brian Rogers, Lyla Taylor, and Chris Reinhard, who chaired the Group. Discussions in Working Group 4 are primarily reflected in Section 8.9.

Working Group 5
Comprised two sub groups, one focused on considerations for quantifying life cycle emissions and the other considerations for assessing the human health and ecological impacts for ERW deployments. The life cycle emission Working Group was composed of Spyros Foteinis, Cara Maesano, Stephen McCord, Morimoto Shinichirou, and Yuan Yao; the outcomes of the Group’s discussion are reflected in Section 10. The human health and ecological impacts Working Group was composed of Maya Almaraz, Stephanie Grand, Fatima Haque, Anu Khan, and Charlotte Levy. The outcomes of this session are partially reflected in Section 6, including a call to action regarding the need for robust, fit-for-purpose guidelines for assessing the ecosystem and human health risks of ERW deployments. Detailed discussion of such guidelines was out of scope for this quantification-focused document and was left for future work.

Following the Working Group sessions, further **joint Working Group-Industry problem solving sessions** were convened to address targeted outstanding questions, generally focused on charting an actionable path forward on challenging topics. A diverse group of industry practitioners participated in these targeted problem solving sessions (note in parentheses the affiliations for all industry practitioner participants). The focus areas and participants of each group were as follows:

Deep soil measurements: desired scientific outcomes and operational challenges.
- Working Group members: Mike Kelland, Noah Planavsky
- Industry practitioners: Mark Baum (Lithos Carbon), Benjamin Möller (ZeroEx)
- Non-Working Group, non-Industry participant: Linah Ababneh

Assessing frameworks for time accounting.
- Working Group members: Freya Chay, Kate Maher, Stephen McCord, Shinichirou Morimoto, Chris Reinhard
- Industry practitioners: Mark Baum (Lithos Carbon), Matthew Gammans (Isometric), Jake Jordan (Mati Carbon), Christina Larkin (Inplanet), Simon Manley (UNDO Carbon), Berta Moya (Carbonfuture)
- Non-Working Group, non-Industry participant: Eli Mitchell-Larson

Constraining secondary carbonate formation in the Near-Field Zone.
- Working Group members: Mathilde Hagens, Frank McDermott, Shinichirou Morimoto, Ian Power
- Industry practitioners: Elisabete Pedrosa (Puro.earth), Ingrid Smet (reverse)

Driving towards actionable requirements for assessing potential changes to soil organic carbon stocks resulting from ERW deployments.
- Working Group members: Maya Almaraz, Becca Neumann, Radomir Schmidt, Arthur Vienne, Bonnie Waring
- Industry practitioners: Viri Alcantara-Shivapatham (Verra), Marta Camps-Arbestain (Shell), Jens Steffen Hammes (Carbon Drawdown Initiative), Maria Mooshammer (Eion Carbon), Katie Sierks (Microsoft)

Accounting for soil baseline heterogeneity.
- Working Group members: Salvatore Calabrese, Mike Kelland, Ian Power, Bonnie Waring
- Industry practitioners: Mark Baum (Lithos Carbon), Jake Jordan (Mati Carbon), Alison Marklein (Terradot), Marya Matlin-Wainer (Isometric), Katie Sierks (Microsoft), Philipp Swoboda (Inplanet)

Developing guardrails and guidelines for assessing CDR associated with counterfactual pH control practices.
- Working Group members: Spyros Foteinis, Noah Planavsky
- Industry practitioners: Marta Camps-Arbestain (Shell), Ben Westcott (UNDO Carbon)
- Non-Working Group, non-Industry participant: Linah Ababneh, Tyler Kukla

Near-term best practice for constraining potential CO_2 evasion from surface water systems.
- Working Group members: Frank McDermott, Becca Neumann, Chris Reinhard, Tao Wen
- Industry practitioners: Elliot Chang (Eion Carbon), Matthew Clarkson (Inplanet), Jens Steffen Hammes (Carbon Drawdown Initiative), Richard Hatz (Puro.earth), Ella Holme (Isometric), Jake Jordan (Mati Carbon), Sasankh Munukutla (Terradot)

The outcomes of these joint Working Group-Industry problem solving sessions were reviewed by Working Group members before being combined with the outputs of Working Group sessions to produce the initial draft of this Foundations document.

A Steering Committee, composed of Freya Chay, Anu Khan, Isabel Montañez, and Noah Planavsky, alongside the Working Group chairs, met for five sessions throughout the course of the community process, and provided guidance and feedback on process governance.

Development and drafting of this document was led by Jenny Mills of Cascade Climate. Hara Wang and Jenny Mills co-architected and ran the community process. The technical facilitation team at Cascade who led Working Group and Working Group-Industry targeted problem solving sessions was composed of Jenny Mills, John Sanchez, Noemma Olagaray, and Hara Wang. Jenny Mills, John Sanchez, Noemma Olagaray, Hara Wang, Alison Tune, Noah Anderson, and Brad Rochlin authored and edited sections of the document.

An earlier draft version of the Document was open for review in July 2024 to all Working Group members, industry practitioners and other stakeholders involved in the community process. The following Working Group members are particularly thanked for providing detailed reviews: Salvatore Calabrese, Christiana Dietzen, Stephanie Grand, Kirsty Harrington, Rachael James, Yoshiki Kanzaki, Mike Kelland, Maria Val Mart, Isabel Montañez, Becca Neumann, Ian Power, Pete Raymond, Tom Reershemius, Tim Jesper Suhrhoff, Lyla Taylor, Sara Vicca, and Shuang Zhang. Representatives from the following industry, government and not-for-profit organizations also participated in the review: Carbon 180, Carbon Drawdown Initiative, Carbonfuture, Carbonplan, ClimeRock, Climeworks, Inplanet, Isometric, Lithos Carbon, Mati Carbon, Shell, Silica, Terradot, Veolia, United States Department of Energy, and the National Institute of Advanced Industrial Science and Technology of Japan.

In addition to the reviewers, we would like to give very special thanks to Mike Kelland for drafting of Section 6 and consultation on Section 7.5, Jake Spertus for consultation on statistical methods discussed in Section 7, and Phil Renforth for detailed reviews of Working Group Session discussion syntheses.

1.4 Use and Citation of this Document

To acknowledge and credit this work, please use the following citation: Mills, J. V., Sanchez, J., Olagaray, N. Y., Wang, H., and Tune, A. K., 2024; *Foundations for Carbon Dioxide Removal Quantification in ERW Deployments*, Cascade Climate.

If you identify any errors or have any suggested updates to this Document, please email foundations@cascadeclimate.org.

2 Framework for netCDR Quantification

2.1 Introduction to Enhanced Rock Weathering

Enhanced rock weathering (ERW) involves the spreading of alkaline feedstocks on agricultural soils; the feedstock may or may not be mixed into the topsoil. Over time, the feedstock dissolves in soil porewater, releasing base cations like Mg^{2+} and Ca^{2+} and removing H^+ from solution, generating alkalinity. Carbon dioxide removal (CDR) occurs due to the 'carbonic acid system' response to this alkalinity generation (Eq. 2.1.3 and Eq. 2.1.5).

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad (Eq.\ 2.1.1)$$

$$K_H = \frac{CO_2(aq)}{CO_2(g)} \qquad (Eq.\ 2.1.2)$$

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \leftrightarrow 2H^+(aq) + CO_3^{2-}(aq) \qquad (Eq.\ 2.1.3)$$

$$DIC = [H_2CO_3]^* + [HCO_3^-] + [CO_3^{2-}] \qquad (Eq.\ 2.1.4)$$

The carbonic acid system is continuously responding to shifts in solution chemistry. The addition of excess base cations and removal of H^+ following feedstock dissolution shifts the balance of the carbonic acid system towards HCO_3^- and CO_3^{2-} (Eq. 2.1.3), generating a disequilibrium between dissolved CO_2(aq) and atmospheric or soil CO_2(g). In accordance with Henry's Law (Eq. 2.1.1, Eq. 2.1.2), CO_2 from the pore space or atmosphere will dissolve into porewater to re-establish equilibrium; notably, CO_2(g) in the soil profile is often much higher than in the atmosphere due to soil respiration.

The amount of CO_2 sequestered is dependent on the feedstock mineralogy and the cations and anions produced during dissolution. For example, the carbonic acid weathering of forsterite can consume up to 4 moles of CO_2 per mole of Mg_2SiO_4 (shown here as a congruent weathering reaction):

$$\begin{array}{rl} & Mg_2SiO_4(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + H_4SiO_4(aq) \\ & 4H_2CO_3(aq) \rightarrow 4H^+(aq) + 4HCO_3^-(aq) \\ + & 4CO_2(g) + 4H_2O \rightarrow 4H_2CO_3(aq) \\ \hline \end{array}$$

$$Mg_2SiO_4(s) + 4CO_2(g) + 4H_2O \rightarrow 2Mg^{2+}(aq) + 4HCO_3^-(aq) + H_4SiO_4(aq) \quad (Eq.\ 2.1.5)$$

Production of acidity or removal of base cations (and replacement with acidity) in solution will drive the carbonic acid system away from HCO_3^- and CO_3^{2-}, leading to CO_2 outgassing.

2.1.1 Excess Base Cations and Alkalinity Generation

Feedstock dissolution and the release of excess base cations generates alkalinity that can be quantified using two different frameworks: proton balance and charge balance. We use these two alkalinity frameworks interchangeably throughout this document to be intentionally inclusive. While geochemists may prefer one over the other, they are considered equivalent and we treat them as such in this context (Middelburg et al., 2020; Wolf-Gladrow et al., 2007).

The proton balance framework of alkalinity is referred to as total alkalinity and is the proton balance relative to a ‘zero point’ set to a pKa of 4.5 (Dickson, 1981):

$$
\begin{aligned}
A_T = {} & [HCO_3^{\,-}] + 2[CO_3^{\,2-}] + [B(OH)_4^{\,-}] + [OH^-] + [HPO_4^{\,2-}] + 2[PO_4^{\,3-}] + [SiO(OH)_3^{\,-}] \\
& + [NH_3] + [HS^-] + \ldots - [H^+] - [HSO_4^{\,-}] - [HF] - [H_3PO_4] - \ldots \qquad (Eq.\ 2.1.1.1)
\end{aligned}
$$

Where the ellipses represent additional ions that may be more minor or negligible in concentration.

The charge balance framework of alkalinity is derived from Dickson’s work and is called the explicitly ‘conservative form’ of total alkalinity (Wolf-Gladrow et al., 2007), where in this case ‘conservative’ refers to conservative ions and alkalinity is defined as the difference between the total charge of conservative cations and conservative anions:

$$
\begin{aligned}
TA_{ec} = {} & [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] + \ldots - [Cl^-] - [Br^-] - [NO_3^{\,-}] \\
& - \ldots TPO_4 + TNH_3 - 2TSO_4 - THF - THNO_2 \qquad (Eq.\ 2.1.1.2)
\end{aligned}
$$

where the ellipses represent additional ions that are expected to be more minor in concentration and the TXX variables stand for the total contributions of the associated anions. This ‘conservative form’ is derived from the principle of charge neutrality, i.e., the sum of all charges is zero (Wolf-Gladrow et al., 2007).

Carbon removal associated with ERW deployments can thus be thought of through two interrelated lenses: that of acid-base reactions and proton balance, or that of excess base cation release and charge balance. As seen in Eq. 2.1.5 and Eq. 2.1.3, although the consumption of H^+ and production of HCO_3^- during feedstock dissolution is ultimately an acid-base reaction, the release of Mg^{2+} (or other base cations depending on the feedstock) can be used to track CDR using charge balance arguments. Embracing a cation and charge balance frame, netCDR quantification for an ERW project can be thought of as an exercise in quantifying how many excess base cations have been released from a feedstock, if they remain in solution, and how those base cations are variably charge-balanced by dissolved inorganic carbon (or have locked up inorganic carbon in a carbonate mineral lattice) through space and time. This can be done by tracking weathering products (i.e., excess cations) in deployment waters, monitoring their movement through different reservoirs in the soil profile with solid-phase mass balance techniques, or by trying to follow the carbon directly by monitoring the export of DIC from deployment soils or changes in the soil CO_2 efflux. We discuss the details of such measurement approaches in Sections 7.4-Section 7.6. It is important to note that there are processes which will not change alkalinity but will change the carbon balance (e.g., CO_2 degassing) and processes that will change base cation concentrations but not change the carbon balance (e.g., cation sorption that does not exchange acidity), which are further discussed in later sections.

2.1.2 Durability

Weathering products are transported through the soil profile and into downstream systems–groundwater, rivers and streams, and in many cases ultimately the ocean. The generation of DIC and its durable storage in downstream systems is critical for CDR efficiency. In open systems, the residence time of carbon spans many orders of magnitude, from the subsecond (e.g., aqueous carbonate system equilibration), monthly to yearly (e.g., dissolution of feedstocks on a field), centennial to millennial (e.g., storage of bicarbonate in the ocean), to the geologic (e.g.hundreds of millions of years of storage in carbonate rocks) (Hartmann et al., 2013; Hilton and West, 2020). The length of time that it takes a feedstock to dissolve, and the time until transport and durable storage (storage in a long residence time reservoir), is a key tension in open system CDR.

There are two primary durable storage pathways for CO_2 removed through weathering reactions: (1) storage as a carbonate mineral in downstream systems (Eq. 2.1.2.1); and (2) storage as dissolved inorganic carbon (DIC) in a long residence time reservoir (Eq. 2.1.4). Dissolved inorganic carbon includes all of the dissolved species of the 'carbonic acid system': dissolved CO_2, carbonic acid (H_2CO_3, which will only be present in small quantities), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (Eq. 2.1.3 and 2.1.4).

$$Ca^{2+}(aq) + 2HCO_3^{-}(aq) \leftrightarrow CaCO_3(s) + CO_2 + H_2O \qquad (Eq.\ 2.1.2.1)$$

The durability of carbonate mineral storage will be site dependent and require careful consideration of the many variables that allow for carbonate storage on geologic timescales, further outlined in Section 9.1.1.

2.2 Terminology of CDR

Throughout this Foundations document, concepts and terminology are used that have been developed and/or repurposed for use in the carbon removal market. We provide context for some of these concepts and how they apply to ERW; however, this should not be viewed as an exhaustive list of relevant terminology.

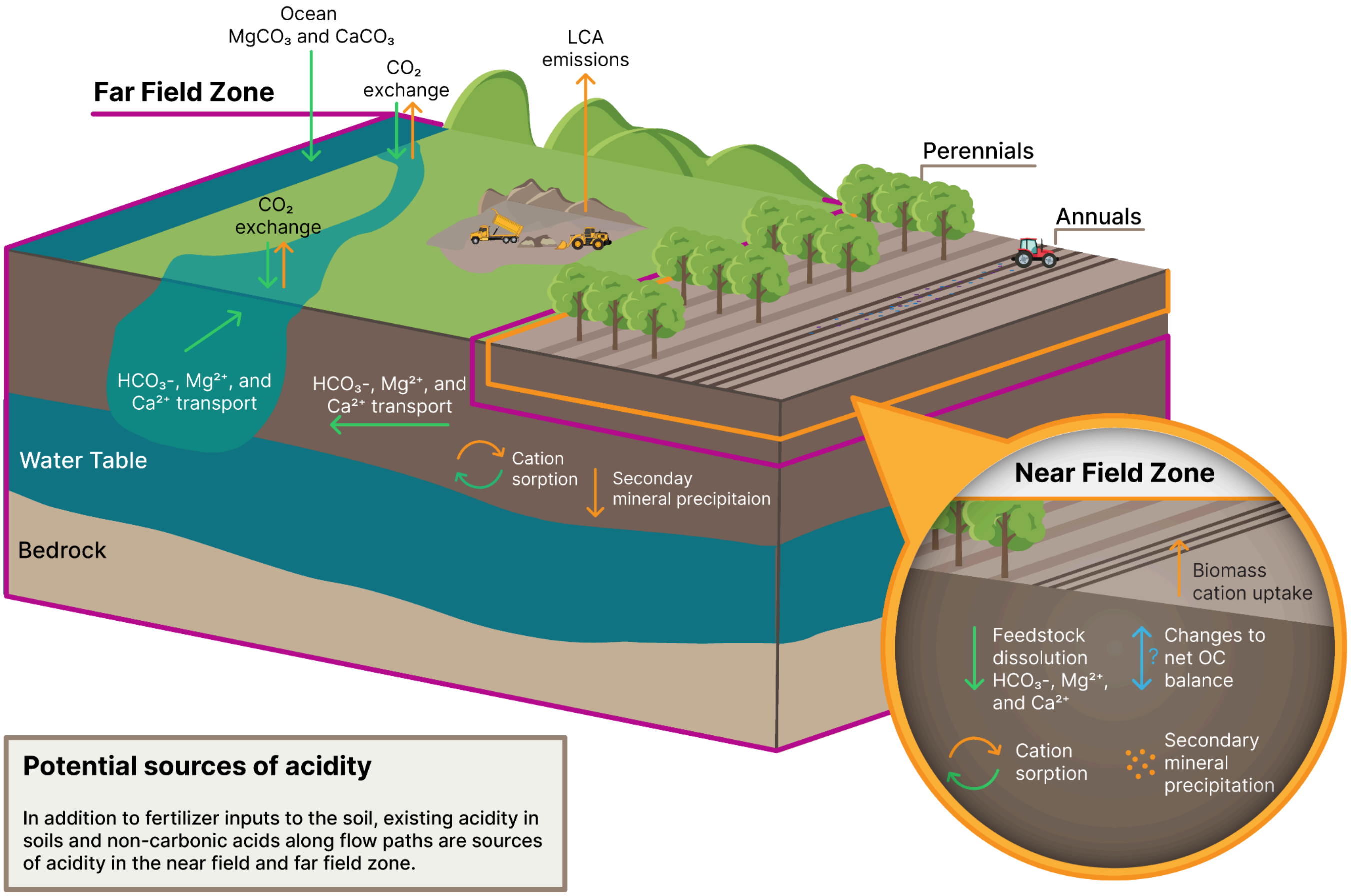
CDR in ERW deployments can be quantified at multiple stages of the deployment leading to different CDR estimates. In this document, we refer to **maximum potential CDR, potential CDR, and netCDR** as distinct estimates of CDR. We use **maximum potential CDR** as the maximum amount of CDR that could occur based on the feedstock composition and chemistry. Maximum potential CDR is calculated according to the modified Steinour equation (Section 6.2.2) as an estimate that does not take into account additional ERW considerations such as slow dissolution rates, losses, lags, etc. We use **potential CDR** to describe CDR driven by feedstock dissolution in the Near-Field Zone, before accounting for any subsequent carbon losses or inefficiencies (more on the NFZ in Section 2.3.1). This is equivalent to $CO_2e_{\text{Feedstock Dissolution}}$ (Section 5.4.1.2) in the term balance equation and is based on the amount of feedstock that has been observed to dissolve during the reporting period. We use **netCDR** to describe the potential CDR, minus the transient cation or carbon losses and any reductions in efficiency, minus any permanent losses in the NFZ and Far Field Zone (FFZ), and minus all process emissions (see full equation Section 5.4). It is to be expected that maximum potential CDR > potential CDR > netCDR.

Carbon storage in open systems takes place in 'pools' or 'reservoirs' where carbon has a long **residence time**, or the average time that carbon is estimated to spend in the reservoir. For ERW, reservoirs where DIC has longer residence times include long residence time groundwater and the ocean. In some systems, carbonates that form in the NFZ and along water flow paths may also have long residence times. When carbon is estimated to have a significant residence time (a normative decision -- see Section 9.1 for discussion) in a reservoir due to geochemical (e.g., thermodynamic or kinetic limitations) and/or physical (e.g., slow transport) processes that retain carbon in a region, this is referred to as a **durable** reservoir (sometimes discussed as permanence in the carbon removal market). Durable reservoirs for ERW are further discussed in Section 9.1.

Losses, **time lags**, and **reversals** are all reductions in netCDR that may refer to similar physicochemical processes but differ in their location and time scale. **Losses** are explicitly present in netCDR quantification and refer to a permanent loss of carbon in the NFZ and/or FFZ, i.e., they are a source of carbon to the atmosphere. In ERW quantification, this may be directly observed as a decrease in DIC, an increase in CO_2(g), or cation loss from the dissolved phase. **Time lags** are transient reductions in netCDR in the NFZ that occur after feedstock dissolution. They are the result of physicochemical processes that delay the export of DIC and cations from the NFZ as a result of ERW. Time lags may either be resolved in subsequent reporting periods if they are monitored for, or treated as losses in netCDR if they are not. In the FFZ, processes that may be a time lag and delay the delivery of DIC and cations to a durable reservoir are treated as losses as they are usually not directly monitored at this time. **Reversals** are permanent re-releases of removed carbon from the durable reservoir where the carbon was stored (e.g., pumping water from a groundwater system used for durable storage).

A key aspect of ERW quantification is comparing the deployment site to a **counterfactual** baseline. In ‘open system’ CDR projects, the ecosystem where the CDR project is occurring may already be removing carbon naturally, and the CDR project is intended to enhance the carbon uptake of that ecosystem. The **counterfactual** represents what would have happened in the absence of a deployment; i.e., quantifying the netCDR from a project must take into account a forward-looking, counterfactual baseline scenario as its base case.

2.3 Conformance Zones: Near-Field Zone and Far-Field Zone



Potential sources of acidity

In addition to fertilizer inputs to the soil, existing acidity in soils and non-carbonic acids along flow paths are sources of acidity in the near field and far field zone.

Figure 1. Net (negative) emissions associated with an ERW deployment are considered across three zones: 1) the Near-Field Zone (orange inset), which encompasses the upper portions of the soil profile; 2) the Far-Field Zone (purple inset), which includes the lower vadose zone, groundwater, and all downstream systems; and 3) life cycle (LCA) emissions, which include all emissions associated with the production, transport, and spreading of the alkaline feedstock. Modified from Calabrese et al., (2022). Green arrows represent the positive fluxes of DIC generated from ERW and orange arrows (or dots in the case of mineral precipitation) represent losses from the flux of DIC generated from ERW. Note that the precipitation of carbonate minerals will be both a loss and source term (see Eq. 2.1.2.1). Changes to SOC are depicted as a blue arrow due to the variable responses of SOC to alkaline feedstock addition.

The overall framework for ERW quantification and carbon accounting presented here divides the full system into two non-spatially overlapping “conformance zones”, which we define as the **Near-Field Zone** and the **Far-Field Zone**.

The Near-Field Zone (NFZ; depicted in the orange box in Figure 1) is the region of the upper soil profile in which the ERW deployment must be directly tracked through empirical measurements, accounting for feedstock dissolution, alkalinity sinks, and other carbon fluxes that impact netCDR. This includes directly tracking both the magnitude of these fluxes and the timescale over which they occur.

As weathering products and DIC travel further down the soil profile, they are then exported into the Far-Field Zone (FFZ; depicted in the purple box in Figure 1). Section 4 provides a detailed discussion of how the spatial extent of the NFZ and boundary between the Near-Field and Far-Field Zones can be defined in a site-specific way. The FFZ encompasses the entirety of the flow path traveled by the weathering flux en route to durable storage after exiting the NFZ. This can include deeper portions of the soil profile and lower vadose zone, groundwater systems, surface waters, and the ocean. While weathering and the subsequent export of carbon and alkalinity out of the NFZ can and should be empirically measured, models and geochemical calculations must be used to constrain carbon dynamics in the FFZ (see Section 9).

We consider the Near-Field and Far-Field Zones separately as they can represent vastly different spatial scales and time horizons, present fundamentally different monitoring challenges, and can thus have very different uncertainty profiles regarding the magnitude of carbon impact through time. The FFZ encompasses much larger spatial scales and longer time horizons over which to consider both reactions and transport, and as such, represents a more significant monitoring (and modeling) challenge.

The other key category of carbon fluxes that must be quantified is project **life cycle emissions**, which can take place both upstream of the deployment and throughout the project lifetime (Section 10). These emissions are considered and estimated separately from NFZ and FFZ carbon dynamics.

These conformance zones are used to develop the high-level term balance presented in Section 5.2 where netCDR is quantified according to:

$$CDR_{Net,\,RP} = CO_2e_{NFZ,\,RP} + CO_2e_{FFZ,\,RP} - CO_2e_{LCA\ emissions,\,RP} \qquad (Eq.\ 5.2.1)$$

where $CDR_{Net,\,RP}$ is the net CO_2 removed by the ERW deployment during the reporting period, $CO_2e_{NFZ,\,RP}$ is the net additional CDR in the NFZ during the reporting period, $CO_2e_{FFZ,\,RP}$ is the calculated net additional CDR in the FFZ assigned to the reporting period, and $CO_2e_{LCA\ emissions,\,RP}$ is the calculated life cycle emissions assigned to the reporting period.

2.3.1 Overview of the Near-Field Zone

Although the ERW deployment is initiated with soil baseline sampling and the actual spreading of feedstock, no carbon can be removed from the atmosphere until the feedstock dissolves and alkalinity is released from the mineral lattice into the soil system (Section 8.2). We consider feedstock dissolution to represent the initiation of carbon removal, or when *potential* CDR is generated. However, feedstock dissolution is not the end of the NFZ story (Section 5.4.1 and Section 8).

The NFZ hosts a suite of biogeochemical processes that can lead to both permanent and transient losses of base cations, and therefore alkalinity and carbon, as well as direct losses of carbon. For example, base cations can be incorporated into secondary carbonate minerals and other phases that commonly form within the soil profile, removing alkalinity from the system and therefore reducing carbon removal efficiency (e.g., Eq. 2.1.2.1, also see Section 8.5, Section 8.6). Shifts in soil chemical and physical properties induced by ERW deployments can also result in changes to the net carbon flux through connected biogeochemical pathways (e.g., by influencing the soil *organic* carbon balance). For this reason, additional measurements or models are required in the NFZ beyond tracking feedstock dissolution to quantify these permanent and transient sinks of alkalinity and carbon as part of carbon removal deployments. The significant NFZ processes discussed here include: pH dynamics and non-carbonic acid weathering (Section 8.3), cation sorption (Section 8.4), secondary carbonate formation (Section 8.5), secondary silicate and other secondary phase formation (Section 8.6), alkalinity loss due to biomass uptake (Section 8.7), and changes to the net organic carbon balance (Section 8.8).

Importantly, these biogeochemical processes may lead to permanent or transient changes to the net carbon balance, and the timescales of reversal for transient carbon or alkalinity sinks can vary from seasons to decades. This leads to consequential questions about the temporal dynamics of CDR, and how to develop a consistent accounting framework that can account for carbon gain and loss processes that occur over very different timescales in ERW quantification (Section 5.3).

Table 1. Components of the NFZ term balance. Here we present a summary of the carbon fluxes relevant for quantifying ERW in the Near Field Zone and their considerations. Note that the first row describes the integrated weathering flux which integrates the other components listed and is relevant for Endmember Approach 1 (excluding the row on changes to soil organic carbon).

Description of term	Considerations for CDR quantification	Recommendations for near-term path forward
Integrated weathering flux The cumulative weathering signal of the dissolved phase, including the integrated effects of feedstock dissolution, cation sorption, secondary carbonate formation, secondary silicate formation, and alkalinity loss due to biomass uptake.	The integrated weathering flux is only required for the aqueous phase approach and is part of one endmember approach for constraining the NFZ balance. If not measuring the integrated weathering flux, the components of carbon sources and losses must be accounted for individually (see below).	• Measure dissolved weathering products directly as they are generated in, and exported from, the NFZ. • Aqueous phase measurements should be taken at the end of the NFZ (or in drainage waters or downstream catchments) in order to calculate a net export flux of weathering products.
Feedstock dissolution The dissolution of minerals in the feedstock after application on the deployment site (potential CDR).	Impacted by temperature, pH, variable water content and fluid residence time, kinetic inhibitors and dissolved phases that enhance rates, the formation of secondary phases, and the impacts of biological processes.	• Collect direct empirical measurements that capture alkalinity release in the solid phase via solid-phase, mass balance-based approaches. • It is highly recommended that feedstock application rates be empirically constrained by measuring the soil concentration of an immobile element or isotope ratio before and after feedstock application.
pH/non-carbonic acid weathering Chemical weathering done by acids other than carbonic acid such as sulfuric, nitric, or organic acid, or in low pH soil.	• Weathering by non-carbonic acids does not lead to base cations charge-balanced by DIC, but does neutralize acidity that may have otherwise reacted with bicarbonate and caused CO2 degassing. • In strongly acidic soils (pH < 4.5-5, pCO_2 dependent), the cations released by weathering are charge-balanced by very little bicarbonate.	• Any non-carbonic acid weathering in the NFZ should be removed from netCDR. • Constrain non-carbonic acid weathering directly through aqueous phase measurements or estimate strong acid addition/production, fully discount from netCDR, and account for degassing. • For now, assume organic acids will be degraded following reaction with silicate minerals and generate an equivalent amount of DIC as carbonic acid weathering (Working Group 2). Do not include in the term balance. • To account for low pH weathering, monitor for declines in exchangeable and bound acidity.

Description of term	Considerations for CDR quantification	Recommendations for near-term path forward
Cation Sorption Adsorption of cations onto soil particle surfaces (e.g., clay minerals, organic matter, mineral oxides).	Cation sorption can act as a transient alkalinity sink; when base cations exchange for acidic cations on exchange sites, the removal of those cations from solution 'undoes' any CDR they were driving (or equivalently, the proton release into solution drives CO2 evasion). As base cation concentrations in the soil solution decrease or the soil begins to re-acidify, these cations can eventually re-enter the soil solution and drive CDR.	- If $CO_2e_{NFZ, RP}$ is constrained by the time-integrated alkalinity flux at or beyond the end of the NFZ, alkalinity loss from cation exchange processes has already been accounted for–no direct measurement of the exchangeable fraction required. - If feedstock dissolution is constrained independently and netCDR in the NFZ is calculated as the sum of sources and sinks, cation exchange capacity and base saturation or exchangeable acidity should be quantified using established methods.
Secondary carbonate formation Precipitation of carbonate minerals (e.g., calcite) in the soil profile.	Secondary carbonate formation in the soil profile and downstream systems can represent a stable (and measurable) store of atmospheric CO2 for ERW deployments with non-carbonate feedstocks. However, secondary carbonate formation reduces (and for carbonate feedstocks, negates) potential CDR by removing cations and charge-balancing carbonate alkalinity from solution.	- Can be directly monitored through changes in soil inorganic carbon stocks relative to business as usual plots. - Location-specific context will be needed to determine the probability of carbonate formation and how to account for it. - Potential strong acid weathering should be considered if reductions in SIC stocks between reporting periods is observed.
Secondary silicate formation Secondary silicate minerals (e.g., clays), amorphous Si, and Fe/Al oxy-hydroxides can form in many potential deployment sites, though other secondary phases–for example, Ca-phosphates–can be formed in specific systems.	Secondary silicate phases can form quickly (hours to days), and their formation may be spatially and temporally separated from the initial weathering reaction. Their formation will reduce CDR efficiency by removing base cations from solution. It is difficult to identify regimes where secondary silicate or Fe/Al oxy-hydroxide could be assumed to be fully negligible (Working Group 2), and therefore should be accounted for in netCDR.	- Potential quantification options may depend on the secondary phase of interest. - It is not recommended that early-stage commercial deployments be required to independently constrain NFZ alkalinity loss through secondary silicate formation due to challenges associated with direct quantification of secondary silicate phases. - Placing bounds on the potential netCDR loss through stoichiometric arguments may be a good place to start.
Biomass uptake of base cations Plants retrieve nutrients from the soil solution, including base cations such as Ca2+, Mg2+, K+, and Na+; generally accompanied by a release of protons to maintain charge balance within the plant.	Biomass uptake of base cations 'undoes' any CDR that was being driven by the base cations in solution; or equivalently, drives CO_2 evasion.	- Plant uptake should be estimated through direct measurements of the base cation content of relevant biomass, including biomass that is removed from the field. - Sufficient data does not yet exist for use of predictive frameworks to estimate element-specific plant uptake for different crop types under different growing conditions (Working Group 2).

Description of term	Considerations for CDR quantification	Recommendations for near-term path forward
Changes to (soil) organic carbon stocks An increase in soil organic carbon via accumulation or a decrease in soil organic carbon via respiration.	Observations thus far have demonstrated variable responses of SOC to alkaline feedstock addition in field trials, mesocosm studies, and laboratory experiments. Small changes in the balance between photosynthesis and respiration, or a destabilization of existing soil organic carbon stocks, could substantially reduce (or even completely negate) CO_2 uptake by an ERW deployment.There are some soil conditions that are at particularly high risk for SOC loss resulting from an ERW deployment.	● ERW intervention's potential impact on soil organic carbon stocks and the net organic carbon balance is nascent, and we do not yet have enough data to consider the potential for SOC mobilization resulting from an ERW deployment to be sufficiently de-risked (Working Group 2). ● Deployments should not be undertaken under conditions that have been deemed at 'high risk of substantial SOC loss' until sufficient evidence has been generated to de-risk the impact of an ERW intervention on organic carbon cycling in such systems. ● For deployments not considered 'high risk', monitoring of bulk SOC stocks should be implemented on a representative sub-plot within the deployment area and corresponding 'business as usual' or negative control plot. ● We do not recommend that any changes to SOC stocks be directly incorporated into netCDR quantification for commercial ERW deployments at this time. ● SOC monitoring data should be transparently reported in a timely manner.

2.3.2 Overview of the Far-Field Zone

Once the weathering flux is exported from the NFZ, it passes into the FFZ, which we separate into three spatial regimes: the (lower) vadose zone and groundwater systems (Section 9.2), surface water systems (Section 9.3), and marine systems (Section 9.4).

When considering the FFZ, it is first important to identify the ultimate carbon storage reservoir and the probable transport path to that reservoir (Section 9.1). For example, while in many systems carbon will ultimately be stored as DIC in the ocean, some deployment areas may drain into long residence time groundwater systems that can be considered a durable storage reservoir–removing the need to consider potential losses in systems further downstream. Carbon may also be durably stored in carbonate minerals formed in the soil profile or along the flow path.

Importantly, processes operating in the FFZ can lead to carbon gains and losses through time, and net additional CDR can be generated in the FFZ. CDR in the NFZ is dictated by the amount of carbon captured as DIC that charge balances alkalinity released from feedstock dissolution *within the soil profile*. Evolving conditions along the flow path and subsequent reactions can change the alkalinity:DIC ratio. For example, weathering reactions in highly acidic soils will consume protons in the soil profile, but do not lead to any CDR in the NFZ, as the base cations released from the feedstock will not be charge-balanced by DIC. However, when these cations eventually reach a downstream, higher pH surface water system within the

FFZ, the carbonate system can re-equilibrate and drive additional CDR. Similar arguments can be made for non-carbonic acid weathering of alkaline feedstocks (Section 8.3).

Despite this, the carbon quantification framework developed here only considers *net losses* in the FFZ at this time. This conservative approach is taken, as confidently predicting FFZ CDR would require robustly validated, catchment-scale models capable of simulating the site-specific proton, alkalinity, and carbon balance as a function of time for both counterfactual and deployment scenarios. The development of such predictive frameworks remains nascent, but we discuss the outlook for simulating FFZ processes (Section 9) and explore the implications of not including FFZ CDR in project-level quantification–from how this influences our understanding of CDR associated with carbonate weathering and liming (Section 5.5.1), to how we interpret the potential carbon benefits of titrating acidity from soil systems (Section 8.3).

Table 2. Considerations for the FFZ. Fluxes that should be considered for each spatial regime in the FFZ and recommended direction.

Spatial Regime	Fluxes to consider in a comprehensive accounting	Recommended near-term path forward (minimum viable product)
Lower vadose zone and groundwater flow paths	• All the fluxes in the NFZ also apply in this region. • It will be important to understand and identify permanent alkalinity sinks and changes to counterfactual alkalinity generation. • Exchange with the atmosphere is limited or nonexistent.	Largely a priority area for research and development: • Not currently feasible to require monitoring or modeling of processes in the deep vadose zone and along groundwater flow paths in commercial ERW deployments. • Undertaking deep vadose zone monitoring or installing groundwater monitoring wells in a select subset of commercial deployments, where applicable and feasible, is recommended.
Surface water systems	• Outgassing caused by DIC system equilibration. • Carbonate mineral burial. • Changes to organic matter respiration and metabolic activity in stream/river systems, including the influence on aquatic vegetation that directly takes up bicarbonate. • Authigenic clay formation and reverse weathering. • Bedrock interaction with solution and changes to counterfactual alkalinity generation. • Changes to nutrient export and nitrogen cycling.	Focus primarily on: • Outgassing caused by DIC system equilibration. • Carbonate mineral precipitation (assume it doesn't re-dissolve) It is recommended that practitioners assess the potential for net CO_2 loss due to these processes at a minimum in two spatial regimes: in the immediate discharge zone (i.e., the surface water system the weathering flux from a deployment is draining into), and in the major river system of the deployment catchment (i.e., the highest order segment in the deployment catchment).
Ocean	• CO_2 evasion due to carbonic acid system equilibration in the coastal ocean. • Carbon and alkalinity feedbacks due to changes to surface ocean chemistry.	Focus primarily on: • CO_2 evasion due to carbonic acid system equilibration in the coastal ocean. At a minimum, practitioners should derive a conservative assumption of evasion from carbonic acid system equilibration by

	- Carbon and alkalinity feedbacks due to changes to diagenetic reactions in shallow marine sediments. - Long timescale marine carbonate burial.	considering the thermodynamic storage efficiency as a worst-case scenario, assuming complete equilibration with atmospheric CO_2 at representative temperature, salinity, and current atmospheric pCO_2.

2.4 Document Explainer

As discussed in Section 1, this document is the result of a community process to develop guidelines for ERW practitioners with a review of the initial draft. However, there remain some areas where Cascade Climate expertise was used to fill in gaps where it was needed. As a result, there are several different ways that guidance in this document came about, including Working Groups providing recommendations, joint Working Group and other problem solving sessions resulting in recommendations brought to the Working Groups, Cascade Climate filling in recommendation gaps, and places where there is not yet a direct recommendation. As a result of this melded process, it is impractical to identify the path of each individual recommendation; however, practitioners should be aware that recommendations came through these varied pathways and draft language was reviewed by Working Group members.

There are three groupings of guidance present in this document. The first are areas where there is ‘no recommendation at this time’ due to the lack of clarity in the literature and state of ERW. Potential forward approaches may be presented, but definitive recommendations are not provided. The second is a ‘recommendation’, which is the current suggested path forward out of the provided approaches. The final is 'best practice’, which is presented when there is an established best practice that should clearly be followed.

We also include calls to action at several locations within this guidance that indicate areas where advancement could be made to reduce substantial uncertainty or open questions in ERW quantification. Finally, there are nods throughout the guidance to opportunities for research and development (R&D), which are listed chronologically in an R&D appendix for ease of reference.

3 Guidelines for Site Characterization

When approaching a new ERW project location, arguably the single most important step in CDR monitoring and quantification is to 'know your system'. In practice, this means being able to answer a series of questions that can provide justification for choices made during CDR quantification and serve to guide a given quantification approach.

In the NFZ, these questions include, but may not be limited to:

- What types of soils are present at the deployment site? What is the soil pH, buffer pH, CEC, base saturation, total alkalinity, SOC & SIC concentration, texture, bulk density, etc.? What is the pH, total alkalinity, and/or DIC concentration of soil porewater? What are the concentrations of other cations and anions of interest in soil porewater? How do these parameters vary with time (e.g., seasonally)? How do they vary spatially?

- How deep is the soil? How do soil physical and chemical properties vary with depth? What are the depths and character of soil horizons? At what depths are there significant changes in the horizontal subsurface structure?

- Are there abrupt changes in soil permeability (e.g., clay layers, plow pans or other indurated layers, caliche, fractures) that will impact how water moves through the soil profile?

- What is the hydrologic regime of the system? How much precipitation does the site receive and what does this look like seasonally? What is the expected irrigation scheme? Do you have access to data on irrigation water chemistry?

- Where does water go when precipitation lands on the soil surface? How significant is overland flow, subsurface preferential flow, etc? What are likely flow paths through unsaturated soil and into groundwater (if applicable)? Are there tile drains or other engineered modifications to flow?

- What is the land use history? What is the prevalence and history of inputs for agronomic pH control, fertilizer use, and crop rotation?

- What is the expected crop regime during the deployment interval? What is the rooting depth? What are tillage practices? How will the feedstock be incorporated into the soil?

- How does this baseline soil chemistry, water chemistry, water balance, and anticipated water movement through the soil impact signal resolvability of different monitoring approaches? Are different monitoring approaches required in treatment and control plots (inclusive of business as usual and negative control plots, Section 5.5.3.1)? Given these site specific conditions, where does it make sense to install monitoring infrastructure (e.g., where / at what depth should lysimeters be installed, etc.)?

In the FFZ, these questions include, but may not be limited to:

- What is the intended durable storage reservoir; is it carbonate minerals, dissolved inorganic carbon stored in a sufficiently long residence time groundwater system, or dissolved inorganic carbon in the ocean?

- If the anticipated storage reservoir is a long residence time groundwater system, do you have sufficient evidence to demonstrate that fluids infiltrating through soils of the deployment site predominantly drain into a flow path that has a mean residence time in excess of the durability threshold (Section 9.1)?

- If waters draining from a deployment site are ultimately transported to the ocean, what is the most probable path they take to get there? What does the regional flow system look like? What is the stream and river system that the deployment ultimately drains into (if any)?

- What monitoring and data already exists along the FFZ flow path? What monitoring approaches would be additive and informative for justifying transport and/or storage durability in the FFZ?

- What CDR losses or additional removals might be happening beneath the NFZ boundary but still within the vadose zone at the deployment site? How deep is the unsaturated zone and the potential for extending NFZ processes and fluxes with depth? Are secondary precipitates a concern in the unsaturated FFZ beneath the NFZ?

- How deep is groundwater, and therefore where will weathering products encounter reduced CO_2(g) and O_2(g) fluxes? When and where will weathering products be transported by saturated flow rather than unsaturated flow?

- At the catchment scale, what is the distribution of groundwater residence times? How might stream or watershed drainage water chemistry measurements be interpreted? Is there historic information on C-Q (concentration-discharge) relationships for the catchment to aid in water chemistry interpretation?

Some of this initial period of site-specific information gathering can happen with desk studies that look into previously published literature, large compilation datasets, or from data provided by farmers. However, collecting other site-specific information may require a pilot study to characterize baseline conditions and site characteristics. Ideally, there will be multi-year data available for a location. The importance of practitioners intimately understanding the ERW system for a given deployment location cannot be overstated.

4 Defining the Near-Field Zone

As described in Section 2, the Near-Field Zone (NFZ) is operationally defined as the region of the soil profile in which project developers must directly track and account for weathering, alkalinity sinks, and other carbon fluxes that impact netCDR. In an idealized framing, after weathering products pass out of the NFZ, carbon losses do not directly influence atmospheric CO_2 concentrations until the weathering products return to a downstream surface water system (Section 9). As such, below the lower depth of the NFZ, transient alkalinity loss processes in the soil profile (e.g., cation sorption or transient carbonate precipitation) are not incorporated into the carbon accounting framework proposed here. Net carbon or alkalinity losses following this export from the NFZ–in the lower vadose zone, groundwater and surface water systems, and in the marine environment–are considered separately as components of the FFZ carbon balance (Section 9).

Defining the NFZ requires a judgment of the depth range through which direct measurements are critical for quantifying netCDR. Although the depth to which carbon cycling is significant in an ecosystem is ultimately a normative and somewhat subjective decision, it has large implications for both the operational difficulty of an ERW deployment and on the timing and magnitude of calculated netCDR. There was consensus amongst Working Group 1 that it is critical to include deeper soil processes, including cation sorption and secondary mineral precipitation, in CDR quantification. Datasets representing these processes in deeper soils are urgently needed for accurate parameterization and validation of soil models that represent ERW processes (Section 8.10). Such data are also critical for realistically quantifying net carbon removed for a given project, and will be central for iterative improvement of frameworks for assessing the NFZ in ERW project design.

Given the operational demands of taking deeper soil measurements, the discussion and recommendations presented here aim to strike a balance between ensuring that enough data are collected to capture and help elucidate the core components of the net carbon balance (Section 8) throughout the soil profile, without posing an infeasible operational burden on early-stage ERW projects.

4.1 Site-Specific Considerations for Defining the Near-Field Zone

The spatial extent over which the weathering flux should be tracked through the soil profile may vary substantially between different deployment contexts. Below, we detail potential approaches and considerations for how the lower depth of the NFZ could be defined in a site-specific way, along with advantages and challenges associated with each approach.

Approach 1: The NFZ ends at the depth of the water table. Terminating the NFZ at the water table is a convenient mechanistic distinction in that it aligns with sharp changes in weathering regimes, redox conditions, fluid transport processes, and the rate at which CO_2 exchanges with the atmosphere (molecular diffusion of CO_2 is orders of magnitude slower in saturated systems than in air (Haynes, 2014; Jähne et al., 1987)). However, water table depth varies immensely between different regions (Fan et al., 2013) — in some systems, groundwater is reached within 10's of centimeters, while in others this would entail tracking fluxes 10's of meters into the critical zone. For such deep water tables, direct measurements would be both infeasible and of diminishing utility. The water table depth is also not fixed in many areas, with marked seasonal fluctuations or changes through time, further complicating the operational implementation of a NFZ definition based on the water table depth (Fan et al., 2007). However, this definition may be ideal for systems with shallow water tables.

Approach 2: The NFZ ends at the estimated rooting depth of the cropping system. Biological processes associated with plant roots have a strong impact on both weathering reactions (Verbruggen et al., 2021; Vicca et al., 2022) and the geochemical conditions in the rhizosphere (Pett-Ridge and Firestone, 2017), and plants directly take up cations (and small amounts of DIC (Enoch and Olesen, 1993)) through their root systems. It could thus be argued that cation and carbon fluxes should at least be tracked through the depth of the rooting zone. However, this may also be operationally infeasible in some systems, as while the root systems for most commercially cultivated agricultural crops do not extend much below 1 meter (Jackson et al., 1996; Ordóñez et al., 2018), the root systems of some crops–particularly perennials and trees–can extend several meters deep (Smith et al., 2005; Stone and Kalisz, 1991). This definition may be ideal for systems with relatively shallow rooting depths and deep water tables.

Approach 3: The NFZ ends at the depth at which diffusive exchange of CO_2 between the atmosphere and soil water is sufficiently slow. This definition has the advantage of restricting the NFZ to a depth where the ERW project will immediately impact atmospheric CO_2 concentrations—any transient or permanent losses of carbon or alkalinity that occur above this depth would result in a near-immediate release of CO_2 to the atmosphere, undoing the associated carbon removal. This definition supports the assumption that permanent alkalinity losses below this depth of sufficiently slow diffusive exchange would not be considered a carbon loss in netCDR quantification until the dissolved weathering flux re-enters contact with the atmosphere in a surface water system, and transient alkalinity sinks below that depth may not result in a reduction in netCDR at all.

While theoretically compelling, this definition is challenging to implement in practice due to the potential high temporal variability of this boundary. Modeling work would need to be done to determine how this depth varies as a function of time for a given soil (soil diffusivity is a function of both the physical properties of the soil and water content (e.g., Moldrup et al., 1999)). Furthermore, the depth at which diffusive exchange with the atmosphere may occur on the order of hours or days could in practice extend well beyond a meter, rendering this approach operationally challenging for project developers.

Approach 4: The NFZ ends at a soil horizon boundary, such as at the estimated average lower depth of the final B-horizon across the field. Generally, using soil horizons to define the base of the NFZ could be a reasonable and accessible method given that important soil properties being measured (e.g., pH, base saturation, bulk density) and soil processes relevant for cation and carbon accounting in ERW deployments often exhibit discontinuities at soil horizon boundaries. B-horizons often represent illuviated soil layers in which secondary minerals have accumulated over time and can have elevated cation exchange capacity, and thus represent an important region to observe in quantifying carbon removal through enhanced weathering (e.g., Weil and Brady, 2016). Similarly, in soils with calcic horizons, the base of the NFZ could be defined to encompass those horizons, as areas of increased probability of long-lived secondary carbonate formation.

One primary challenge with implementing this method is that determining the depth of particular soil horizons at a given site may be challenging in practice, given the somewhat subjective nature of horizon identification and given that horizon depths can vary across a field or deployment site. Nevertheless, we would encourage the consideration of using soil horizons to define the NFZ in early-stage deployments.

Approach 5: The NFZ ends at the tillage depth, plus a small (e.g., 10 centimeter) buffer. This choice reflects the fact that measurements should at a minimum extend to the depth at which the feedstock is incorporated (i.e., via tillage) within the soil profile, along with a buffer to account for potential deeper mixing and spatial heterogeneity in tillage depth at the field scale. The advantage of this approach is its operational simplicity, in many cases only requiring sampling of shallow soils within the traditional "agronomic" zone (~30 centimeters). However, prescribing this approach as the NFZ across all deployments is problematic, given that it excludes the effects of important soil processes that should be readily measurable in the field and that will have a clear impact on netCDR calculations (e.g., cation sorption and secondary mineral formation). This is particularly true prior to rigorous and widely accepted validation of predictive models of soil carbon and alkalinity dynamics that would allow for modeled constraints on deeper soil processes. On the other hand, this definition may be beneficial for systems where a plow pan or shallow clay layer limits water infiltration significantly past the regularly plowed layer.

Approach 6: The NFZ ends at a predetermined, fixed soil depth (e.g., 30 centimeters or 1 meter). This approach has the advantage of being generalizable to a wide variety of fields, and has the operational benefit of creating more predictability in the sampling process. Developing high-level protocols and methodologies independent of the context of any particular deployment site will likely need to lean on setting fixed depths for the end of the NFZ, at least as a default approach until further site-specific information is provided. The clear downside of this approach is that any choice of fixed depth will be a semi-arbitrary decision, may be largely independent of the details of any particular soil system, and may miss processes within the soil column that have a substantial impact on the timing and magnitude of netCDR.

4.2 Considerations Based on Field Hydrology

Often, the simplifying assumption is made that the movement of water and solutes through the soil occurs solely through vertical infiltration. However, some soil systems and crop management regimes plainly violate this assumption. Here, we outline some of these cases and provide recommendations for how to delineate the NFZ in these systems.

The **presence of hardpans, plow pans, caliche layers, or other soil layers may prevent substantial deeper vertical infiltration** of water through the soil profile. This presents two interrelated challenges: (1) sampling beneath this layer may be operationally infeasible; and (2) the flow path of water and dissolved weathering products may be lateral along the impermeable or semi-permeable soil layer instead of through the layer. In these cases, it may be operationally necessary for the NFZ to extend only down to this layer. However, it is important to consider the likely flow path of water when designing a sampling strategy and to account for NFZ fluxes (e.g., cation sorption and secondary mineral formation) along that flow path. Notably, there may also be localized areas of high permeability or preferential flow within otherwise low permeability layers; these should be considered when determining the likely flow path.

Similarly, the **presence of a high water table** may necessitate an exception if a methodology or protocol defines a default NFZ depth and the water table is shallower than the prescribed depth. In such cases, we recommend that the water table depth be considered the end of the NFZ.

One significant example of a crop management regime where multiple of these hydrological considerations may be important is in rice paddies. The hydrology of rice paddies is complicated—the plowing of saturated soils often creates a plow pan that prevents vertical water infiltration, but raised "bunds" that form boundaries around the flooded field perimeter stay unflooded, so water tends to runoff horizontally in the field and infiltrate vertically downward into the bund, where hydraulic conductivity is higher (Neumann et al., 2009). In addition, cracks often form over time after plowing events, which form preferential flow paths for fluid infiltration within the field itself (Neumann et al., 2009). This complexity means that it is difficult to assign a fixed depth across the field that represents the end of the NFZ. To appropriately capture the reactive transport of weathering products through the NFZ, some level of monitoring of deeper portions of the soil profile within the bunds is likely needed in such systems.

In general, project developers should be cognizant of field hydrology when making and justifying sampling locations and interpreting measurements (Section 3).

4.3 Operational Considerations and Challenges with Deeper Measurements

ERW quantification practices from field trials and early commercial deployments often focus measurements on shallow soils, given both the greater ability to resolve a weathering signal and the operational challenges of taking deep samples. While it is critical that the ERW community prioritizes deeper measurements in the coming years in order to better understand alkalinity dynamics in the soil profile, this must be done while transparently navigating tradeoffs associated with operational feasibility. Here, we highlight some of the operational challenges encountered by both project developers and academic researchers when routinely taking deeper soil measurements.

While shallow soil cores can often be extracted by hand using push cores or augers, collecting deep soil cores may not be easily integrated with traditional agronomic practice, and may require bringing heavy machinery (e.g., power augers) to the field site. Heavy equipment may pose a risk of soil compaction, and access roads must exist to accommodate the size and weight of a drill rig and towing vehicle. Additional challenges exist in perennial cropping systems (e.g., sugarcane), where sampling events occur with crops still in the soil, making it challenging to bring machinery on-site for deep sampling without causing potential damage to the crop. More broadly, it was stressed by practitioners with field experience that a requirement for deeper sampling would impose longer timelines and higher labor costs on each sampling event, given that sampling a particular deployment may require a multi-day effort instead of being a shorter, simpler task.

One final important challenge with deep measurements is that the parameters being measured at depth, from cation concentrations on the exchangeable fraction to soil inorganic carbon, are often highly spatially variable, and so high sampling densities will likely be needed to detect a field-scale change in these parameters above the baseline soil variability. **In particular, one-off or sporadic deep cores that do not account for baseline variability of the parameters being measured, as well as the analytical error of measurement techniques, may provide a qualitative sense of the in-field alkalinity dynamics but have limited utility compared to more statistically robust and quantitative analyses for which uncertainty can be reported.** A large number of deep samples may be required to constrain each component of the NFZ term balance at the field scale.

Given these challenges, it is important that projects maximize the likelihood that deep measurements yield high-quality data that can meaningfully contribute to our collective understanding of deeper soil processes and help quantify CO_2 removal outcomes. These operational challenges are not impossible to overcome, and must be seriously considered in the coming years as an upfront investment so that the community has the datasets it needs to rely more heavily on models for predicting feedstock dissolution and cation transport, storage, and exchange in the soil column for ERW deployments undertaken at scale (Section 8.10).

4.4 Synthesis and Call to Action

The considerations outlined in Section 4.1-4.3 demonstrate that site-specific factors should play a strong role in determining the spatial extent of the NFZ, as informed by an initial site characterization (Section 3). All site-specific considerations used to delineate the NFZ should be clearly justified and documented for a given deployment.

In some cases, the decision of how to define the NFZ may have substantial impacts on the overall netCDR quantification, both in terms of the magnitude of tonnes quantified and the time horizon over which these tonnes are achieved (Section 5.3). Comparative analyses that demonstrate the implications of choosing different definitions of the NFZ on the same field would be a helpful step to guide decision making and future protocols and methodologies.

Recognizing the simultaneous importance and operational challenge of taking deeper measurements, a near-term approach that balances the imperative to sufficiently characterize the system with operational constraints could be to focus comprehensive sampling that includes direct characterization and monitoring of deeper soils on targeted representative subplots of larger deployments and/or more highly monitored demonstration sites.

In order for the data to be quantitatively useful, deeper soils must be sampled at a sufficient density to resolve a signal above baseline spatial variability of measured parameters; a smaller number of demonstration sites where the necessary level of sampling resolution is achieved in representative treatment-control blocks (Section 7.2) is preferable to sporadic deep measurements that cannot meaningfully inform quantitative CDR estimates.

Near-term quantification protocols and methodologies could consider taking a hybrid approach, in which the NFZ is defined to a shallower (but still site-specific) depth on most fields, but on a small representative subset of each deployment the NFZ is set deeper (i.e., secondary mineral precipitation and cation sorption dynamics are quantitatively constrained at depth). For example:

- On a majority of the deployment area, the minimum depth of the NFZ could be set *to the deeper of* a) 20 centimeters, or b) the tillage depth plus a 10 centimeter buffer. A depth of 20 centimeters (or 8 inches) is commonly recommended for “surface soil” agronomic samping (e.g., USDA, 2022). In addition, it is important to ensure measurement to at least the depth at which the feedstock is incorporated through tillage, with a 10 centimeter buffer to account for both potential additional vertical feedstock transport and spatial heterogeneity in tillage depth. As per above, this definition should be informed in practice based on site-specific considerations (e.g., site hydrology).

- On a small representative subset of the deployment area, a deeper definition of the NFZ boundary is utilized, e.g., between 60-100 centimeters, or the end of a relevant soil horizon. This depth is intended to interrogate secondary mineral precipitation and cation sorption, where soil porewater is still very likely in rapid diffusive exchange with the atmosphere.

Importantly, solid-phase mass balance methods to quantify feedstock dissolution (see Section 8.2) may not be able to accommodate a sampling depth of the full NFZ and still be able to resolve a signal. If this is the case, project developers are encouraged to sample a shallower depth interval to constrain feedstock dissolution; however, these measurements must be supplemented with other methods of constraining cation sinks and alkalinity export between the ‘feedstock dissolution zone’ measurement depth and the end of the NFZ. As a general rule, it may be challenging to generate resolvable signals if an entire deep core is homogenized; separate analysis of different depth intervals is recommended whenever analyzing deep soil cores.

In the context of commercial deployments, we strongly recommend that in the near-term, these “deeper NFZ” subset fields be included in the MRV cost of the deployment, given the central importance of deep-soil processes to the ultimate netCDR quantification. Quantified carbon removal outcomes and measurement costs may be substantially different in fields with shallow versus deeper NFZs. At this stage of development in the ERW pathway, this is advantageous in that it allows for the direct comparison of measurement costs and quantification outcomes in each NFZ regime, but may also add complexity to project contracting and analytical cost per ton of CDR.

5 Overview of netCDR Quantification

5.1 Defining a Single Deployment

In this quantification framework, a “deployment area” is defined as a field or group of fields that represent the statistical population to which a single ERW treatment is applied and for which net carbon removal will be estimated. It is the grouping at which an overall statistical analysis will be performed (a quantification of netCDR with uncertainty), and for which a single project design document should be specified.

All fields or field areas within the same deployment must have broadly consistent:

- Time of feedstock application.
- Composition of applied feedstock.
- Geographic area.

The concept of a deployment area is distinct from its stratification—once defined, a deployment area can additionally be stratified to create distinct field areas that share certain characteristics, as per the recommendations in Section 7.3.

5.2 High-Level CDR Term Balance

In this framework for ERW carbon accounting, CDR is quantified over discrete time intervals that we will refer to as reporting periods (RP). In each reporting period, netCDR is quantified according to the following term balance:

$$CDR_{Net,\,RP} = CO_2e_{NFZ,\,RP} + CO_2e_{FFZ,\,RP} - CO_2e_{LCA\ emissions,\,RP} \quad \text{(Eq. 5.2.1)}$$

Where:

- $CDR_{Net,\,RP}$ is the net CO_2 removed by the ERW deployment during the reporting period.

- $CO_2e_{NFZ,\,RP}$ is the net additional CDR in the NFZ during the reporting period (Section 5.4.1).

- $CO_2e_{FFZ,\,RP}$ is the calculated net additional CDR in the FFZ assigned to the reporting period (Section 9). **Importantly in the quantification framework presented here, only net carbon loss in the FFZ is considered. This value is thus always negative.** FFZ CO_2 losses are amortized across reporting periods as described in Section 5.3.2.

- $CO_2e_{LCA\ emissions,\,RP}$ is the calculated life cycle emissions assigned to the reporting period. Emissions are amortized across reporting periods as described in Section 10.3.

Each of these terms can be further broken down into the difference between a treatment term and a counterfactual (CF) term:

$$CO_2e_{NFZ,\,RP} = CO_2e_{Treatment\ NFZ,\,RP} - CO_2e_{CF\ NFZ,\,RP} \quad \text{(Eq. 5.2.2)}$$

$$CO_2e_{FFZ,\,RP} = CO_2e_{Treatment\ FFZ,\,RP} - CO_2e_{CF\ FFZ,\,RP} \quad \text{(Eq. 5.2.3)}$$

$$CO_2e_{LCA\ emissions,\,RP} = CO_2e_{Treatment\ LCA\ emissions,\,RP} - CO_2e_{CF\ LCA\ emissions,\,RP} \quad \text{(Eq. 5.2.4)}$$

Where:

- The terms representing the "Treatment" are statistical estimates of the quantity of CO_2 removed from the atmosphere (or in Eq. 5.2.4, emitted to the atmosphere as life cycle emissions) in reporting period RP, as measured or estimated in the scenario where alkaline feedstock has been applied.

- The terms representing the "Counterfactual" are statistical estimates of counterfactual CO_2 fluxes if the ERW deployment had not occurred (Section 5.5). In order to keep track of avoided emissions separately from atmospheric removals, these terms must be nonnegative (Section 5.5.4).

All terms in Eq.s 5.2.1 to 5.2.4 are expressed in units of tonnes CO_2.

5.3 Time Accounting

A prevailing challenge across CDR pathways is that CO_2 emissions and removals do not all occur simultaneously with the initiation of a project. The carbon balance of an ERW deployment is arguably best thought of as a timeseries of carbon 'gains' (removal from the atmosphere) and losses through time. Upstream LCA emissions occur before and during the initial spreading of the alkaline feedstock. Feedstock dissolution will occur over a period of years. Following the release of alkalinity through feedstock dissolution, the transport and storage of cations in the soil profile can lead to non-negligible lags between feedstock dissolution and when DIC is produced and exported from the NFZ (Amann et al., 2020; Kanzaki et al., 2024). Carbon can continue to be lost and gained as the weathering products are transported through downstream systems to an eventual durable storage reservoir (Section 9). It is thus important to develop a consistent carbon accounting framework that can account for processes that occur over different timescales, and informs when carbon benefits can be credibly claimed over the course of a project lifetime.

More broadly, for any given CDR pathway, it is important to differentiate between when carbon is actually removed from the atmosphere, and when carbon credits are awarded in the context of a commercial CDR deployment.

We propose the following frame for considering when CO_2 has been removed from the atmosphere due to an ERW intervention:

- Potential CDR is generated when base cations are released into solution through feedstock dissolution (or when a non-carbonate feedstock mineralizes to form a carbonate mineral).

- Carbon removal has occurred when base cations released from the feedstock are charge-balanced by dissolved inorganic carbon (DIC) in a fluid in diffusive exchange with the atmosphere. This may occur in soil porewaters, or in downstream surface water systems (though net carbon removal generated in the FFZ is not considered in the accounting framework presented here, Section 5.4). This CDR is maintained as long as the base cations and charge-balancing DIC remain in solution or reach a permanent storage reservoir that is not in contact with the atmosphere over the timescale of the durability threshold (e.g., long duration groundwater reservoirs, Section 9.1).

- For non-carbonate feedstocks, carbon removal has also occurred when base cations released from the feedstock have formed a secondary carbonate mineral, incorporating 1 mole of CO_2 per mole of Ca^{2+} or Mg^{2+}.

Ideally, carbon credits that are used to offset emissions should be awarded in an ex-post manner, after atmospheric CDR actually occurs. This is most clearly guaranteed by issuing credits as CDR is achieved through time. However, a range of operational and normative choices, as well as precedent from other CDR pathways, may also play a role in determining when credits are issued for CDR deployments.

The choice of a time accounting framework is ultimately a normative decision, but one that has many nuanced and interlocking implications. Importantly, developing cohesive frameworks for time accounting within and across CDR pathways is very much a work-in-progress and critical challenge for the broader CDR community in the coming years. In this section, we lay out a series of potential frameworks for time accounting in ERW, along with the advantages and practical implementation challenges associated with each.

5.3.1 Near-Field Zone time accounting frameworks

We first introduce a series of frameworks for considering when CDR is generated in the NFZ. A common thread to all of these frameworks is that *potential* CDR is generated upon feedstock dissolution, and thus crediting should not be considered until alkalinity release from the feedstock has been empirically demonstrated. These proposed frameworks largely differ in the details of how the potential for transient and permanent alkalinity sinks within the NFZ are treated.

In almost all of the approaches below, the temporal dynamics of carbon loss and gain in the FFZ and the amortization of LCA emissions are considered separately from the NFZ (Section 5.3.2). Amortized life cycle emissions (Section 10.3) and FFZ net predicted carbon losses assigned to a reporting period are incorporated at the time of credit generation.

At this stage of development of the ERW pathway, we do not recommend that the temporal dynamics of downstream carbon gains and losses be considered explicitly. Instead, given the relatively higher level of uncertainty around the timing of carbon dynamics in the FFZ, we recommend making the conservative assumption that estimated net FFZ losses occur when CDR is generated in the NFZ (see Section 5.3.2 for further consideration of amortizing FFZ carbon loss).

5.3.1.1 Approach 1: Credit upon feedstock dissolution

In this approach, carbon credits are assigned when base cation release and/or associated DIC generation due to feedstock dissolution has been measured within the NFZ. This time accounting method does not consider transient sinks of alkalinity in the soil profile (e.g., cation sorption or the formation of secondary carbonates that later dissolve). Expected permanent losses in the NFZ are subtracted from netCDR at the time of credit generation as projected or estimated percentages of the potential carbon removal generated by feedstock dissolution.

There are two primary disadvantages to this framework. First, there can be context-specific time lags on the order of months-to-years between feedstock dissolution and when DIC is produced and exported from the NFZ–i.e., when CDR is considered to occur (Amann et al., 2020; Kanzaki et al., 2024). Crediting at feedstock dissolution in many systems will thus result in credits being issued before CDR has occurred and significant temporal uncertainty as to when the credited CDR will actually lead to a reduction in atmospheric CO_2.

Second, this approach requires that permanent losses and reductions in CDR efficiency within the NFZ must be estimated before they can be measured empirically, and so conservative assumptions have to be made about the magnitude of each of these fluxes (Section 5.4, Section 8). Improved soil models and frameworks for model validation are required to confidently estimate the magnitude of potential NFZ losses in a site-specific way.

5.3.1.2 Approach 2: Consider temporal dynamics within the Near-Field Zone

This method requires detailed tracking of the temporal dynamics of netCDR until weathering products are exported from the NFZ (Section 4). Instead of crediting upon feedstock dissolution, carbon credits are assigned when released cations that are charge-balanced by dissolved inorganic carbon are either a) exported from the NFZ, or b) remain in porewater within the NFZ. Secondary carbonate accumulation within the NFZ can also be credited as CDR after appropriately accounting for the reduction in CDR efficiency (Section 8.5).

One way of considering NFZ carbon dynamics is that in each reporting period, carbon credits are issued corresponding to the potential CDR associated with alkalinity release from the feedstock during the reporting period, tempered by the *change* in each soil stock that can represent a reduction in netCDR. The change in carbon sink terms during the reporting period (e.g., change in base cations in the exchangeable fraction, inorganic carbon content, cations incorporated into secondary clays, plant uptake, soil organic carbon stocks) is calculated for the integrated soil profile in the NFZ.

The NFZ term balance described in Section 5.4.1.2 reflects this framing. Independently constraining potential CDR associated with alkalinity release from the feedstock, alongside changes in any transient or permanent sinks of alkalinity within the NFZ (represented by Endmember Approach 2), should in theory yield an equivalent mass balance to directly measuring the time-dependent export of dissolved-phase weathering products and associated DIC from the NFZ (in addition to any net additional DIC stored within the NFZ at any given time; represented by Endmember Approach 1). This has yet to be rigorously demonstrated in an ERW field trial or deployment. Pursuing this method intercomparison–comparing solid-phase mass balance results with those from aqueous phase monitoring of DIC and weathering products–at a range of well-instrumented sites should be a key priority for the ERW community in the near-term.

This time accounting framework attempts to most closely and conservatively mirror when the atmosphere feels the effect of the ERW intervention, so that credits are issued in an ex-post manner. The magnitude of each potential transient or permanent reduction in CDR efficiency within the NFZ is empirically constrained and incorporated into netCDR quantification.

5.3.1.3 Approach 3: Hybrid Near-Field Zone time accounting methods

A key tension with Approach 2 is its implications on cash flows and financing for commercial ERW projects. Delaying carbon removal crediting until base cations released from the feedstock and charge-balancing DIC have been exported from the NFZ, or are stored as dissolved species within the

NFZ, means that netCDR and associated cash flow from the sale of carbon credits may be delayed by a period of years from initial feedstock spreading. During discussions involving both representatives from the technical Working Groups and market practitioners, it was repeatedly highlighted that this time delay in the near-term could prove to be a potentially prohibitive financial bottleneck. Importantly, time delays between feedstock application and credit generation are also inherent to Approach 1 (crediting upon feedstock dissolution); for most ERW feedstocks there will be a significant time delay between feedstock application and complete dissolution. However, given the fact that *potential* CDR is not generated until feedstock dissolution, there was much greater consensus amongst Working Group and market practitioner participants that CDR should *not* be credited before feedstock dissolution.

Thus, this section explores a series of time accounting frameworks that attempt to still take into account the time dynamics of the NFZ following feedstock dissolution, but without waiting to strictly assign credits until NFZ CDR is realized.

Time discounting of netCDR generation. Theoretically, one could envision a system in which operators produce a prediction of netCDR through time, and CDR is credited at the time of feedstock dissolution, with temporal discounting applied to future net gains and losses in CDR. The question of how to value carbon removal that will occur in the future is a normative question that parallels ongoing field-wide discussions about the value of short-duration removals, and would likely involve some version of assigning a discount rate that reflects the social cost of carbon (Balmford et al., 2023; Cullenward et al., 2020; Fearnside et al., 2000; Matthews et al., 2023; Parisa et al., 2022).

Importantly, this type of economic discounting would break the claim of “physical equivalence” between a tonne of CO_2 removed and cumulative radiative forcing impacts (Chay et al., 2022), and thus require careful discussion and consensus-building around how to translate projected carbon removals and emissions into reductions in climate damages and then net present value.
While this may be worth exploring in the future, this method is largely infeasible today given our insufficient ability to currently model CDR from source to sink (i.e., from the dissolution event to durable storage in the ocean or a long residence time groundwater system; Section 9).

Guardrail-based time accounting. In this approach, CDR can be considered to occur when alkalinity is released from the feedstock, but only under certain conditions. One example is considering CDR to be generated with feedstock dissolution under conditions when there is a very high probability that the weathering flux will be exported from the NFZ within a threshold time interval (e.g., 10 years).

Analogous frameworks for time accounting exist in CDR pathways that utilize waste biomass feedstocks (e.g., Belmont et al., 2022; Gammans et al., 2024). When using waste biomass for CDR, the atmosphere feels the effect of the CDR intervention only at the time when CO_2 from the biomass would have been counterfactually released to the atmosphere via biomass decay. A recently released protocol accounts for this by creating a binary threshold—any CO_2e from the biomass that would have been released within a 15 year time period can be credited immediately, and anything beyond that cannot be credited at all (Gammans et al., 2024). A clear counterfactual of sufficiently decay (or combustion) is required to enable this type of accounting.

Considering the potential to apply an analogous approach to ERW deployments, this is likely infeasible given that we do not currently have a sufficient predictive understanding of the controls on alkalinity storage in and transit through the soil profile to predict export timescales with high precision.

Consider NFZ temporal dynamics, with some crediting at dissolution. Here, credits are issued for a fixed percentage of the potential CDR generated upon feedstock dissolution (e.g., 25-50%), while waiting to credit the remaining CDR until cations are observed to be exported from the NFZ, or actively driving CDR within the NFZ. This would functionally entail maintaining an operationally-defined “buffer pool” of uncredited potential CDR, held back until the magnitude of NFZ loss processes and the timescale of realizing NFZ carbon removal are empirically determined.

Importantly, in this method, project developers still need to do the same temporal tracking and NFZ measurements described in Approach 2 above (Section 5.3.1.2), such that the magnitude of NFZ loss can be quantified, and the correct number of credits remaining after deducting these losses can be released from the buffer pool.

To operationalize this method in an ERW deployment, project developers should keep track of both a) the cumulative number of credits issued upon dissolution in the deployment, as well as b) the cumulative number of tonnes of CDR demonstrated through detailed temporal tracking and NFZ measurements. Additional credits are only released from the buffer pool when the cumulative number of tons of CDR demonstrated in the NFZ is greater than the cumulative number of credits issued upon dissolution; this represents CDR that has not yet been credited, and so double counting can be avoided.

While this time accounting framework does not rely on the existence of sufficiently validated models to the same degree as the other hybrid approaches above, an informed decision needs to be made regarding the percentage of credits held back in the buffer pool. The size of the buffer pool should be determined by a conservative estimate of the magnitude of permanent sinks in the NFZ (i.e., more credits should not be issued than will be eventually realized).

Given our current level of understanding, this would necessarily be a somewhat arbitrary and normative choice, but we strongly recommend that if this approach is pursued, the buffer pool should be no less than 50% of potential credits, and any assumptions used to justify a buffer pool size in a protocol or methodology should be articulated explicitly.

5.3.1.4 General recommendation for Near-Field Zone time accounting

For near-term commercial deployments, we recommend that protocols and methodologies follow Approach 2 above, considering temporal dynamics within the NFZ. This approach most closely allows for crediting when CDR is biogeochemically realized, does not rely on predictive modeling to estimate NFZ fluxes, and ensures that each NFZ loss process is constrained through empirical measurement.

It is important to note that the operational difficulty and financing challenge represented by this time accounting framework substantially increases as the depth of the NFZ increases (Section 4) and will vary substantially between different deployment contexts. Within a given deployment environment, when project developers are required to track the temporal dynamics of cation and carbon stores over a greater depth interval, they will likely need to wait longer until carbon removal is realized and credits can be issued. As one suggestion to balance operational feasibility with the need to monitor relevant processes in deeper soils, see the recommended approach for defining the extent of the NFZ in Section 4. However, practitioners should also be cognizant of how characteristics of the deployment environment–microclimate, soil characteristics, and cropping system–will impact both the appropriate spatial extent of the NFZ and likely time lags between feedstock dissolution and netCDR generation within or export from the NFZ (Section 3).

Lastly, if time accounting Approach 2 is not pursued given challenges surrounding cash flows and financing, we believe that hybrid approaches which require consideration of temporal dynamics and empirical measurement of NFZ processes (e.g., the buffer pool scheme described above) are an improvement from issuing credits upon feedstock dissolution. However, it is important to note that these time accounting proposals still need to be pressure tested in practice; as such, we recommend a pilot period to test the efficacy of these frameworks before they are implemented commercially.

5.3.2 Far-Field Zone loss amortization

For each deployment, FFZ losses must be estimated using the methods and principles outlined in Section 9.

These net carbon losses in the FFZ must then be assigned to, or amortized across, reporting periods. The recommended, easiest, and most conservative approach is to deduct calculated potential FFZ losses associated with quantified NFZ carbon removal at the time of credit generation.

Notably, in some systems, CO_2 losses in downstream systems may not occur until decades after the weathering flux is exported from the soil profile. In addition, CO_2 losses due to marine carbonate precipitation will occur gradually in the decades to centuries following the initial weathering event. Whether and how declines in CDR efficiency associated with long-term marine carbonate precipitation should be included in netCDR is discussed in Section 9.4.3.

Process participants thus discussed the potential to deduct the components of downstream losses that are justifiably argued to occur well after the end of the project lifetime equally across a project lifetime, as opposed to proportionally at the time of credit generation for NFZ CDR (i.e., projected downstream loss for a given tonne of NFZ CDR is realized in the reporting period the NFZ CDR is claimed). This would include losses from long-term marine carbonate precipitation by default; a project developer would need to provide justification based on residence time arguments that other FFZ losses would occur well after the project lifetime (e.g., due to transit through a groundwater system with a residence time longer than the project lifetime).

Importantly, in this accounting, care would also need to be taken to ensure that the downstream losses realized in the later years of the project lifetime are not greater in magnitude than the netCDR being generated in those later reporting periods (as if so, this portion of downstream losses would never be taken into account). Similarly, provisions would also need to be put in place for early project termination.

Given the substantially more straightforward accounting, as a default it is recommended that net CO_2 losses in the FFZ are allotted proportionally at the time of crediting. Projects that do amortize downstream losses across the project lifetime should be accompanied by clear justification based on the estimated timescale of downstream losses in the project design document.

5.3.3 Life cycle emissions amortization

There are two forms of life cycle emissions associated with an ERW deployment: upstream emissions that occur before or during the deployment event, and ongoing emissions that occur over the lifetime of the project.

Ongoing emissions should be accounted for in the reporting period in which they occur.

It is recommended that upstream emissions be allowed to be amortized across a portion of the potential CDR of the deployment. At the beginning of the project (before feedstock is spread), a project-specific potential CDR should be calculated, representing the potential CDR generated by the feedstock expected to dissolve within the lifetime of the project (Section 6.2.1). Upstream life cycle emissions may be amortized proportionally as credits are issued across the first 50% of this CDR potential.

This is a practical middle ground between two endmember approaches also discussed by process participants:

- Upstream life cycle emissions are amortized proportionally over the entire weathering curve, subtracted proportionally to credits issued in each reporting period. The challenge with this accounting scheme is that the entire feedstock may not weather, which would mean that LCA emissions are not fully accounted for.
- All life cycle emissions are taken into account in the first reporting period(s) of the deployment in which they occurred. This is maximally conservative and closest to when the atmosphere feels the effect of the life cycle emissions, but is arguably overly punitive given that it does not conform with current precedent in other CDR pathways (e.g., direct air capture). Any acceptance of this endmember approach is likely contingent on the creation of amortization frameworks and best practices adopted across CDR pathways at the industry level that more readily account for when the atmosphere feels the impact of a project emission.

5.4 CDR Term Balance Equations

5.4.1 Near-Field Zone term balance equation

In this section we lay out the term balance for quantifying net carbon removal in the NFZ ($CO_2e_{NFZ,RP}$, Eq. 5.2.1, Section 5.2); the fluxes of cations and carbon that must be considered in the FFZ are delineated in Section 5.4.2 and Section 9.

NFZ CDR can be quantified as the additional DIC that has been exported from the NFZ relative to a counterfactual baseline, plus CDR occurring in the NFZ as dissolved weathering products and precipitated secondary carbonates. Changes to the soil organic carbon balance should also be included in this term balance where applicable (Section 8.8). Note that this definition is represented by the time accounting framework in Section 5.3.1.2 (Approach 2).

Within the NFZ, it can be helpful conceptually to think about two endmember approaches for empirically constraining CDR:

Endmember Approach 1: Direct measurement of dissolved weathering products or DIC produced. CDR is calculated as the export of carbonate alkalinity above a counterfactual baseline through aqueous-phase measurements of carbonate system parameters and/or major ion concentrations at the end of the NFZ (or in drainage / catchment waters past the NFZ). To additionally quantify CDR occuring within the NFZ, practitioners can generate an estimate of additional DIC within the NFZ relative to the counterfactual baseline, via direct measurements at a series of depths.

Endmember Approach 2: Independently constrain feedstock dissolution and each term balance component. Instead of directly measuring changes in alkalinity or DIC in the aqueous phase, the potential CDR associated with cations released through feedstock dissolution is calculated in each reporting period, tempered by the change in each potential carbon loss term relative to the last reporting period. After accounting for each potential loss term, the remaining CDR from feedstock dissolution should represent the magnitude of additional DIC in and exported from the NFZ.

The term balance equations presented in these endmember approaches allow for the consideration of DIC in the NFZ as part of a holistic accounting of generated CDR. Importantly, in the solid phase mass balance approach, DIC in the NFZ is counted as CDR since there is no measurement of DIC in the NFZ to subtract from the term balance. Therefore, the dissolved phase approach includes the approach to calculate an estimate of the additional DIC in the NFZ.

Practitioners should be cognizant of the higher vulnerability of DIC in the NFZ to losses, lags, and reversals. Similar considerations apply to carbonate minerals that form in the NFZ, as in agricultural soils they are vulnerable to subsequent dissolution and non-carbonic acid dissolution. At the current state of ERW, we are considering the formation of DIC and secondary carbonates in the NFZ from ERW to be CDR. It is important for practitioners to capture dynamics in the project period and explicitly discuss reversal risk, possibly projecting out subsequent precipitation and dissolution dynamics to determine whether one should consider further downstream dynamics of the carbon and alkalinity that is stored within the carbonate lattice. If carbonates are a primary storage pathway in the NFZ at a project location, one needs to be much more cognizant of the long-term durability of those carbonates, specifically with regard to potential changes in land use (e.g., fertilizer application or changing root depth).

A note on secondary carbonates (discussed in more detail in Section 8.5). The formation of a secondary carbonate mineral removes two moles of alkalinity from solution, but stores one mole of CO_2 in the mineral lattice. In Endmember 1, the reduction in CDR efficiency from the removal of alkalinity from solution is reflected in the measurement, but the additional CDR represented by the CO_2 stored in the mineral lattice is not. This carbonate-based CDR may be incorporated into the term balance by directly measuring carbonate formed (Section 8.5.3). In Endmember 2, depending on the details of the quantification method, the reduction in CDR efficiency from the removal of alkalinity from solution may not be captured by the feedstock dissolution measurement. Direct quantification of (potential) carbonate formation may be required to account for the net reduction in CDR efficiency associated with any secondary carbonate formation (Section 8.5.3).

For either endmember, changes to the net organic carbon balance would need to be accounted for separately from the inorganic carbon flux measurements represented in the endmember approaches. As discussed in Section 8.8, it is currently recommended that project developers be cognizant of, and monitor for, potential changes to the net organic carbon balance as a result of an ERW deployment, but that practitioners should not be required to incorporate potential net organic carbon loss into the (inorganic) netCDR quantification. Instead, organic carbon gains and losses should be tracked separately (Manning et al., 2024), and constraining scenarios in which ERW deployments are likely to lead to meaningful loss of organic carbon relative to counterfactual practice–either transiently or over longer timescales–should be a key priority for the pathway in the coming years (Section 8.8). The potential for biogeochemical changes induced by ERW deployments to lead to net additional accumulation of organic carbon also emphasizes the coming need to navigate between different carbon quantification and crediting regimes (e.g., soil organic carbon, standing biomass (e.g., in forested settings), and ERW) to avoid overcounting while providing a more holistic accounting of the overall carbon balance (Section 8.7).

Within each endmember, a wide array of measurement approaches and techniques can be used (Almaraz et al., 2022; Campbell et al., 2023; Clarkson et al., 2024)—the goal here is to present two different approaches for considering the inorganic term balance, spelled out in more detail in the following sections.

5.4.1.1 Endmember approach 1: Direct measurement of dissolved weathering products

When directly measuring dissolved weathering products, a project developer must estimate:

a. The total time-integrated export of carbonate alkalinity or DIC from the NFZ for the reporting period; $\sum_{time} DIC_{Export,\,RP}$ (Section 8.1). Note that direct measurements of DIC need not be taken; rather, DIC may be calculated from measurements of carbonate system parameters. Monitoring other dissolved weathering products (e.g., major ions) is also useful.

b. Optionally, the concentration of DIC spatially integrated throughout the NFZ at at the time of quantification; $\sum_{volume} DIC_{NFZ,\,RP}$ (Section 8.1).

c. Optionally, any additional carbon removal that has occurred due to secondary carbonate precipitation; $CDR_{Secondary\ carbonates,\,RP}$.

NFZ CDR generated in each reporting period using this method can be calculated through the following term-balance equation:

$$CO_2e_{NFZ,\,RP} = \sum_{time} DIC_{Export,\,RP} + \sum_{volume} DIC_{NFZ,\,RP} - \sum_{volume} DIC_{NFZ,\,Prev\,RP}$$

$$+ CO_2e_{Secondary\ Carbonates,\,RP} \quad \text{(Eq. 5.4.1.1.1)}$$

Where:

- $CO_2e_{NFZ,\,RP}$ is the NFZ CDR during the reporting period (Eq. 5.2.2).
- $\sum_{time} DIC_{Export,\,RP}$ is the CO_2 removal represented by time-integrated DIC export from the NFZ during the reporting period. This can be calculated from a time series of porewater or drainage water chemistry measurements coupled with constraints on the water flux at the end of the NFZ in a treatment plot, compared to porewater or drainage water measurements in a representative control plot (Section 8.1).
- $\sum_{volume} DIC_{NFZ,\,RP}$ is the CO_2 removal represented by the concentration of DIC in porewater spatially integrated throughout the entire NFZ. This can be estimated via a series of porewater chemistry measurements at a range of depths in the NFZ, and using an interpolation technique to estimate concentrations throughout the NFZ. (**Optional.**)
- $\sum_{volume} DIC_{NFZ,\,Prev\,RP}$ is the same NFZ DIC quantity as the previous term, but for the previous reporting period. For the first reporting period of a given deployment, this represents the DIC concentration spatially integrated throughout the entire NFZ before the deployment has occurred. (**Optional.**)
- $CO_2e_{Secondary\ Carbonates,\,RP}$ is the *additional* CO_2 removal this reporting period due to the precipitation of secondary carbonate minerals in the NFZ (measured as the difference in NFZ soil inorganic carbon stocks in the current reporting period relative to NFZ inorganic carbon stocks in the previous reporting period–Section 8.5). In this endmember approach, this term can either be directly measured or assumed to be zero. (**Optional.**)

All terms in Eq. 5.4.1.1.1 are expressed in units of tonnes CO_2.

Note that this equation implicitly requires the estimation of CO_2e fluxes for the treatment scenario relative to the counterfactual scenario; each term represents the difference between the change in the associated parameter in treatment areas, minus the change in that parameter in control areas. This corresponds to the high-level term balance in Section 5.2:

$$CDR_{NFZ,RP} = CO_2e_{Treatment\ NFZ,\,RP} - CO_2e_{CF\ NFZ,\,RP} \quad \text{(Eq. 5.2.2).}$$

5.4.1.2 Endmember approach 2: Independently constrain feedstock dissolution and each term balance component

In this endmember, the potential CDR associated with alkalinity release from the feedstock during a given reporting period is calculated alongside changes in soil stocks that represent a reduction in netCDR. At each reporting period, project developers generate a new estimate of how each term in the below term-balance equation **has changed since the last reporting period** (e.g., how much alkalinity is tied up on sorption sites, or how much net new carbonate formation is in the soil profile during the time of the reporting period). The change in each term during the reporting period (e.g., change in base cations in the exchangeable fraction or change in soil inorganic carbon stocks) is calculated for the integrated soil profile in the NFZ.

NFZ CDR quantified for a reporting period using this method can be calculated through the following term-balance equation:

$$CO_2e_{NFZ,\,RP} = CO_2e_{Feedstock\ Dissolution,\,RP} - CO_2e_{Biomass\ Uptake,\,RP} - CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\,RP} - CO_2e_{Sorption,\,RP} - CO_2e_{Secondary\ Carbonates,\,RP} - CO_2e_{Secondary\ Silicates,\,RP} \quad \text{(Eq. 5.4.1.2.1)}$$

Where:

- $CO_2e_{NFZ,\,RP}$ is the NFZ CDR during the reporting period (Section 5.2).

- $CO_2e_{Feedstock\ Dissolution,\,RP}$ is the potential “theoretical maximum” CDR generated through the release of base cations from the alkaline feedstock in the current reporting period (Section 8.2). In this presentation, $CO_2e_{Feedstock\ Dissolution,\,RP}$ assumes that base cations released through dissolution are fully charge balanced by bicarbonate; corrections for the soil solution DIC:Alkalinity ratio and non-carbonic acid weathering are included in the $CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\,RP}$ term.

- $CO_2e_{Biomass\ Uptake,\,RP}$ is the decrease in CDR over the reporting period due to cation uptake into biomass that is removed from the system (Section 8.7).

- $CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\,RP}$ is the decrease in CDR over the reporting period due to alkalinity generation that is not charge-balanced by bicarbonate (including the impact of non-carbonic acid weathering) (Section 8.3).

- $CO_2e_{Sorption,\,RP}$ is the decrease in CDR over the reporting period due to base cation sorption on soil exchange sites, or equivalently, a reduction in exchangeable acidity (Section 8.4).

- $CO_2e_{Secondary\ Carbonates,\,RP}$ is the decrease in CDR over the reporting period due to the precipitation of secondary carbonate minerals (Section 8.5). Note that secondary carbonate minerals represent a sink of CO_2 from the atmosphere for non-carbonate feedstocks, but the reduction in CDR efficiency due to the removal of alkalinity from solution must still be accounted for.

- $CO_2e_{Secondary\ Silicates,\,RP}$ is the decrease in CDR over the reporting period due to the formation of secondary silicate minerals and other secondary phases (Section 8.6).

All terms in Eq. 5.4.1.2.1 are expressed in units of tonnes CO_2. As above, note that each term should be computed separately for the treatment scenario (as measured on treatment fields; $CO_2e_{Treatment\ NFZ,\,RP}$) and for the counterfactual scenario (as measured on control fields; $CO_2e_{CF\ NFZ,\,RP}$). The difference between $CO_2e_{Treatment\ NFZ,\,RP}$ and $CO_2e_{CF\ NFZ,\,RP}$ yields $CO_2e_{NFZ,\,RP}$.

The guardrails and requirements for accounting for each of these listed fluxes are considered in detail in Section 8. As described above, **many of these terms may be either positive or negative**, depending on the direction of change of the corresponding flux in the given reporting period. In addition, some terms may be excluded for some or all reporting periods, as detailed in Section 8.

5.4.2 Far-Field Zone term balance equation

Guidelines for determining the durable storage reservoir for the CO_2 removed by an ERW deployment and the associated spatial scope of the FFZ are discussed in Section 9.1. Broadly, a project should consider net carbon losses in three spatial regimes: the lower vadose zone and along groundwater flow paths, surface water systems, and the ocean. A term balance equation for the FFZ can thus expressed as:

$$CO_2e_{FFZ,\,RP} = CO_2e_{Groundwater,\,RP} + CO_2e_{Surface\,Water,\,RP} + CO_2e_{Oceans,\,RP} \quad \text{(Eq. 5.4.2.1)}$$

Where:

- $CO_2e_{FFZ,\,RP}$ is the calculated net additional CDR in the FFZ assigned to the reporting period. **Importantly, in the quantification framework presented here, only net carbon loss in the FFZ is considered. This value is thus always negative.**
- $CO_2e_{Groundwater,\,RP}$ is the net change in CDR relative to the counterfactual due to permanent alkalinity sinks in the lower vadose zone and along groundwater flow paths (Section 9.2). In the framework for CDR quantification presented here, this will always be a reduction in CDR, and thus should be a negative value.
- $CO_2e_{Surface\,Water,\,RP}$ is the net change in CDR relative to the counterfactual due to permanent alkalinity sinks and CO_2 evasion in surface water systems (Section 9.3). In the framework for CDR quantification presented here, this will always be a reduction in CDR, and thus should be a negative value.
- $CO_2e_{Oceans,\,RP}$ is the net change in CDR due to carbonic acid system re-equilibration and any permanent alkalinity sinks in the ocean (Section 9.4). In the framework for CDR quantification presented here, this will always be a reduction in CDR, and thus should be a negative value.

All terms in Eq. 5.4.2.1 are expressed in units of tonnes CO_2, and should be nonpositive values. However, we note that while these terms are separate in this equation, in reality, processes in one part of the FFZ may affect other processes, and there may be scenarios where the individual terms are positive even if $CO_2e_{FFZ,\,RP}$ is negative.

Recommendations regarding the cation and carbon fluxes that should be explicitly quantified in each of these FFZ environments as part of project-level netCDR for ERW deployments, including current capabilities and path forward, are discussed in detail in Section 9. Guidance for amortizing reductions in CDR efficiency in the FFZ across reporting periods is provided in Section 5.3.2.

5.5 Defining a Counterfactual Baseline

Establishing a counterfactual baseline is a key element of determining the additionality of a project. Only net additional CO_2 removal should be credited as part of a CDR project, so the project needs to be compared against the baseline of netCDR that would have occurred had the project never been established (Millock, 2013). Determining an accurate counterfactual is nuanced and complex—from defining the counterfactual practice, to practically estimating carbon outcomes as a result of that practice.

We begin this section with a discussion of one of the core components and outstanding debates of defining counterfactual CDR in agronomic systems: how to consider and quantify the net (potentially negative) emissions associated with liming for soil pH control. The section then walks through the key elements of defining a counterfactual baseline for an ERW deployment: defining the counterfactual scenario, quantifying the netCDR of that counterfactual, and integrating estimates of the counterfactual baseline into netCDR calculations.

5.5.1 CDR and liming

The practice of applying alkaline rock powder to agricultural soils to adjust soil pH for improved crop production is well-established and is a common commercial practice in many regions. This most commonly takes the form of the addition of fine-grained carbonate minerals (agricultural lime, or ag-lime) to raise soil pH levels. This established practice is functionally enhanced rock weathering with carbonate feedstocks. Depending on the timeframe considered and a number of site-specific factors, liming can represent a net source or sink of CO_2 (Hamilton et al., 2007; Oh and Raymond, 2006; West and McBride, 2005).

Carbonate weathering has the potential to produce 2 moles of charge-balancing DIC for every mole of Ca^{2+} or Mg^{2+} released into the soil solution. One of these moles of DIC will be released from the carbonate mineral itself, meaning a maximum of one mole of CO_2 is removed from the atmosphere. However, the mole of carbon contained within the carbonate mineral also means that carbonate weathering can be a net source of CO_2 to the atmosphere (over certain timescales), or net neutral if a carbonate mineral is re-precipitated in the soil profile or in a downstream system.

For example, if $CaCO_3$ weathers in low-pH soils, the weathering reaction will remove acidity from the soil, but the carbon contained within the $CaCO_3$ will be released to the atmosphere, making the liming reaction an immediate net source of CO_2. However, when the weathering products reach a downstream surface water system with higher pH, the carbonate system will re-equilibrate and the cation may then be charge-balanced by DIC. Equivalently, the reduction in acidity being exported from the soil profile could drive CDR by reducing CO_2 evasion downstream. As such, in some contexts, liming could be a CO_2 source initially but an eventual sink of CO_2 downstream. Indeed, measurements in the Mississippi River watershed have demonstrated a significantly enhanced bicarbonate flux over the past 50 years, attributable in part to large-scale agricultural liming (Raymond et al., 2008).

For ERW deployments that lead to a change in agronomic pH control practice, it is important to consider the CDR of that counterfactual practice. Many regulatory agencies (e.g., EPA, Defra) currently provide guidance on the emissions factors associated with agricultural liming, which assume that liming practices lead to net CO_2 emissions *in all scenarios*. Although this is a conservative assumption from the perspective of emissions accounting, this is not a conservative assumption from the perspective of netCDR quantification. The guidance outlined in the following sections calls for a deliberate tracking or conservative estimation of the net emissions associated with counterfactual liming practices.

5.5.2 Defining a counterfactual scenario

For ERW deployments in agricultural systems, the counterfactual scenario represents the ‘business as usual’ (BAU) suite of agronomic practices that would have been employed had the project not been established. This can include agronomic pH control, cropping and tillage practices, fertilizer use, and irrigation practices. Defining a counterfactual scenario can be challenging–someone must decide what a farmer would have done without being able to actually observe it.

Defining the counterfactual agronomic pH control practice is of particular importance, as the practice of applying alkaline rock powder to agricultural soils is a widespread commercial practice in many regions and, depending on the deployment context and timescale considered, can drive netCDR (Section 5.5.1). We thus focus the majority of this section on recommendations and guardrails for defining the counterfactual agronomic pH control scenario, but start with high-level guidance on other components of counterfactual agronomic practice that may require particular consideration.

Alongside this counterfactual agronomic practice, in some cases counterfactual feedstock use should also be considered, particularly for existing ‘waste’ feedstocks that were not mined or produced specifically for an ERW deployment. For example, feedstocks that would have otherwise been stored in an outdoor tailings pile in contact with atmospheric CO_2 could drive some amount of CDR in the counterfactual use case (Khalidy and Santos, 2021; Pullin et al., 2019; Wilson et al., 2014, 2009). To be fully comprehensive, deployments should consider whether the counterfactual feedstock use could drive non-negligible CDR, and–if so–quantify the counterfactual CO_2 uptake over at least the project lifetime of the ERW deployment. Any quantified CDR from the counterfactual feedstock use scenario should be subtracted from netCDR as part of the counterfactual baseline.

5.5.2.1 Cropping and tillage practices

Any land-use change as a result of the ERW deployment should be reflected in the counterfactual baseline scenario. In the case that financing for the deployment led to different decisions regarding crop selection or farming practice (e.g., a shift in tillage practice to enable spreading and mixing of the ERW feedstock), the counterfactual practice should be included in the counterfactual scenario and implemented in any BAU plot, Section 5.5.3.

5.5.2.2 Fertilizer use

Some ERW feedstocks will provide micro- and macro-nutrients to the soil system, and improved agronomic pH control may increase the nutrient use efficiency of the cropping system (Beerling et al., 2018; Skov et al., 2024; Swoboda et al., 2022). It is thus possible and even likely that over time, ERW deployments will be accompanied by a shift in fertilizer use. There is significant potential to achieve reductions in both direct and indirect greenhouse gas emissions from a reduction in fertilizer use (particularly from nitrogen-based fertilizer), and these avoided emissions should be quantified and possibly credited through fit-for-purpose crediting schemes (Alberta Environment and Protected Areas, 2023; Millar et al., 2013). The counterfactual fertilizer use practice (i.e., business as usual) should be used in the counterfactual scenario.

5.5.2.3 Irrigation

It is also plausible to envision scenarios where irrigation practices are changed to accommodate an ERW deployment (e.g., previously rain-fed fields are irrigated to maintain higher dissolution rates). In this case, the counterfactual irrigation practice should again be included in the counterfactual scenario defined for a deployment.

5.5.2.4 Agronomic pH control

The counterfactual scenario defined for agronomic pH control practice should consist of an estimated counterfactual application rate, application frequency, and composition of the liming agent. Importantly, different materials can be used for agronomic pH control, including calcium carbonate, dolomitic carbonates, and calcium or magnesium hydroxides. Silicate feedstocks have also been used for pH and nutrient management in some regions–most notably Brazil (Manning and Theodoro, 2020; Ramos et al., 2017)–but also in other geographies (e.g., Gillman et al., 2002; Van Straaten, 2021, 2006, 2002). As shorthand in the following section, we refer to counterfactual agronomic pH control by any of these methods as 'liming'.

There is no set method for defining counterfactual liming practice that will apply across all deployment scenarios. In deciding what liming practices to adopt, farmers are striking a balance between 'optimal' pH control from an agronomic perspective (e.g., maximizing nutrient use efficiency and yield) and economic and operational considerations. Records of historic agronomic pH control practices can thus be an informative lens in determining what agronomic practices would have been in the absence of the ERW project. If historical, site-specific liming records are available for the deployment site, they can be utilized to establish the counterfactual scenario by projecting the historic decision making on liming application rates into the future.

However, historical records can be difficult to come by as a result of landowner changes, land-use changes, and incomplete record-keeping. Regional liming records are available in some areas but may not be representative of site-specific decision-making. Thus, if historical records are not available, and clear evidence does not exist that liming is absent from regular commercial practice for the deployment site, we recommend that practitioners assume the site would have been limed in a manner consistent with commercial practice for the area. This would entail assuming the use of a farmer's historical liming agent, or that recommended as default by local agronomists or extension agents, to bring the soil buffer pH up to the average soil buffer pH of other fields of a similar crop type within a regional radius of 50 km. Calculations should be performed to translate between this assumed target pH and a defined counterfactual management scenario that defines an application rate and frequency for the liming agent. It is also justifiable to assume the soil would have been limed to achieve the target pH recommended by local agronomists or agricultural agencies; considering the average soil pH for a crop type in a localized region is simply an option that may better represent realistic liming decisions, as commercial crops are limed at lower-than-recommended rates in many regions.

5.5.2.5 Reporting

Before a deployment begins, a counterfactual management practice scenario should be clearly articulated, along with justification that either refers to relevant records or articulates the assumptions and calculations used to define the scenario. Project developers are also encouraged to report 'sense checks' on this counterfactual, such as a comparison to average liming rates (or sales of liming agents) in the region, or a comparison between reported historic liming rates and fertilizer use.

5.5.3 Quantifying the netCDR of a counterfactual scenario

Once a counterfactual scenario is defined, project developers then need to quantify the netCDR associated with that scenario.

5.5.3.1 Counterfactual Near-Field Zone CDR

We begin by considering how to estimate NFZ CDR ($CO_2e_{CF\ NFZ,\ RP}$, Eq. 5.2.2) for a given counterfactual management practice scenario.

As a default, we recommend that the counterfactual scenario is implemented on a business-as-usual (BAU) plot, and that $CO_2e_{CF\ NFZ,\ RP}$ is quantified through monitoring of the BAU plot. Here we define a BAU plot as a control plot on which all counterfactual management practices are implemented, including any counterfactual agronomic pH control practice.

Assuming that BAU plots are sufficiently representative of their corresponding treatment areas (Section 7.2.2), BAU plots provide the ability to directly monitor carbon and alkalinity fluxes in the counterfactual scenario through time, and represent a dynamic baseline to which to compare time-varying fluxes in the treatment plot (e.g., aqueous cation or carbonate system measurements, or changes to organic carbon cycling). In addition, BAU plots may allow for observation of potential agronomic co-benefits of ERW treatment compared to counterfactual management practices.

While monitoring BAU plots is the recommended approach for quantifying $CO_2e_{CF\ NFZ,\ RP}$, there are a few ways in which maintaining and comparing measurements against BAU plots may be operationally difficult:

- In some cases, maintaining BAU plots could be particularly operationally taxing, such as for smaller farms on which delivering and spreading both ag-lime and an additional ERW feedstock could represent an economically impractical operational burden.

- As a default, $CO_2e_{CF\ NFZ,\ RP}$ should be monitored and calculated in the same manner as $CO_2e_{Treatment\ NFZ,\ RP}$ (Eq. 5.2.2). However, mobile/immobile tracer techniques used to quantify feedstock dissolution in treatment plots may be difficult or impossible to use to quantify carbonate dissolution in a BAU plot, given the lack of relevant immobile tracers in carbonate feedstocks. Therefore, an alternative quantification method may need to be used in the BAU plot in some circumstances (Section 8.2).

- Using BAU plots that have been amended with ag-lime as the baseline from which to compare changes in soil inorganic carbon (SIC) stocks presents an operational complication, as shallow soils may contain undissolved carbonate amendments. In these cases, we recommend focusing SIC stock measurements below the shallow soil layer where the carbonate minerals in the liming agent have been incorporated (Section 8.5.3).

Negative control plots, on which all counterfactual management practices are implemented except for counterfactual pH control, offer an alternative way of establishing a dynamic baseline for time-varying fluxes, but are more problematic than BAU plots under most scenarios.

Because negative control plots do not fully implement the business-as-usual scenario, there could be a marked departure from counterfactual conditions, particularly in cases where the negative control plot becomes substantially more acidic over time through continued nitrogen-based fertilizer use without continued ag-lime application. In general, negative control plots are recommended as a potentially informative supplement to a BAU plot (particularly for research studies), but not as the sole control plot used. Note, throughout this document we use ‘control plot’ as an umbrella term to refer to either a “business as usual” (BAU) plot or a negative control.

If a project *cannot* establish a BAU plot, then a conservative estimate of $CO_2e_{CF\ NFZ,\ RP}$ due to the liming practice may be developed by assuming that all of the applied liming agent dissolves and drives netCDR at 100% field efficiency (e.g., assuming no secondary mineral precipitation, negligible plant uptake, assuming rapid transport of alkalinity out of the NFZ, ignoring base cation sorption to exchange sites, etc.). This calculation may be adjusted for non-carbonic acid weathering in the BAU plot using the same methods as the treatment. This theoretical estimate of $CO_2e_{CF\ NFZ,\ RP}$ must be assigned to a time interval or reporting period(s); the simplest, most conservative assumption is to assign the entire calculated counterfactual carbon removal to the reporting period in which the counterfactual liming event would have occurred.

If a conservative estimate of $CO_2e_{CF\ NFZ,\ RP}$ from the liming counterfactual is pursued, then it should be accompanied by a negative control plot to observe the rest of the counterfactual scenario and provide a baseline to any time-varying fluxes.

Due to a lack of fully validated or benchmarked models (or even the existence of accepted validation/benchmarking frameworks) that could estimate the amount of CDR occurring from a counterfactual pH control practice, using reactive transport models of the soil profile coupled to models of downstream processes is not currently an acceptable method for quantifying the counterfactual netCDR (Section 8.10).

5.5.3.2 Counterfactual Far-Field Zone CDR

All terms within the FFZ term balance should be calculated for the counterfactual scenario to estimate $CO_2e_{CF\ FFZ,\ RP}$ (Eq. 5.2.3). For any site-specific model runs that are used to calculate FFZ losses given the treatment practice, corresponding site-specific model runs should be performed representing the counterfactual scenario. Net FFZ carbon removal should be calculated as FFZ CO_2 fluxes to the atmosphere in the treatment scenario in excess of FFZ CO_2 fluxes in the counterfactual scenario (where both terms on the R.H.S. should be negative, representing losses):

$$CO_2e_{FFZ,\ RP} = CO_2e_{Treatment\ FFZ,\ RP} - CO_2e_{CF\ FFZ,\ RP}.$$

5.5.3.3 Counterfactual life cycle emissions

The same framework and methods for emissions accounting (e.g., emissions factors) that are used to calculate life cycle emissions for the treatment scenario should also be used to calculate the life cycle emissions of the counterfactual scenario $CO_2e_{CF\ LCA\ emissions,\ RP}$ (Eq. 5.2.4). In addition, the same method for amortizing upstream emissions for a deployment across reporting periods should be used for both treatment and counterfactual LCA emissions.

The LCA emissions of maintaining the BAU plot should be considered within the system boundary of the ERW project as a whole and allocated to $CO_2e_{Treatment\ LCA\ emissions,\ RP}$. However, when estimating the LCA emissions of the counterfactual scenario, the emissions associated with that counterfactual practice, not the BAU plot, should be used (e.g., if the transportation pathway for the small quantity of ag-lime used in the BAU plot differs from that which would normally be used, the ‘business as usual’ transportation would be used in calculating the counterfactual LCA emissions).

5.5.4 Complexities with counterfactual carbon accounting

Following the high-level term balance in Eq. 5.2.2 under ideal circumstances, project developers could directly calculate $CO_2e_{CF\ NFZ,\ RP}$, the netCDR occurring within the NFZ in the counterfactual scenario. However, depending on the methods used to quantify the counterfactual–i.e., measurements on a BAU plot or a theoretical calculation–there are important nuances and accounting decisions that may have a substantial impact on calculated netCDR in practice.

5.5.4.1 Direct observability of treatment and counterfactual CDR

For many fluxes in the NFZ term balance (Section 8), a dynamic, time-varying baseline must be established that reflects ‘natural’ or ‘baseline’ fluctuations in the parameters being measured. As a simple example, if a project developer is taking measurements of dissolved Ca^{2+} in soil porewater over time, determining a CDR signal requires calculating the difference between $[Ca^{2+}]$ in the treatment porewater and baseline porewater $[Ca^{2+}]$.

However, when using measurements on a business-as-usual plot as a dynamic baseline, it is important to note that BAU plot measurements represent the aggregate effect of both natural baseline fluctuations **and** counterfactual weathering products that are driving CDR in the counterfactual scenario (assuming that the BAU plot is sufficiently representative of the corresponding treatment plot; Section 7.2.2).

In order to to directly calculate $CO_2e_{CF\ NFZ,\ RP}$, we would need an independent constraint on baseline $[Ca^{2+}]$ without the influence of the counterfactual liming practice. Similarly, $CO_2e_{Treatment,\ NFZ,\ RP}$ cannot be calculated independently from $CO_2e_{CF,\ NFZ,\ RP}$ without an independent measure of baseline $[Ca^{2+}]$.

However, monitoring of a BAU plot can still be used to derive:

$$CO_2e_{NFZ,\ RP} = CO_2e_{Treatment\ NFZ,\ RP} - CO_2e_{CF\ NFZ,\ RP} \qquad \text{(Eq. 5.2.2)}$$

For any given NFZ flux,
$CO_2e_{Treatment,\ NFZ,\ RP} = [treatment\ plot\ observations] - [baseline\ of\ natural\ fluctuations]$, and
$CO_2e_{CF,\ NFZ,\ RP} = [BAU\ plot\ observations] - [baseline\ of\ natural\ fluctuations]$.

The baseline of natural fluctuations cancels out when calculating netCDR so that:
$CO_2e_{Net\ NFZ,\ RP} = [treatment\ plot\ observations] - [BAU\ plot\ observations]$.

In order to isolate $CO_2e_{Treatment\ NFZ,\ RP}$ or $CO_2e_{CF\ NFZ,\ RP}$, one option could be to implement a negative control plot alongside the BAU plot. Monitoring a negative control plot is also imperfect, however, in the case of significant drift in soil pH over time (Section 5.5.3).

5.5.4.2 Separate accounting of avoided emissions

Many carbon crediting frameworks explicitly call for the separating accounting of *removals* of CO_2 from the atmosphere from *avoided emissions* that may have occurred as a result of the project. It is possible that some amount of the calculated $CDR_{Net,\ RP}$ will represent avoided emissions.

In this section, we discuss a framework for how to identify and quantify the avoided emissions that may be wrapped up in the netCDR calculation, so they can be tracked separately from removals and credited with fit-for-purpose accounting schemes. Properly calculated avoided emissions still represent very real tonnes of CO_2 that aren't entering the atmosphere, and may still be used against climate targets elsewhere, e.g., as reductions to Scope 3 agricultural emissions (Bhatia et al., 2011).

Much of this discussion is predicated on how an "avoided emission" is defined. Here we utilize the definition that an avoided emission is an *anthropogenic* flux of CO_2 to the atmosphere that would have occurred in the counterfactual scenario, but does not occur in the treatment (Johannes et al., 2021). Namely, a human activity *would have* directly led to the emission in the counterfactual, and this activity ceases in the treatment scenario.

The approach recommended here is to separately calculate netCDR for the NFZ, FFZ, and life cycle (LCA) emissions (Eq. 5.2.1), and quantify any avoided emissions in each of these parts of the system.

Consider a deployment where the LCA emissions in the counterfactual scenario ($CO_2e_{CF\ LCA,\ RP}$) are greater than the LCA emissions for the treatment ($CO_2e_{Treatment\ LCA,\ RP}$). For example, this could occur in an endmember case where an alkaline feedstock was already being applied to a field, but an innovation has led to significantly lower life cycle emissions in the treatment scenario relative to the counterfactual. In this case, the CDR occuring in the NFZ is the same in the treatment and control, so any difference between CDR calculated in the counterfactual and treatment scenarios represents avoided emissions rather than removals—the difference is solely due to a reduction in LCA emissions. As a general rule, we consider any counterfactual LCA emissions that are in excess of treatment LCA emissions to represent avoided emissions. These avoided emissions should not be included in netCDR and should instead be accounted for separately.

Another potential example of avoided emissions would be a deployment where the counterfactual liming practice would have led to net emissions in the NFZ (e.g., the mole of CO_2 contained in the carbonate feedstock is released), but the treatment practice of applying a silicate feedstock leads to net removals in the NFZ. In this example, $CO_2e_{Treatment\ NFZ,\ RP}$ is positive (representing net removals), while $CO_2e_{CF\ NFZ,\ RP}$ is negative (representing net emissions). In this case where $CO_2e_{CF\ NFZ,\ RP}$ is a net emission, the entire absolute value of $CO_2e_{CF\ NFZ,\ RP}$ represents avoided emissions because the counterfactual liming practice is a direct human activity that can be attributed to emissions. Thus, $CO_2e_{CF\ NFZ,\ RP}$ should be capped at zero in the netCDR calculation, and the avoided NFZ emissions accounted for separately.

Thus, we recommend following these general rules for avoided emissions quantification:

- Any net emissions represented by $CO_2e_{CF\ NFZ,\ RP}$ (i.e., the counterfactual liming practice as an emissions source in the NFZ) are avoided emissions; as discussed above, these avoided emissions may not be directly calculable in all circumstances. In practice, negative values of $CO_2e_{CF\ NFZ,\ RP}$ should be tracked as avoided emissions, and $CO_2e_{CF\ NFZ,\ RP}$ should be capped at zero in the calculation of $CO_2e_{NFZ,\ RP}$.

- Any LCA emissions in the counterfactual ($CO_2e_{CF\ LCA,\ RP}$) in excess of LCA emissions in treatment ($CO_2e_{Treatment\ LCA,\ RP}$) represent avoided emissions.

- Any FFZ losses in the counterfactual scenario in excess of FFZ losses in the treatment represent avoided emissions, although they may be realized after a time delay.

There may also be other avoided emissions that are not included in the bounds of the netCDR calculation. For example, a reduction in nitrogen fertilizer use as a result of the ERW deployment would represent avoided emissions. Although not included within the netCDR of an ERW deployment, we encourage the tracking, reporting, and appropriate crediting of such negative emissions as part of a holistic understanding of the greenhouse gas emissions of agricultural systems.

To summarize, the recommended approach to integrating counterfactual CDR into netCDR quantification is to calculate the net CO_2 contributions from the NFZ, FFZ, and LCA emissions separately, representing the difference between the treatment and counterfactual scenarios in each case. Then, determine whether there are avoided emissions included in any of these terms according to the rules above, and separate those emissions from the netCDR calculation.

5.6 Statistical Methods, Uncertainty Quantification, and Discounting

A core component of calculating netCDR for an ERW deployment is the quantification of associated uncertainty. There are many sources of uncertainty in ERW quantification, including the analytical error of all measurement techniques used, sampling uncertainty due to both baseline soil spatial variability and temporal variability, uncertainty in the composition of the feedstock, and sub-sampling uncertainty (i.e., how subsamples are chosen from a larger soil sample for analysis).

The datasets needed to quantify CDR in ERW deployments can be highly complex, often with many different parameters measured at several points in time. Parameters can also co-vary with complex spatial correlation structures. It is therefore likely that more simplistic statistical tests, like Student t-tests or simple parametric confidence intervals, will not be able to accommodate this high-dimensional data, and that closed-form expressions for the standard error or statistical power will be difficult or impossible to develop analytically. Instead, some degree of simulation, re-sampling, or novel statistical model development may be required.

This section aims to break down the task of uncertainty quantification into a series of interrelated steps and provide considerations and recommendations for each component. This includes:

- A discussion of the use of both frequentist confidence intervals and Bayesian modeling for uncertainty quantification, along with advantages and drawbacks of each approach.
- Considerations for propagating error through netCDR quantification.
- A recommended framework for consistent uncertainty discounting.
- A potential causal inference driven approach to CDR quantification.
- Approaches for validating statistical models.

5.6.1 Frequentist approaches to uncertainty quantification

One approach to quantifying uncertainty for an estimate of netCDR from a given deployment (we'll reference this estimate as $\hat{\theta}$) is to create a confidence interval for netCDR with a significance level α. This is a frequentist approach to uncertainty characterization—if one was to repeat the process of collecting a sample of in-field measurements and develop a confidence interval many times, the fraction α should represent the proportion of these confidence intervals that contain the true netCDR value θ.

When nonparametric approaches are used to develop a confidence interval, or when asymptotic assumptions can be justified (e.g., via the Central Limit Theorem), a strong advantage of using confidence intervals is that they do not require making modeling or distributional assumptions that are likely hard to justify in practice (e.g., normality of a particular parameter) (Stanley et al., 2023).

There are several potential methods for generating this confidence interval, which might include:

- A Wald interval: $\hat{\theta} \pm z_{\alpha/2}\hat{SE}(\hat{\theta})$, where $z_{\alpha/2}$ is the $\alpha/2$ quantile of the standard normal distribution, and $\hat{SE}(\hat{\theta})$ is an estimate of the standard error of netCDR. This is fairly simple and asymptotically justified by the central limit theorem for a wide range of estimators $\hat{\theta}$, given the assumption that the population doesn’t contain extreme outliers. However, it requires a consistent estimate $\hat{SE}(\hat{\theta})$ of the standard error, which may be difficult to derive analytically when the estimator is a complex function of the data.

- Percentile intervals of the non-parametric bootstrap: the empirical $\alpha/2$ and $(1 - \alpha/2)$ quantiles of the bootstrap distribution of $\hat{\theta}$. A bootstrap distribution can be estimated by resampling from the original data with replacement some large number of times, recomputing $\hat{\theta}$ each time on the resampled data. It does not require any analytical calculations to derive a standard error estimate, but is more computationally intensive than a Wald interval and provides no insight into sources of variation (i.e., a decomposition of $SE(\hat{\theta})$ into the variances of inputs and sample sizes). Given the complexity of ERW data, the non-parametric bootstrap can be a powerful tool for developing confidence intervals.
- Other methods for creating a confidence interval are possible, but should be justified theoretically and/or via finite sample performance (as described below–Section 5.6.5).

5.6.2 Propagation of error

Given a set of estimators representing each soil parameter needed to calculate components of the CDR term balance (Section 5.4.1), proper error propagation methods must be used to quantify uncertainty in overall netCDR of the deployment. Error propagation can be done theoretically through asymptotics and independence assumptions (e.g., using the delta method, which approximates the variance of an estimator via the first-order terms in a Taylor expansion) or numerically.

Independence assumptions for each soil parameter being estimated need to be justified. If two different parameters are not independent (e.g., bulk density and soil inorganic carbon), they should be jointly measured (e.g., by measuring properties on the same core) and their full joint distribution passed through the appropriate error propagation method (e.g., the nonparametric bootstrap).

5.6.3 Bayesian approaches to uncertainty quantification

Another approach to quantifying uncertainty is by creating a Bayesian model, where Bayes’ theorem is used to take all available deployment data into account to generate a posterior distribution, explicitly assigning a probability distribution to netCDR that has occurred in the deployment. Given the complexity and number of parameters involved in calculating the term balance, this may take the form of a hierarchical Bayesian model, in which the parameters of the model are also modeled as distributions and also updated using Bayes’ theorem.

The use of Bayesian modeling for uncertainty quantification in ERW deployments has advantages and disadvantages compared to the frequentist confidence interval approach described above. Bayesian approaches require prior distributions to be assigned to a range of relevant parameters, which may represent important assumptions that often cannot be justified on empirical grounds, and may have a large impact on the final netCDR quantification. In addition, if two different project developers are each using their own Bayesian model, their different choices of prior distributions will lead to different quantification outcomes, even given the same deployment data.

However, it can also be argued that there is a real benefit to making input assumptions explicit as stated prior distributions, and that the full set of prior information available should be brought to bear on netCDR quantification. For example, in frequentist approaches, necessarily sample sizes are determined via estimation of the baseline variance of the parameter of interest (Section 7.4.1.1); however, there exists uncertainty in this baseline variance estimate, which is ignored in the frequentist approach, but can be included and given a prior distribution using a Bayesian model (Brus et al., 2022).

If Bayesian models are used, all model priors should be explicitly stated in a project design document, with corresponding justification based on pre-existing data and assumptions about the system. In addition, each term within the NFZ term balance (Section 5.4.1) must still be empirically measured and a sample size determination should be provided for each NFZ parameter, e.g., using established performance-based Bayesian sample size criteria (Brus et al., 2022).

Given the early stage of the ERW pathway, we consider transparency and documentation of the statistical approach utilized, and collective investigation and iteration upon these statistical approaches, to be more important than standardizing around any given statistical approach today. In the coming years, the statistical methods applied to ERW deployments will undoubtedly evolve as we gain experience quantifying CDR from larger-scale field trials and early commercial deployments.

5.6.4 Uncertainty discounting for carbon removal crediting

Uncertainty discounting is an important component of the translation of netCDR to carbon credits. After a robust quantification of netCDR uncertainty, discounting involves conservatively issuing credits at the lower-bound of a confidence interval of prescribed coverage probability, or at a pre-defined and conservative percentile of a posterior distribution.

To ensure fairness and consistency in how carbon accounting is done across ERW deployments, it will ultimately be important to determine a standardized level of uncertainty discounting that is shared across commercial deployments and credits issued. While we provide recommendations below for how early-stage protocols and methodologies might approach this today, there are a few core challenges that arise when attempting to determine a shared level of uncertainty discounting.

First, depending on the methods used to characterize uncertainty in netCDR quantification, the level of discounting will have different interpretations in subtle but important ways. For example, given the goal of calculating something akin to 90% certainty in a ton of CDR generated, consider the difference between quantifying netCDR uncertainty with a confidence interval versus with a Bayesian posterior distribution:

- Discounting at a chosen percentile of Bayesian posterior distributions for netCDR (e.g., the 10th percentile of the distribution) would imply a belief that there is a 90% chance that the true value of netCDR is greater than or equal to the number of credits issued.

- Discounting at the lower bound of a confidence interval of given coverage probability (e.g., the lower bound of a two-sided 80% confidence interval). The coverage probability of a confidence interval describes the likelihood that the generated interval contains the true netCDR value. This discounting approach would imply that if a very large number of CDR deployments were to occur, where CDR is credited at this lower bound of an 80% confidence interval, fewer than 10% of these crediting events will overestimate carbon removal. It does *not* mean that in any single deployment, the probability of over-crediting is 10%, but instead constrains the long-run behavior.

These differing interpretations pose a subtle barrier to applying consistent discounting practices across all commercial deployments.

Second, in discussions with working group members and market practitioners, it was emphasized that prematurely setting a conservative discounting level may be overly punitive or prevent early-stage projects from being able to get off the ground and bring down uncertainty over time. The ERW community simply has not done full-stack carbon removal quantification many times before, so as we better characterize uncertainty across a range of measurement approaches and field conditions, we may be better equipped to more confidently assert a standardized discounting level that is actionable in practice.

More broadly, the ERW community will need to learn-by-doing–i.e., pursuing netCDR magnitude and uncertainty quantification in a range of deployment contexts. We strongly advocate for the transparent reporting and sharing of data, methods, and results, including for deployments where no credits are issued because the confidence interval overlaps with zero and/or a statistically significant signal is not found.

5.6.4.1 Recommendation for uncertainty discounting

As a default, we recommend that crediting of CDR should occur at the lower bound of a two-sided 80% ($\alpha = 0.2$) confidence interval. Assuming the interval is valid, this ensures that over the long run, fewer than 10% of crediting events will overestimate carbon removal. In the case that Bayesian models are used, then carbon removal credits may be issued corresponding to the 10th percentile of a posterior distribution for net carbon removal, noting the differing interpretation described above.

In both cases, there is a strong requirement that all deployments must demonstrate a weathering signal from the data–ideally using their pre-registered statistical methods and sampling plan (Section 7.1). Most straightforwardly, because crediting occurs at the lower bound of an 80% two-sided confidence interval, a signal is demonstrated when this lower-bound is greater than zero. This corresponds to a hypothesis test of the null that no CDR has occurred (i.e., that netCDR is no more than zero).

If no signal can be detected from the data that is discernable from baseline variability and analytical error, no carbon removal should be considered to be generated in the associated reporting period.

5.6.5 Validation of statistical methods

It is important that any novel statistical models or estimators for netCDR be subjected to rigorous validation. This is to ensure both that:

- There is no bias in the estimation of netCDR (i.e., on average, the estimator is correct).
- The uncertainty in the estimate is well characterized.

The statistical methods used for any deployment should be justified and clearly documented; methodological details, including derivations and worked examples as well as method validation results, should be transparently reported. Example avenues for validating the statistical approach include:

- **Theoretical justification (asymptotics)** - the bias and variance of estimators used or developed must be theoretically calculated and demonstrated. Any assumptions made should be justified.

- **Empirical justification via synthetic data (finite sample performance)** - in such a process, a large number (e.g., 10,000) of synthetic datasets are generated that represent the underlying statistical process being modeled and for which the correct answer is known. Then, the proposed statistical method for net carbon removal quantification is tested on each synthetic dataset to derive the following performance characteristics: bias, root mean squared error, confidence interval coverage, and expected confidence interval width. Robustness to deviations from any distributional assumptions should also be demonstrated.

5.6.6 Demonstrating causality and causal inference

Demonstrating the additionality of CDR generated by an ERW deployment means showing that the observed carbon removal effect would not have occurred in the counterfactual scenario; the changes to the carbon balance were caused by the intervention itself. Thus, it can be argued that ERW deployments should demonstrate and quantify a *causal* relationship between alkaline feedstock application and $CO_2e_{NFZ,RP}$ (Eq. 5.2.1). We explore the implications of applying a causal inference frame and associated statistical methods to ERW quantification here.

Simply observing a greater CDR effect on a treatment plot than on a corresponding representative BAU plot does not suffice to demonstrate causality; particularly for soil parameters with a high degree of baseline temporal and spatial variability (e.g., aqueous DIC concentrations or soil organic carbon stocks), the observed effect on a treatment plot relative to the control may potentially be due to confounding factors.

For a more comprehensive discussion of experimental design requirements to demonstrate causality in ecological field studies, see Hurlbert (1984). Here, we highlight two components of project design that must be considered for ERW deployments in order to demonstrate a statistically significant causal effect, which are further discussed in Section 7.2.3.

First, systematic bias in the way that field areas are assigned to either the control or treatment could influence their relative outcomes. Theoretically, the field areas receiving the control versus treatment should thus be assigned at random, even if the total amount of treatment area is much larger than the control area. This presents an immediate challenge in ERW deployments, due to operational challenges and the potential for contamination of control plots if they are placed downhill or downwind of treatment plots. The location of control plots can thus likely not be fully randomly assigned in real-world deployments. Instead, we recommend that practitioners be cognizant of the need to minimize systematic bias in the assignment of control plot areas, even while design decisions are made to minimize the potential for contamination and to ensure controls are representative of treatment areas. The approach used to define treatment and control areas should be transparently documented.

Second, even as care is taken to ensure representativeness, there will inevitably be a great deal of variability inherent within different field areas of the same deployment. Underlying spatial and temporal variability may lead to substantially different measured outcomes even for two fields that are assigned to the exact same treatment; other confounding variables will influence observed outcomes on each field. When statistical causal inferences are drawn despite only having one replicate assigned to each of the control and treatment, this is known as pseudoreplication (Hurlbert, 1984). As an analogy, one could not draw causal conclusions about the efficacy of a drug based on outcome data from only two patients, one given the drug and one given the control, even if the two patients were shown to have similar characteristics.

Thus, multiple paired control and treatment areas would ideally be created to help differentiate between the inherent spatial and temporal variability within and between field areas, and netCDR that has actually been caused by the treatment. These replicates should be interspersed (e.g., all of the control plots should not be spatially grouped in one area of the deployment). This could take the form of a stratified design in which the deployment area is subdivided into relatively homogeneous regions, which are then each split into a treatment and control area.

A deployment design with multiple paired treatment and control areas may present real operational challenges in practice, which are described in more detail in Section 7.2.3; these challenges must be carefully weighed against the need to sufficiently account for the random differences (confounders) between any given control and treatment pair. To avoid pseudoreplication, the sample size used in statistical analysis when estimating $CO_2e_{NFZ,\,RP}$ and its standard error should be taken to be the number of replicates rather than the total number of measurements taken.

In addition to project design, practitioners would also need to use statistical methods and estimators from causal inference to rigorously demonstrate and quantify the causal effect and associated uncertainty. One such approach would be to estimate the average treatment effect (ATE) for a deployment. Conceptually, each field area has two potential outcomes–one representing CDR over time had it received treatment, and one representing CDR over time had it received the control (i.e., business as usual practices, Section 5.5.2). In reality, exactly one potential outcome is observed for each field in the deployment.

Practitioners could aim to estimate the ATE for the deployment, which represents the netCDR per hectare that would be observed had every field in the deployment been assigned to treatment (rock spreading), minus the CDR per hectare had every field been assigned to control. $CO_2e_{NFZ,\,RP}$ could be calculated as the average treatment effect (ATE) across all control-treatment pairs, multiplied by the number of pairs represented in the deployment. With a design that is stratified at the block level (Section 7.3), the estimate and inference would need to reflect this stratified design. For example, generating a stratified estimate of the ATE and its standard error involves computing means and variances within strata and combining across strata by taking a weighted sum (e.g., Imbens and Rubin, 2015, Chapter 9.5).

Ultimately, while explicitly leveraging causal inference methods and project designs may be difficult today, we encourage more conversations across the CDR community about whether each individual deployment should rigorously demonstrate and statistically estimate a causal impact, or instead if it should be sufficient to simply quantify the change observed in a treatment relative to a control. At the very least, project developers and academic researchers alike should be explicit about what the quantification represents and the conclusions that can be drawn given the project design and statistical analysis.

6 Feedstock Characterization

Characterization of the alkaline feedstock proposed for use in an ERW context is a critical component of deployment planning. Outlined here are recommendations for a suite of minimum requirements for feedstock characterization, which serves two purposes:

- **Assessing CDR potential:** Determining the feedstock's capacity to take up atmospheric CO_2 through mineral weathering reactions.

- **Identifying potential health and environmental impacts:** Assessing risks associated with the feedstock's chemical composition, mineralogy and particle size distribution.

To ensure responsible deployment, all feedstock characterization steps outlined here should be completed, and the suitability of the feedstock confirmed based on the results, before field application commences. Importantly, while this section does discuss relevant feedstock characterization steps to understand potential health and safety risks, this document does not represent comprehensive guidance for performing ecosystem and human health risk assessment, monitoring, and mitigation.

In the future, it could be highly beneficial for the geochemical CDR community to align around more formalized standards and regulations for feedstock and source rock characterization. These could potentially be modeled off of mineral reserves reporting standards, such as those stewarded by the Committee for Mineral Reserves International Reporting Standards (CRIRSCO) and standards of disclosure for mineral projects used by stock exchanges (e.g., Canada’s National Instrument 43-101).

6.1 Characterization Frequency

The frequency with which a feedstock should be sampled and characterized depends on the heterogeneity of the feedstock source with respect to key variables (e.g., major oxide content, mineralogy), as well as site-specific factors. Project developers should construct a feedstock sampling plan that considers the following factors:

- **Feedstock heterogeneity:** The inherent variability of the feedstock's properties (chemical composition, mineralogy, particle size) across the source material.
    - Factors influencing heterogeneity may include the variable geology of the deposit, processing history, and storage conditions. Through an initial characterization of the feedstock source (e.g., deposit or discrete pile) with subsampling that represents the entirety of the pile or deposit, an estimated coefficient of variation for each parameter in a feedstock pile or quarry output should be developed to inform the necessary frequency of future sampling.

- **Sampling location:** The number and location of sampling points within the feedstock source (e.g., quarry, stockpile).
    - A sufficient number of samples should be collected from various locations to capture variability across the feedstock source.

- **Sample collection methods:** The procedures used to collect representative samples from the chosen locations.
    - This may involve specific techniques for handling large or heterogeneous materials. Methods used to subsample larger piles should be clearly documented in any Project Design Document.

- **Analytical requirements:** The sampling plan should ensure enough material is collected to conduct all requisite analyses, and consider the analytical precision of characterizations when calculating a requisite sample density.

At this stage, in addition to robust initial feedstock source characterization, it is highly recommended that practitioners characterize their feedstock on an ongoing basis–at minimum, once per every deployment (see Section 5.1). As a default, a tonnage-based requirement for ongoing characterization, in which the feedstock is re-characterized for every X tonnes spread (e.g., every 1,000 or 5,000 tonnes), could be justified in protocols or methodologies. This tonnage threshold could be revised upwards or downwards depending on demonstrated variability within a particular feedstock source.

6.2 Recommended Minimum Suite of Characterizations

6.2.1 Characterization of CDR potential

The potential CDR of a feedstock application is a critical metric for ERW projects. It is recommended that practitioners calculate both a maximum potential CDR based on the elemental composition of the feedstock and a project-specific CDR potential that captures the likely CDR potential over the *project lifespan*. This quantification should be based on the results of physical, chemical, and mineralogical analyses conducted on representative samples.

The following measurements and calculations are recommended at a minimum:

6.2.1.1 Chemical composition

Concentrations of the major elements calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), sulfur (S), phosphorus (P), aluminum (Al), silicon (Si), and iron (Fe) must be determined using established analytical methods.

6.2.1.2 Mineralogical composition

The mineralogical composition of the feedstock must be determined to more accurately predict the CDR potential of the feedstock through consideration of the expected dissolution kinetics of constituent mineral phases, as well as to assess potential health and safety risks such as the presence of asbestiform minerals or problematic concentrations of potentially toxic trace elements (Section 6.2.3). The relative abundance of constituent crystalline minerals and (inferred) amorphous phases should be determined using established quantitative analytical methods.

For silicate feedstocks specifically, the abundance of carbonate minerals within the feedstock must also be determined, using quantitative analytical methods suitable for the material. When estimating netCDR, practitioners must appropriately account for the differing CDR efficiency of carbonate minerals. If the carbonate content of the feedstock is less than the detection limit of the analytical method used, then practitioners should assume a carbonate content equal to the detection limit.

6.2.1.3 Particle size distribution

The feedstock's particle size distribution (PSD) should be characterized using established analytical methods capable of measuring the entire size range, from particles with a diameter of greater than 2.0 mm to those with a diameter of 2.5 µm or less. This is done both to inform estimates of feedstock dissolution rate and to characterize respirable particles (diameter <10 µm) that can pose a health and safety risk.

Specific surface area measurements (e.g., BET) can be used in addition to PSD measurements to better characterize surface roughness and reactive surface area when assessing or modeling the feedstock's CDR potential.

6.2.1.4 Moisture content

The gravimetric water content of the feedstock should be determined immediately prior to application (i.e., from a sample taken at the deployment site) using established analytical methods. This is particularly important when gravimetric methods are used to monitor feedstock application rate. Any estimations of feedstock application rate that are reported or assumed in CDR quantification must appropriately account for this water content and associated uncertainty.

6.2.2 Calculating CDR potential of a feedstock

One simple approach for calculating the maximum CDR potential of a feedstock is using a modified Steinour equation (Renforth, 2019):

$$E_{pot} = \frac{M_{CO_2}}{100} \cdot \left(\alpha \frac{CaO}{M_{CaO}} + \beta \frac{MgO}{M_{MgO}} + \varepsilon \frac{Na_2O}{M_{Na_2O}} + \theta \frac{K_2O}{M_{K_2O}} + \gamma \frac{SO_3}{M_{SO_3}} + \delta \frac{P_2O_5}{M_{P_2O_5}}\right) \cdot 10^3 \cdot \eta$$

where CaO, MgO, SO_3, P_2O_5, Na_2O and K_2O are elemental concentrations expressed as oxides, M_x is the molecular mass of each oxide; α, β, γ, δ, ε, and θ are pH-dependent coefficients that consider the relative contribution of each oxide (Supplementary Figure 9, (Renforth, 2019)); and η is the molar ratio of CO_2 sequestered per divalent cation in the feedstock (Renforth, 2019). The η used should reflect the feedstock used (e.g., silicate versus carbonate) and predicted durable storage location of the CO_2 removed (e.g., as DIC in seawater versus as a carbonate mineral).

Note also that if CDR associated with only a subset of base cations will be considered in the project-level CDR quantification (e.g., Ca^{2+} and Mg^{2+}, but not Na^+ or K^+), the maximum CDR potential calculation should be modified to reflect only those cations.

Practitioners are encouraged to calculate and report a maximum potential CDR for their feedstock using this modified Steinour equation, and should document and provide site-specific justification for the coefficients used. However, this calculation represents a fairly coarse upper bound on potential CDR given the elemental composition of a feedstock. The details of the feedstock mineralogy, particle size distribution, and deployment conditions will play a substantial role in determining the CDR potential in practice, particularly over the project's lifetime. In the coming years, improved and sufficiently validated models of feedstock dissolution in soils may be able to meaningfully improve the accuracy of a priori estimates of a feedstock's CDR potential over a given time interval.

Even in the absence of model advancements, we encourage practitioners to use the feedstock mineralogy, particle size or specific surface area, and first-order site characteristics (e.g., soil pH and climate) to estimate a dissolution rate, which–when coupled with the anticipated project lifetime–should yield a more realistic estimate of the deployment's CDR potential. This **'project-specific' CDR potential** should be calculated and used when amortizing across the potential CDR of a deployment (e.g., when amortizing LCA emissions–Section 5.3.3).

6.2.3 Analyses for Health and Safety Assessment

It is clear that fit-for-purpose ecosystem and human health safety guardrails for ERW deployments are urgently needed.

This section outlines analyses required to assess potential health and ecological risks associated with the feedstock. Given the scope and focus of this document, the aim here is not to provide a comprehensive assessment of all possible risks to ecosystems and human health. For example, expectations for ongoing monitoring for heavy metal accumulation in soils and drainage waters are not covered in this section, which focuses only on feedstock characterization. Nor do we summarize existing regulations that apply to ERW deployments in different geographies, or develop specific thresholds or guardrails to mitigate potential environmental harms.

Until comprehensive cross-jurisdictional requirements exist, we opt to outline a set of baseline feedstock characterizations that are crucial for assessing these risks. Project developers must follow all applicable jurisdictional and international regulations pertaining to human and environmental health and safety, and document a proposed adherence plan in a Health and Safety Risk Assessment.

6.2.3.1 Health and Safety Risk Assessment (HRSA)

Based on the results of the mandatory analyses for health and safety outlined below, practitioners should produce a Health and Safety Risk Assessment (HSRA) prior to project initiation. This HSRA should:

- **Evaluate potential human health hazards** associated with the feedstock based on the chemical composition, mineralogy, and particle size distribution. This includes assessing risks from exposure to dust (including respirable crystalline silica), heavy metals, and potential radioactive materials.

- **Identify potential environmental risks** associated with the feedstock, considering potential impacts on soil, water, air quality, organisms, and biodiversity.

- **Demonstrate compliance** with all applicable environmental and health & safety regulations in the relevant jurisdictions for the intended deployment of the feedstock, referencing specific regulations and providing evidence of adherence.

- **Develop and outline mitigation strategies** to ensure safe handling, transportation, and application of the feedstock. These strategies should address all identified health and environmental risks and may include:

    - **Engineering controls:** Implementing measures to minimize worker *and community* exposure.
    - **Personal protective equipment (PPE):** Specifying the required PPE for workers handling the feedstock, based on identified hazards.
    - **Worker training programs:** Developing and implementing training programs to educate workers on the safe handling procedures and potential health risks.
    - **Waste management plan:** Outlining procedures for the safe disposal of any waste generated during handling, transportation, or application of the feedstock.

6.2.3.2 Chemical composition

The release of potentially toxic trace elements from applied feedstocks presents risks due to the potential for uptake into agricultural crops, accumulation in soils, and leaching into groundwater. Concentrations of the following potentially harmful trace elements should be determined using established analytical methods: antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), uranium (U), vanadium (V) and zinc (Zn).

Practitioners should include a calculation or demonstration in their HSRA that the use of feedstock for enhanced weathering at the projected application rate and application frequency is safe for the soil and crop system, and complies with jurisdictional regulations. This includes conservative assumptions about potential Cr(III) oxidation to Cr(VI) in the deployment environment.

6.2.3.3 Mineralogical composition

Feedstocks must be analyzed for asbestos and asbestiform minerals, according to established analytical methods sensitive enough to meet regulatory limits for environmental applications in the relevant jurisdiction for the deployment (e.g., OSHA 1910 Subpart Z for asbestos regulations in the United States).

Additionally, due to the acute risk of silicosis for those involved in feedstock spreading, the risk presented by respirable silica should also be considered and mitigated against. The feedstock should be analyzed to quantify the respirable crystalline silica (RCS) fraction (including quartz, cristobalite, and tridymite) using established analytical methods. If the RCS fraction is not analyzed, practitioners should assume that RCS is present, take appropriate mitigation measures, and follow local regulations.

Practitioners should also consider the potential impact of rapid shifts in biogeochemical conditions, such as the effects of rapid pH increase, on soil biodiversity. This is particularly relevant for fast dissolving feedstocks, such as those containing hydroxide and oxide minerals.

6.2.3.4 Radionuclide content

Naturally occurring radioactive elements can be present in some rock types, including mafic and ultramafic feedstocks. While the natural radioactivity levels in these rocks are typically low, crushing and processing feedstock may potentially enhance their release rates.

Thus, feedstock sources must initially be analyzed for radioactivity to assess potential radiological risks. The analytical method chosen should be sensitive enough to detect activity levels below regulatory limits for environmental applications in the relevant jurisdiction for the deployment (e.g., see OSHA 1910 Subpart Z for US regulations regarding ionizing radiation).

6.2.3.5 Particle size distribution

As per above, the feedstock's PSD must be characterized using established analytical methods, ideally that are capable of measuring respirable particles with a diameter of 2.5 µm or less. If approaches that cannot determine PSD into the single digit micron range are used, practitioners must make conservative assumptions when assessing potential risk (e.g., anything within or below the smallest size class measured is assumed to be respirable).

Importantly, all practitioners must follow relevant jurisdictional and international regulations governing air quality, the production of respirable particulate matter, and associated mitigation and safety measures. Practitioners should document the regulations considered and propose an adherence plan in a Health and Safety Risk Assessment (Section 6.2.3).

7 Sampling Requirements

7.1 Pre-Registration

Before beginning a new deployment, all statistical methods and a full sampling plan should be pre-registered: for example, in a project design document. Pre-registration incentivizes careful consideration of the project design beforehand, supports the proper data collection, and ensures that analyses or groupings cannot be altered to produce a more favorable estimate of CDR after data is collected. It also avoids a "specification search", whereby multiple analyses or groupings are checked and the one producing the largest estimate/lower confidence bound is chosen.

This pre-registration can occur after a round of pilot sampling to initially characterize the deployment area, but should occur before rock spreading or any further sampling rounds. Ideally, data from pilot sampling, other sampling campaigns, and/or existing agronomic data will be used to justify design decisions (e.g., the choice of stratification and/or sample sizes at baseline and follow-up).

Elements of the statistical methods and sampling plan that should be pre-registered include:

- The fields and coordinates in the area representing the deployment.
- All blocking and other stratification performed (Section 7.3), including how strata were determined and the size and location of each stratum. The number of homogeneous pairs created should be clearly indicated, as well as the location and size of the treatment area and control area within each block.
- Sampling pattern design (e.g., random, grid, transect, etc.).
- Number of samples for each parameter measured, with power analysis or other justification for this choice.
- Sampling depth.
- Sample handling and laboratory analysis techniques, including protocols for drawing cores, compositing (if any), shipment and storage, sample preparation, analysis method/instrument, and method for determining analytical error (e.g., QA/QC protocols, measurement standards, replication).
- All calculations that will be performed on the data to calculate net carbon removal, including the functions used to map data to CDR, additional uncertainties in the parameters of those functions (e.g., variable or poorly constrained coefficients), and any grouping or averaging performed on the data.

Any deviations from the pre-registered plan should be recorded and justified (e.g., in crediting documentation or associated publications).

7.2 Control Plots

As discussed in Section 5.5.2, calculating netCDR for a deployment requires defining an appropriate counterfactual. At this stage of the ERW pathway, maintaining some type of control plot is an integral component of quantifying netCDR relative to the counterfactual baseline.

Importantly, throughout this document we use ‘control plot’ as an umbrella term to refer to *either* a “business as usual” (BAU) plot where counterfactual management practices are implemented, *or* a negative control on which no pH control amendments are applied, but counterfactual management practices are otherwise implemented (Section 5.5.3.1). As detailed in Section 5.5.3, we strongly recommend that deployments implement BAU plots as a default, and negative control plots be included for supplementary data and only act as a substitute for a BAU plot when circumstances require.

7.2.1 What is being controlled for

For each deployment, depending on the parameters being measured, it is helpful to specify which soil processes the control plot is aiming to represent as a counterfactual baseline. To give some examples, this may include some combination of:

- Capturing baseline natural weathering and CDR driven by counterfactual management practices.
- Providing a dynamic temporal baseline of counterfactual fluid flow and aqueous chemistry.
- Providing a baseline for cation uptake into biomass as measured by cation concentrations in plant tissues.
- Providing a dynamic baseline from which to compare soil organic and/or inorganic carbon changes.
- Quantifying the impact of the ERW treatment on crop yields.

This identification of the purposes of a control plot and how it will be used as a reference for measurements is an important first step in deciding what constitutes a representative control plot, or when designing a control plot sampling strategy.

7.2.2 Representativeness of control plots

In order for control plots to serve as realistic counterfactuals or points of reference for CDR quantification, it is important that control plots sufficiently represent the treatment areas for which they are intended to serve as a baseline. As described in Section 7.3, each treatment area should be paired with a sufficiently representative control plot, and measurements of carbon removal should be performed separately within each treatment and control area.

In judging ‘representativeness’, it is most important to index on characteristics that will either strongly impact dissolution rates and the transport of weathering products through the soil profile, or that can strongly bias measurements and their interpretation. It is recommended that the following parameters should be shown to be consistent across control areas and corresponding treatment areas to ensure control plots are sufficiently representative:

- Inputs and agronomic practice (tillage, irrigation, etc.).
- Crop type.
- Soil properties that affect field hydrology, including soil texture and soil type, water throughput in irrigated systems, and mean elevation, slope, and aspect. For aqueous phase measurements, it is particularly important for the control plot to have similar discharge characteristics as the corresponding treatment (Section 7.5).
- The initial buffer capacity of the soil, including the mean soil pH, buffer pH, CEC, and base saturation.
- Soil organic carbon and soil inorganic carbon stocks, with particular care taken to ensure representativeness on deployments where SOC and SIC stock changes are being directly quantified.

Depending on what is being measured in the control plot to calculate netCDR and on the context of the deployment site, some of these properties will matter more than others. In addition, given the high degree of heterogeneity within soil systems, even at small spatial scales, there will always be operational and practical complexity to manage in finding field areas that are relatively homogenous across all of these variables. It is thus recommended that care is given in examining how these parameters vary across a deployment site; control and treatment areas are selected in an informed manner; and explicit documentation is included that notes any clear drawbacks or ways in which selected control areas serve as imperfect counterfactuals. Practitioners should also be cognizant of changes to parameters over time with changing land use (e.g., changes to liming practice).

As one form of documentation and representativeness sense check, we recommend that the project design document should include a table in which the parameters listed above are compared for each treatment and control pair. For each continuous covariate listed, the estimated mean for each treatment and associated control should be listed in the table alongside the calculated standardized mean difference. The control could be considered to be 'sufficiently representative' if the standardized mean difference between the treatment and control is less than 10%, a common practice within observational causal inference (e.g., Austin et al 2009).

7.2.3 Location, size, number, and sampling density of control plots

As discussed in Section 5.6.6, commercial ERW deployments must strike a balance between the need for statistical rigor in deployment design and the operational complexities of implementing and maintaining control plots in practice.

Control plot locations should ideally be selected in a way that avoids selection bias, to avoid introducing systematic differences between controls and treatment areas that influence the outcomes measured in treatment versus control plots. Generally in experimental design, this is done via random assignment of the control and treatment—for example, after a large field area is identified that is sufficiently homogenous across the above "representativeness" parameters, a small, randomly assigned subset of that full area could be designated to be a control.

However, this type of random selection is in many cases either not possible or not a good idea in ERW deployments. As an example, control plots placed downhill or downwind of the corresponding treatment area are more likely to be contaminated by feedstock or weathering products exported from treatment plots. Operationally, many farmers may also be resistant to randomly distributed elements across their fields, which may interfere with established practices and workflows. In some cases it may also be important that control plots be located near access roads. We thus recommend that practitioners choose control plot locations that attempt to capture as much of the variability present in the associated treatment plot as possible (e.g., in the above hydrologic and geochemical parameters), while balancing the need to avoid contamination risk and minimize systematic differences between treatment and control areas.

In commercial deployments, the size of control plots will inevitably be much smaller than their corresponding treatment areas. Even so, it is recommended that control plots capture the baseline variability of the treatment plot, even if this necessitates enlarging the control plot.

As discussed in Section 5.6.6, deployments should ideally have several control plots in order to demonstrate a causal effect—the above checks for "representativeness" are inherently imperfect, and there will very likely be confounding variables that lead to temporal variability in the parameters being measured on control and treatment field areas. A greater number of smaller control plots is likely more effective than a small number of large control plots as a means of better capturing in-field heterogeneity. However, this needs to be balanced with the fact that with fewer and smaller control plots, "edge effects" at the boundary of control and treatment plots may be more pronounced, and smaller control plots are also more likely to be contaminated by feedstock blown by the wind.

Collecting statistically meaningful data in control plots for parameters that exhibit high degrees of temporal variability is crucial for being able to interpret these measurements. Sample density in control plots should be large enough to demonstrate a resolvable treatment effect between control and treatment areas, and should reflect the baseline variability of soil parameters being measured in the control plot (e.g., see Section 7.4.1.1).

7.3 Blocking and Stratification

We recommend that stratification be performed within the full deployment area to create "**blocks**", where each block is a subset of the deployment area that is relatively homogenous with respect to the agronomic parameters that may influence weathering rates or CDR efficiency (see list in Section 7.2.2). Blocks should each be divided into a larger treatment area and smaller corresponding control plot. This blocking (or pairing, since each block is of size n=2) is done as a means of ensuring that all control plots are sufficiently representative of their corresponding treatment areas. As discussed in Section 5.6.6, in order to quantify a causal effect, the deployment design should include several blocks (i.e., several treatment and control pairs).

When measuring CDR within any particular block, sub-stratification can also be performed as needed to minimize the influence of within-field spatial heterogeneity, and to increase power and precision of estimates without expanding sample sizes. Further stratification within a block is necessary when different application rates are used across a single treatment area, such that CDR can be initially estimated for each individual region where the application rate is consistent. Variables that are chosen to stratify on should be readily observable or already observed at design time.

Any stratification methods used, along with the field locations of each stratum, should be pre-registered and stay consistent throughout the project lifetime. When stratification is performed, any deployment-wide estimates must weight the estimate based on each stratum's relative area.

7.4 Solid Phase Measurement Guidelines and Sampling Patterns

7.4.1 Types of sampling rounds and sampling density

For clarity, we define the following four types of sampling rounds that could be pursued for an ERW deployment for reference in the discussion that follows:

- **Type A: Pilot Study** - an initial round of sampling taken before any feedstock is spread to assess the baseline spatial variability of parameters being measured to track weathering fluxes. This is done to help inform the required sample size that would be needed to pick up a statistically significant signal above baseline variability and design stratification approach.

- **Type B: Baseline Sampling** - once the required sample size has been determined, this is a round of samples taken before any feedstock is applied to the field in order to set the baseline for the project.

- **Type C: Post-Spreading Sampling** - a round of samples taken after feedstock has been spread, but before meaningful weathering has occurred. This sampling is intended to gain a better understanding of localized heterogeneity in feedstock application rates or post-application feedstock mobilization

- **Type D: Post-Weathering Sampling** - any round of samples taken after some amount of feedstock has weathered, to assess changes against a pre-application or pre-weathering baseline.

7.4.1.1 Determining sampling density and pilot studies

Rather than directly recommending a particular minimum sampling density that would hold across deployment contexts, we strongly encourage pre-registration and transparent uncertainty characterization. Failing to take sufficient samples will result in a lack of resolvable signal, and therefore no net carbon removal quantified. Broadly speaking, the density of required sampling for baseline, post-spreading, and post-weathering rounds should be determined by an estimate of the soil's underlying spatial baseline variability of the parameters being sampled.

Some justification for the chosen sample size for each soil parameter should be provided in a project design document, likely in the form of an explicit or numerical power analysis. If pre-existing data about a deployment site is insufficient to estimate the baseline mean and variance of the parameters being measured for netCDR calculation, then a Pilot Study (Type A sampling) should initially be performed to generate a sample mean and sample variance for each relevant parameter in the soil baseline. This should then inform a sample size for future sampling rounds.

7.4.1.2 Post-spreading sampling

If a project developer's quantification approach involves using solid-phase mass balance methods to determine feedstock dissolution rates, Type C Post-Spreading sampling done in addition to a round of Type B Baseline Sampling could also be undertaken. The goal of this post-spreading round would be, in certain cases, to gain a better understanding of localized heterogeneity in feedstock application rates or post-application feedstock mobilization. As described in Section 8.2, this is also the goal of using an immobile tracer when constraining feedstock dissolution, and as such, a Type C sampling round will be most useful either when there is not a useful immobile tracer in the feedstock, or as an additional check that information from the tracer is accurate (e.g., that the tracer is, in fact, immobile under deployment conditions).

In practice, there was no consensus among Working Group members regarding the utility of post-spreading sampling rounds in the manner described above. Type C sampling rounds would likely take place only days or weeks after spreading occurs. The soil samples may be taken before homogenisation or redistribution of feedstock within soil (e.g., before tilling or rain events can redistribute feedstock), making the sampling round less useful as a check on application rates. If the post-spreading round occurs much later than that, the finest particle size fraction will likely have already reacted with available acidity in the soil profile, making Type C sampling less representative of pre-weathering soil conditions.

Type C sampling (done in addition to baseline measurements) is likely not necessary if other measurement techniques are utilized (e.g., porewater measurements).

7.4.2 Guardrails for common sampling patterns

In addition to any stratification performed, and within any given stratum, common field sampling patterns include simple random sampling, grid sampling, zone sampling, and transect patterns. When developing a sampling pattern for a deployment site, it is important to avoid sampling bias, where the choice of sampling pattern systematically biases the estimate of a given parameter beyond the effects of random sampling error (Ramsey et al., 1995).

To ensure unbiased estimates, sample locations within a field or deployment should ideally be determined through random sampling. Any systematic sampling methods with fixed distances, including grids or transects, can be prone to bias when there are periodicities in the field area (e.g., crop rows), and as such are not recommended unless an argument is made with regards to how potential systematic bias has been mitigated.

7.4.3 Geo-located sampling

Geo-located sampling is a paired sampling method in which the location of each baseline sample (taken during Type B sampling) is recorded with a GPS device, and future sampling rounds (Type D sampling) return to each location within a narrow radius rather than selecting new random locations. Location-paired samples from before and after weathering has occurred are directly compared. When there is less variability at small spatial scales compared to broader field heterogeneity, geo-located sampling can reduce the variance for an equal number of samples in a particular field or deployment. It is recommended that project developers consider the potential benefits of geo-located sampling, particularly for parameters exhibiting a high degree of spatial variability.

However, in the context of commercial ERW deployments, geo-located sampling also creates the potential for “gaming the system”; if sample sites where re-measurements will occur are known in advance, then an operator could in theory apply a greater amount of feedstock to these locations in order to generate a greater number of carbon credits for the deployment. To mitigate this risk, methodologies could mandate that only a certain fraction of total sample sites can be reused (e.g., 50%), or attempt to ensure that those involved in rock spreading are blind to information about where samples will be taken.

7.4.4 Compositing of soil samples

This section covers guidelines for sample compositing, meaning the physical combination of several physical soil samples into a single sample for subsequent analysis. It is important that soil samples are thoroughly homogenized after compositing, before analysis is performed, and proper sample splitting techniques are used.

For clarity, we define two different types of sample compositing for discussion here:

- **Type 1:** A single "sample" is created by combining ~6-20 individual soil cores within a tight radius of a central point, to smooth out variability at small scales.
- **Type 2**: Samples from across a field or deployment are combined, at more substantial spatial distances from each other. This is done to decrease the lab analysis burden, but increases uncertainty

Type 1 sample compositing is strongly recommended during the collection of soil cores, as it is a best practice followed by most agronomic providers and academic researchers, especially in the case of shallow agronomic nutrient sampling. Type 1 compositing may be less feasible if deep cores are being collected.

Type 2 sample compositing can also be pursued, but the resulting larger standard error due to a smaller sample size should be incorporated into uncertainty quantification and discounting of crediting volumes (Section 5.6; Spertus et al., 2021).

7.5 Aqueous Phase Measurement Guidelines

Aqueous measurements for quantifying carbon removal associated with ERW deployments can take many forms, including measurements of soil porewater collected at various depths (e.g., Holzer et al., 2023; Paessler et al., 2023) or sampling drainage waters—such as from catchment waters like proximal streams or the outlet of tile drained systems (e.g., Larkin et al., 2022).

An advantage of aqueous phase measurements is that they integrate the cation and alkalinity fluxes that must be tracked for NFZ CDR quantification down to the depth where samples are collected (see Section 5.4). For example, one sample from a suction lysimeter represents a larger radial sampling volume than a solid core captures depending on the tension of the lysimeter and the surrounding water potential. Done well, they have the potential to directly measure the export of weathering products and charge-balancing DIC from the NFZ over time, thus providing the most direct measure of CO_2 removed from the atmosphere in the soil profile. That said, the integrated nature of the measurement (including the integration of waters traveling along different flow paths and with different residence times in the case of catchment waters) means that supplementary measurements may be required to disentangle the sources and sinks for alkalinity within the soil column for the purposes of calibrating and validating process-based models (Section 8.10).

In addition, quantifying a robust CDR signal from aqueous-phase monitoring can be significantly complicated by spatial and temporal variability and the physical challenges of extracting water from the system. For example, incorporating and operating an array of lysimeters represents a significant logistical challenge, particularly given the need to physically access the site to sample on a frequent, and often non-periodic (i.e., responsive to rainfall events) basis. Soil water content must also be sufficiently high to allow for porewater extraction by suction lysimeters or rhizons.

There is a decades-long history of collecting measurements of porewater, groundwater, and surface waters across the soil science and low-temperature geochemistry communities that practices employed for ERW quantification can build upon (e.g., Singh et al., 2018; Weihermüller et al., 2007). However, best practices for quantifying dissolved carbon and cation fluxes for ERW deployments are context-dependent and very much still under development. Thus, the discussion and recommendations in this section aim to strike a balance between setting guardrails for what we already know should be required for high quality aqueous measurements, while maintaining flexibility for learning and iterative development of measurement strategies over the coming years.

7.5.1 Counterfactual temporal baseline

Establishing a robust temporal baseline of key aqueous phase parameters (e.g., cation concentrations, DIC, total alkalinity, pH) is important in order to distinguish the additive impact of an ERW deployment from existing temporal variability in the soil system. Practitioners must interpret aqueous phase measurements through time against a temporal baseline that reflects the counterfactual scenario—the state of fluid flow and alkalinity movement through the soil profile in the absence of ERW application.

As outlined in Section 7.2 and Section 7.3, it is recommended that practitioners pair each treatment area with a sufficiently representative control plot in terms of soil properties, topography, hydrology, and management practices (note: in most cases, this control will be a 'business as usual' plot–Section 5.5.3.1). The most accurate means of constraining this temporal baseline will often be performing corresponding aqueous phase measurements on the control plot, which will capture the time-varying natural fluctuations in the system. Crucially, this relies on the control plot being both hydrologically similar to the deployment area (e.g., similar flow paths and levels of discharge), and also as much as possible hydrologically isolated from the treatment.

In irrigated systems, operators should also be cognizant of where irrigation water is drawn from and have constraints on irrigation water chemistry.

7.5.2 Site hydrology: understanding soil fluid flow and water balance

Accurately quantifying the flow rate of water through the soil column is a core requirement for quantifying carbon removal via aqueous phase measurements. The calculation of a time-integrated export flux requires knowledge of the concentration of the dissolved species of interest (e.g., cation or inorganic carbon) and the total volume of water exported from the NFZ over a defined period. For example, export of DIC from the NFZ over a given time interval

($\sum_{time} DIC_{Export,\,RP}$; Eq. 5.4.1.1.1) can be calculated as:

$$DIC_{Export} = \int_{time} c(t)\, q(t)\, dt \qquad \text{Eq. 7.5.2.1}$$

where $c(t)$ is the concentration of DIC in soil porewater at the end of the NFZ at time t, and $q(t)$ is the net water flux through the NFZ at time t (Dressing, 2003).

Estimating the water flux $q(t)$ is complicated by both the spatial variability of soil properties affecting field hydrology and infiltration, as well as temporal variability of water fluxes due to precipitation, evapotranspiration, and irrigation rates that change over time. As a default, project developers should at least calculate the time-varying water mass balance of the system, considering net infiltration as the balance between water inputs (e.g., precipitation and irrigation) and losses (e.g., surface runoff and evapotranspiration). Whether more nuanced hydrologic modeling is required should be considered on a site-by-site basis.

The complexity of the hydrologic modeling required to appropriately characterize the fluid flux at a particular site should match the complexity of the field's hydrology. In some fields, the simplistic assumption of roughly vertical fluid infiltration and transport downward through the soil profile may be appropriate. In others, the situation may be more complicated, due to preferential flow paths, high amounts of fluid runoff into surface water, tile drains, drainage ditches, or other physical structures that impede or redirect fluid flow. Thus, we recommend an initial characterization of field hydrology (Section 3).

For simpler field hydrologies that resemble vertical infiltration, considering the time-varying water mass balance may be sufficient. Net infiltration can be calculated from an estimate of water inputs (irrigation inputs and precipitation as measured by a local weather station), consideration of the ratio of surface runoff to net infiltration for a given rain event, and calculation of the evapotranspiration rate (e.g., using the Penman-Monteith equation or other empirical parameterization, informed by weather station measurements (Allen et al., 1998; McColl, 2020; Monteith, 1981)). Although costly, evapotranspiration can also be directly constrained using weighing lysimeters or eddy covariance techniques (Alfieri et al., 2018; Moorhead et al., 2019).

In more complex hydrological cases, the use of 1, 2, or 3D soil unsaturated flow models may be useful, especially when the goal is explicitly to determine the rate of flow past a certain soil depth (e.g., export from the NFZ), or to inform optimal sampling locations in more complex systems. The parameterization of any soil physics / hydrology model should be informed by an initial site characterization, and supplemented by ongoing measurements such as soil water content, soil water potential, or net infiltration (e.g., with a weighing lysimeter). Where available, practitioners should use peer-reviewed and publicly-available models, and always transparently document model assumptions and sources of input data.

7.5.3 Temporal variability and frequency of aqueous measurements

A key challenge of using aqueous measurements to estimate CDR in ERW deployments is the potentially high temporal variability of fluid flux through the soil systems, and daily and seasonal fluctuations in porewater chemistry. In computing estimates of time-integrated fluxes of weathering products, representative concentration measurements need to be assigned to specific time intervals of fluid flow, potentially using a temporal interpolation method to fill in the data gaps. The accuracy of this calculation is in part determined by the frequency of these concentration measurements—whether sufficient measurements are taken to capture temporal variability and transient signals—as well as the specific interpolation methods chosen (Moatar and Meybeck, 2005).

Studies that use a time series of instantaneous concentration measurements to characterize nutrient load in catchments can often substantially underestimate the true load value, due to under-sampling of a substantial proportion of the total fluid flux that occurs during short-duration precipitation events (Cassidy and Jordan, 2011). Given the approach of creating a time series of instantaneous measurements, it is important to be cognizant that concentration varies with net infiltration and evaporation. Measurements and temporal interpolations should take this into account; otherwise, practitioners run the risk of under or overestimating the alkalinity signal through the soil profile. Such temporal interpolation might best be done with process-based models to predict the response of the soil water chemistry to fluctuating soil water dynamics, a key area of R&D moving forward. Protocols and methodologies should allow for flexibility in the temporal measurement cadence used, but measurement collection timestamps should always be reported alongside the data and details on any spatial and temporal interpolation should be transparently reported.

Depending on the climatology of the deployment, there will likely be time periods where there is not sufficient water content in the soil profile to collect porewater samples at all. During such periods, zero export from the NFZ should be assumed, unless an alternate temporal interpolation method for this period can be realistically justified.

While many methods of collecting aqueous phase samples will yield concentration data for a single point in time (or averaged over a short time interval), other methods that collect soil water for more extended periods of time will represent a time-integrated view into concentrations of dissolved species and fluid volumes. For example, this could include the use of ion exchange resins, which have been used to track nitrate and other nutrient leaching from agricultural systems in a time-integrated manner (Apostolakis et al., 2022; Grunwald et al., 2020; Wolf et al., 2022). By capturing more of the water (or, in the case of ion exchange resins, ions) flowing through the soil system, these methods have the advantage of requiring little-to-no temporal interpolation, with the ability to capture more of the temporal variability and transient alkalinity pulses through the soil.

Similarly, proxy measurements or novel sensor development that allow for the use of in-situ soil sensors, such as using electrical conductivity as a proxy for total alkalinity, could allow for the production of a continuous time-series of a given variable of interest, also reducing or eliminating the need for temporal interpolation (Amann and Hartmann, 2022; Paessler et al., 2024; Rieder et al., 2024). Sufficient validation of any in-situ proxies used in place of standard analytical measurements must be demonstrated across a representative array of field conditions.

7.5.4 Spatial variability and density of aqueous soil measurements

Carbon removal calculations making use of soil-based porewater measurements should capture uncertainty due to both the spatial variability of baseline porewater chemistry at a particular depth, as well as spatial variability in the rate of feedstock weathering and alkalinity transport. Several ERW studies to date have observed substantial variability of key weathering indicators in soil porewater at the same depth, at small spatial scales (Holzer et al., 2023; Paessler et al., 2023). Spatially sparse aqueous measurements across large deployment areas will likely not provide a robust quantification of field-wide changes in key weathering parameters (particularly if consideration is not given to underlying soil heterogeneity).

Ideally, deployments would develop a quantitative sense for the baseline spatial variability of the dissolved species being measured (e.g., base cation concentrations) at a single point in time before feedstock is applied to the soil, potentially during a rain event when much of the fluid flux will be occurring. This baseline variability, understood either through direct pre-deployment measurements or extrapolation from similar systems, could be used to inform some form of power analysis to determine the sampling density needed to interpret a signal above baseline variability.

Given the nascent state of the field and operational challenges involved with conducting high density baseline porewater measurements before beginning the deployment, the spatial density of aqueous measurements could also be potentially justified by reference to the underlying variability of the soil properties that dictate hydrology, weathering rates, and transport of weathering products through the soil column. These properties may include:

- Topography.
- Soil pH and buffer pH.
- Cation exchange capacity and base saturation.
- Soil texture, porosity, and permeability.

Where there is more variability in these baseline parameters, a higher spatial density of aqueous measurements is likely required. At a minimum, aqueous measurements should be taken within each treatment and corresponding representative control area (see Section 7.3). We strongly advise that practitioners document their assumptions and justification for aqueous phase sampling density, and apply statistical methods to directly quantify uncertainty due to spatial variability, given their chosen sampling approach.

7.5.5 Measuring field or catchment drainage waters

Measuring a deployment's drainage waters–for example, from tile drains or a low-order stream that the deployment area can be demonstrated to be draining into (Section 9.1.4)–is another method of directly measuring an integrated inorganic weathering signal (Clarkson et al., 2024; Knapp et al., 2023; Larkin et al., 2022).

In these cases, practitioners first need to ensure they have defined the hydrologic boundaries of the watershed and characterized likely ground and surface water flow paths (Section 3). Measurements of field drainage integrate over much larger spatial areas than soil-based porewater measurements, and understanding what deployment areas are being represented in the signal is critical; for example, if a control and a treatment area are not hydrologically isolated, contamination of the ‘control’ waters could attenuate the apparent weathering signal.

Also, there may be a substantial transit time for a weathering signal to travel from the point of feedstock application, through the vadose zone and along groundwater flow paths, to the point of monitoring in drainage waters or in a downstream catchment. Thus, practitioners should attempt to estimate the distribution of flow paths, temporary storage of weathered cations (e.g., via cation exchange sites), and groundwater residence times draining into the specific water being sampled to enable an estimate of the predicted ‘breakthrough time’ when a signal is expected. This is particularly important for efforts aiming to mass balance–for example, measurements of feedstock dissolution in shallow soils with the export of weathering products in drainage waters.

7.6 Gas phase measurement guidelines

Direct measurements of CO_2 fluxes can be another important lens on the soil system and NFZ carbon dynamics. They can be particularly impactful for understanding the net carbon balance, as the vast majority of ecosystem CO_2 exchange for the agricultural systems where ERW is deployed will still be driven by organic carbon fixation (photosynthesis) and respiration (Section 8.8, Friedlingstein et al., 2023; Kantola et al., 2023; Kutsch et al., 2010). In addition, soil CO_2 concentrations exert a primary control on mineral dissolution rates in a manner that is highly dynamic through time (Andrews and Schlesinger, 2001; Perez-Fodich and Derry, 2019; Vargas et al., 2010). Thus, gas-phase measurements represent an important data stream to help improve predictive modeling capabilities over time.

Soil or ecosystem CO_2 exchange can be measured through various approaches that target different spatial scales:

- CO_2 profile measurements from in-situ CO_2 sensors at one or more depths in the soil profile yield direct measurements of in-situ CO_2 concentration and provide a depth-resolved window into soil processes and their response to environmental drivers (Paessler et al., 2023; Vargas et al., 2010). Soil CO_2 fluxes can still be calculated from in-situ CO_2 concentration methods using Fick's first law of diffusion (e.g., Vargas et al., 2010), though the need to constrain soil diffusivity can lead to significant uncertainty in the calculated surface flux (Sánchez-Cañete et al., 2017). A number of different methods can be used to empirically constrain or estimate how soil diffusivity varies as a function of soil and environmental conditions (see Sánchez-Cañete et al., 2017 and references therein), and non-CO_2 gas concentrations may be used to determine additional processes impacting CO_2 concentrations (e.g., Angert et al., 2015)

- Flux towers provide an integrated measurement of net ecosystem exchange (capturing both carbon fixation and respiration) (Baldocchi, 2003; Kantola et al., 2023).

- Flux chambers provide a direct measurement of the net CO_2 flux at the soil surface at a given point in time (for the surface area covered by the chamber), which gives a depth-integrated view of subsurface processes (Chiaravalloti et al., 2023; Dietzen et al., 2018; Myklebust et al., 2008; Pavelka et al., 2018; Stubbs et al., 2022).

While CO_2 uptake due to inorganic weathering reactions will be reflected in the broader gas flux signal of an ERW deployment, resolving the inorganic component will be highly challenging given the significant background of space and time-varying carbon fixation and soil respiration. These organic fluxes are often an order of magnitude or more higher than the inorganic CDR flux (Kantola et al., 2023; Kutsch et al., 2010). In order to quantify the inorganic signal, gas phase measurements at high temporal resolution will be needed, as single or sporadic measurements of CO_2 concentrations or fluxes will likely not be interpretable against the highly dynamic background of soil respiration.

As a broad recommendation for deployments today, soil CO_2 measurements should not be used as a sole means of quantifying CDR in ERW deployments, at least until gas-phase approaches are repeatedly co-deployed with and validated against high quality solid and/or aqueous-phase measurements. However, we strongly encourage the continued collection of high resolution CO_2 concentration and flux data in both laboratory and field settings where possible.

8 Components of the Near-Field Zone Term Balance

8.1 Integrated Weathering Flux

One strategy for constraining the NFZ term balance is to measure dissolved weathering products directly as they are generated in, and exported from, the NFZ. This can integrate the cumulative inorganic weathering signal—including the integrated effects of feedstock dissolution, cation sorption, secondary carbonate formation, secondary silicate formation, and alkalinity loss due to biomass uptake—to the depth in the soil profile or location in the catchment drainage system at which measurements are taken (Clarkson et al., 2024; Holzer et al., 2023; Larkin et al., 2022). As described in Section 7.5, capturing the weathering flux through dissolved phase monitoring requires careful consideration of spatial and temporal variability at the field scale, as well as controlling for counterfactual baseline fluctuations in the parameters being measured.

Aqueous phase measurements should be taken at the end of the NFZ (or in drainage waters or downstream catchments) in order to calculate a net export flux of weathering products, and may also be taken at shallower depths to capture an earlier weathering signal and track any CDR occurring in shallow soils (Section 5.4.1.1).

Given the ultimate goal of constraining the carbonate system and calculating an export of DIC from the NFZ above a counterfactual baseline ($\sum_{time} DIC_{Export,\,RP}$, Eq. 5.4.1.1.1), at least two (and ideally three) carbonate system parameters should be measured out of pH, total alkalinity, DIC, [CO_2], [HCO_3^-], and [CO_3^{2-}] (Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow, 2001). Practitioners should also be cognizant of potential contributions from organic alkalinity when interpreting total alkalinity measurements (Middelburg et al., 2020; Wolf-Gladrow et al., 2007)07). Tracking weathering reactions through measurements of major ions, including both base cations and major anions, may also be used for alkalinity, the latter of which can help constrain the magnitude of non-carbonic acid weathering. Proxy measurements, such as electrical conductivity as a proxy for total alkalinity, have also been proposed, but further work to validate these approaches against standard analytical measurements must be demonstrated across a representative array of lab and field conditions (Amann and Hartmann, 2022; Paessler et al., 2024; Rieder et al., 2024).

When calculating $CO_2e_{NFZ,\,RP}$ (Eq. 5.2.2) (Section 5.2) from base cation concentrations or total alkalinity, the speciation of the carbonic acid system must be considered to convert those concentrations to corresponding DIC (e.g., Bertagni and Porporato, 2022; Turner et al., 1981; Wolf-Gladrow et al., 2007).

Finally, when calculating netCDR from aqueous phase parameters, it is important to disentangle if weathering products are derived from silicate weathering, or from the dissolution of any carbonate minerals that may be present within the feedstock or fertilizers (when working with non-carbonate feedstocks). For each mole of divalent cation released from carbonate mineral dissolution, two moles of DIC can be generated, but only one is derived from the soil atmosphere; the other is released from the carbonate mineral. When using the aqueous phase to calculate netCDR where the counterfactual includes liming, $CO_2e_{CF\,NFZ,\,RP}$ will include the integrated weathering flux of background weathering plus ag-lime dissolution, therefore the DIC derived from the feedstock in any BAU plot measurements should similarly account for disentangling silicate versus carbonate dissolution.

Thus, for feedstocks that contain both carbonate and silicate phases, including silicate feedstocks that may have partially carbonated prior to application, adjustments to the netCDR calculation must be performed to account for the lower CDR potential of carbonate minerals. In the context of commercial deployments, when characterizing the mineralogy of a silicate feedstock, practitioners should determine the weight percentage of carbonate phases. As a default, we recommend conservatively assuming that all carbonate phases in the feedstock preferentially dissolve first, and interpreting dissolved phase measurements accordingly. Isotope tracers (e.g., ^{87}Sr / ^{86}Sr) can also be helpful for partitioning the relative contribution of carbonate versus silicate weathering (Andrews and Jacobson, 2017; Clarkson et al., 2024; Gaillardet et al., 1999; Larkin et al., 2022 and references therein).

8.2 Feedstock Dissolution

The prediction and modeling of mineral (particularly silicate) dissolution rates in soil systems remains a key outstanding challenge in ERW quantification and Earth sciences more broadly. There are many complex and interrelated processes that can exert a strong influence on dissolution kinetics in soils, such as temperature, pH, variable water content and fluid residence time, kinetic inhibitors and dissolved phases that enhance rates, the formation of secondary phases, and the impacts of biological processes (see Oelkers et al., 2018; White and Brantley, 1995).

It is extremely well documented that dissolution kinetics observed in field settings can diverge from those predicted from laboratory measurements by several orders of magnitude (Drever and Clow, 2018; Richards and Kump, 2003; White and Brantley, 2003). These markedly slower field dissolution rates have been attributed a range of mechanisms, including decreased reactivity of the mineral surface over time (e.g., due to coatings from secondary phases (Maher et al., 2016; Navarre-Sitchler et al., 2011; Nugent et al., 1998; Oelkers et al., 2018) and changes in surface roughness at the mineral interface (Navarre-Sitchler and Brantley, 2007)) as well as factors related to aqueous chemistry (e.g., the interplay between water infiltration rates, fluid residence time, and mineral saturation states (Maher, 2010; Maher et al., 2009)). Such details are often not well-represented in laboratory experiments (Calabrese et al., 2022; Li et al., 2017; White and Brantley, 2003).

Given that robustly validated models capable of predicting dissolution kinetics do not yet exist, particularly for silicates (Section 8.10), direct empirical measurements that capture alkalinity release from feedstock dissolution are a critical part of ERW quantification. This can take the form of either dissolved phase measurements of weathering products (Section 8.1), or solid-phase measurements in surface soils that aim to constrain feedstock dissolution in a more isolated way.

In the presentation of the NFZ term balance in Eq. 5.4.1.2.1, $CO_2e_{Feedstock\ Dissolution,\ RP}$ represents the potential CO_2 removed, assuming that all cations released from the feedstock are charge-balanced by bicarbonate (i.e., 2 moles of CO_2 removed for every mole of divalent base cation released). In reality, the chemistry of the soil solution will dictate the speciation of the carbonate system, and therefore the true change in DIC per unit of alkalinity addition. This reduction in CDR due to charge balance by carbonate ions or non-DIC anions is taken into account in the term $CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\ RP}$ (Section 8.3).

In recent years, solid-phase, mass balance-based approaches–long used to constrain natural weathering rates (Brantley and Lebedeva, 2011; Brimhall et al., 1991; Fisher et al., 2017; Riebe et al., 2003)–have been applied in an ERW context (Kantola et al., 2023; Reershemius et al., 2023; Suhrhoff et al., 2024; Wolf et al., 2022). In such approaches, the loss of base cations from feedstock-amended surface soils relative to an immobile tracer is measured over time, yielding a time-integrated signal of feedstock dissolution. The use of solid-phase mass balance methods to constrain in-situ weathering rates has been demonstrated in both mesocosm and field studies within the past year (Beerling et al., 2024; Kantola et al., 2023; Reershemius et al., 2023).

When using solid-phase mass balance approaches, one core challenge is the need to pick up a resolvable signal. This is a function of the analytical uncertainty of the measurement technique, the amount of feedstock applied and fraction that has dissolved, the depth to which the feedstock is mixed and method applied (i.e., the ratio of added feedstock to soil), and baseline soil concentrations and variability of the chosen immobile tracer (Suhrhoff et al., 2024). Care should be taken in deployment and sampling design to ensure signal resolvability.

Another key challenge is precisely constraining the amount of feedstock that has been applied to a given sampling location due to inevitable inhomogeneities in application rate and potential mixing or post-application transport. It is highly recommended that feedstock application rates be empirically constrained by measuring the soil concentration of an immobile element or isotope ratio before and after feedstock application. Some feedstocks (e.g., wollastonite, carbonates) may not have sufficient concentrations of immobile tracers to produce a resolvable signal; measurements of base cation loss can still be performed, but should ideally be coupled with secondary constraints on local feedstock addition rates (e.g., Beerling et al., 2024). In addition, it is important to ensure that the tracer used is actually immobile under the conditions of the deployment (e.g., considering pH, redox state, etc.).

One alternative approach for tracking feedstock dissolution involves measuring the addition of base cations to the exchangeable fraction over time, which can be a proxy to determine how much alkalinity has been released from the feedstock (Dietzen and Rosing, 2023). This has the important advantage of being easily integrated into typical agronomic practice, as cation exchange capacity and base saturation are commonly performed agronomic measurements. However, increases in base cations in the exchangeable phase that replace exchangeable or bound acidity (thereby releasing acidity into the soil solution) do not represent active CDR (Section 8.4), and it may be challenging to differentiate changes to the exchangeable fraction due to feedstock dissolution from other controls on cation sorption. In addition, as the base saturation of the soil system increases, a lower percentage of base cations released through feedstock dissolution will be incorporated into the exchangeable fraction, decreasing the ‘information richness’ of the exchangeable fraction as a proxy for dissolution. While this method may therefore be difficult to utilize today for direct quantification of feedstock dissolution, it could represent an important and readily-available form of empirical validation for eventual model-reliant ERW quantification.

8.3 pH Dynamics and Non-Carbonic Acid Weathering

The weathering of silicate and carbonate minerals will consume protons and generate alkalinity. The extent to which that alkalinity is charge-balanced by DIC is pH and pCO_2 dependent. This sets up a question of spatiotemporal scope when considering the impact of porewater pH and non-carbonic acid weathering on CDR efficiency. CDR in the NFZ is dictated by the amount of carbon captured as DIC that charge balances alkalinity released from feedstock dissolution *within the soil profile*. Non-carbonic acid weathering, or chemical weathering done by acids other than carbonic acid such as sulfuric, nitric, or organic acids, does not lead to base cations charge-balanced by DIC, but does neutralize acidity that may have otherwise reacted with bicarbonate and caused CO_2 degassing as seen in these reactions (Taylor et al., 2021):

$$CaSiO_3 + H_2O + H_2SO_4 \rightarrow Ca^{2+} + H_4SiO_4 + SO_4^{2-}$$

$$CaSiO_3 + H_2O + 2HNO_3 \rightarrow Ca^{2+} + H_4SiO_4 + 2NO_3^{-}$$

$$CaSiO_3 + H_2O + 2H_3A \rightarrow Ca^{2+} + H_4SiO_4 + 2H_2A^{-}$$

Quantifying organic acids is difficult (Jones et al., 2003), and often the simplifying assumption is made that organic acids will degrade over short timescales (e.g., Jones, 1998). At this stage, Working Group 2 agreed that it is valid to assume that organic acids will be degraded following reaction with silicate minerals and generate an equivalent amount of DIC as carbonic acid weathering.

There are additional reservoirs of acidity in the soil system that can also reduce netCDR including bound (also called residual) and exchangeable acidity, and their presence or removal contributes to the total buffer capacity of the soil. Exchangeable acidity is measured in an equivalent manner to the cation exchange capacity and is functionally the inverse of base saturation (cation exchange sites will either be occupied by acidic or base cations). Bound acidity is ‘bound’ on the surfaces of soil minerals or organic matter, and is dictated by pH-dependent surface speciation or complexation reactions; bound acidity is the difference between total buffer capacity of the soil and exchangeable acidity. Both residual and exchangeable acidity may include hydrogen and/or aluminum depending on the pH.

Analogously, as weathering products exported from the NFZ are transported downstream, they will continue to react and the carbonic acid system will re-speciate, potentially driving net additional CDR in the FFZ. But while the NFZ can be directly measured, reactive transport of cations and carbon in the FFZ must be modeled, with associated significantly higher uncertainties on the magnitude and timing of net carbon gains and losses.

The conservative approach is thus to solely consider carbon removal in the NFZ, and only include estimated net carbon losses in the FFZ in netCDR. This has important implications, particularly for acidic soils where feedstock dissolution rates will often be highest and the potential for beneficial agronomic impact will be substantial. In soils with a pH greater than about 6.2, cations released by weathering are variably charge-balanced by bicarbonate in the soil profile. For alkaline soils (pH > 8), a non-negligible portion of the cations released will be charge-balanced by carbonate, reducing CDR efficiency in the NFZ that could be regained through re-speciation downstream. For lower pH soils (<~6.2) where the base cations are not fully charge-balanced by bicarbonate (Dietzen and Rosing, 2023), more CDR than suggested by the DIC at the base of the weathering zone could again be achieved if those base cations are transported to a more buffered/higher pH system in the FFZ. In strongly acidic soils (pH < 4.5-5, pCO_2 dependent), the cations released by weathering are charge-balanced by very little bicarbonate, yielding little CDR in the NFZ ($CO_2e_{Feedstock\ Dissolution,\ RP} \sim CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\ RP}$). Under these conditions, weathering will only drive netCDR by decreasing the proton flux from the soil profile, thereby potentially reducing CO_2 evasion downstream. The core question when weathering mobilizes base cations that are not charge-balanced by DIC in the NFZ is whether the impact of proton buffering by the weathering reaction can be considered in the quantification of netCDR.

CDR generated in the FFZ *could* be calculated by considering the proton balance on a catchment scale (i.e., from the soil profile to downstream surface water and marine systems), but this presents a significant counterfactual challenge: how has the ERW intervention changed alkalinity fluxes relative to the counterfactual scenario? In the case of non-carbonic acid weathering neutralizing acidity in the soil profile, was that acidity going to react with bicarbonate downstream, driving evasion, or would it have reacted with another carbonate or silicate rock along the flow path? Understanding the *timing* of FFZ CDR generation would also require good constraints on the transit time of the weathering flux: when will the weathering products mix with downstream surface water systems? To further complicate matters, the counter-ions that charge balance base cations in non-carbonic acid weathering reactions–particularly nitrate–can also be removed from the system by biotic reactions downstream (e.g., via denitrification or assimilation), again raising the possibility of those base cations driving additional CDR.

Accounting for CDR in the FFZ would thus require sufficiently rigorous and validated models of catchment-scale reactive transport to quantify the net CO_2 flux from downstream river/stream and ocean systems for both counterfactual and ERW scenarios (Section 9). Based on assessments from Working Groups 2, 3, and 4, such sufficiently validated, catchment-scale models do not yet exist; thus, it is recommended that practitioners utilize conservative accounting and only consider CDR that is generated in the NFZ, along with any net carbon loss in the FFZ. Any non-carbonic acid weathering in the NFZ should be removed from netCDR.

There are multiple potential approaches to quantify the reduction in CDR efficiency due to soil solution pH and non-carbonic acid weathering ($CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\ RP}$):

- If dissolved-phase measurements are made of the integrated weathering flux exported from the NFZ (Section 5.4.1.1), DIC export can be constrained through either direct measurements of DIC or measurement of two or more carbonic acid system parameters.
    - Quantification of integrated DIC export from the NFZ (relative to the counterfactual) is sufficient for netCDR quantification, but the magnitude of non-carbonic acid weathering can be constrained through either measurement of non-DIC counter-ions (i.e., nitrate, sulfate, chloride, and dissolved phosphorus) (Kantola et al., 2023) or base cations–increases in base cation concentration without associated DIC production is evidence for non-carbonic acid weathering (Hamilton et al., 2007; Larkin et al., 2022).
- If solid-phase measurements are used to constrain feedstock dissolution (Section 5.4.1.2), the amount of DIC generated per mole of alkalinity released from the feedstock must be independently constrained, including the impact of non-carbonic acid weathering.
    - Importantly, soil solution (porewater) pH is not equivalent to soil pH (e.g., Kanzaki et al., 2023). Deriving an aqueous phase pH and carbonic acid system speciation from solely solid-phase measurements is not a trivial problem. At this stage of the pathway, taking both solid and aqueous phase samples to inform the carbon, alkalinity, and proton balance from multiple perspectives is strongly recommended.

- In the absence of direct measurements of porewater pH or other carbonic acid system parameters, one potential path forward is to (1) independently estimate the magnitude of strong acid addition to–or production in–the system, and fully discount that acidity generated from netCDR, and (2) account for degassing due to acidity already present in the soil system by considering changes to exchangeable acidity.

- Methods to independently constrain the magnitude of non-carbonic acid weathering include:

    - Measurement of the flux of non-DIC counter-ions (i.e., nitrate, sulfate, chloride, and dissolved phosphorus) from the NFZ.

    - For soil systems where it can be justified that the nitric acid produced through nitrification is the dominant contributor to non-carbonic acid acidity, an estimate of non-carbonic acid weathering may be developed from documented NH_4-based fertilizer application rates. By default, practitioners should assume 100% of the ammonium applied is nitrified; to move away from this assumption, nitrogen-use efficiency (i.e., the amount of applied nitrogen that is taken up into biomass) could be measured for the deployment. Sulfuric acid production through sulfide oxidation should also be considered for feedstocks containing appreciable reduced sulfur.

- After accounting for strong acid weathering, practitioners must still account for any reduction in CDR efficiency due to the re-equilibration and speciation of the carbonic acid system, including contributions from the release of exchangeable and bound acidity in the NFZ as soil surfaces respond to changing solution chemistry. Two considerations come from this:

    - 1) Monitoring for declines in exchangeable and bound acidity–the exchangeable component of which is included in the $CO_2e_{Cation\ Sorption}$ component of the term balance (Section 8.4)–should account for any reduction in CDR efficiency due to the reaction of bicarbonate with acidity released from soil surfaces.

    - 2) In alkaline soils, where a non-negligible portion of alkalinity will be charge-balanced by CO_3^{2-}, an additional correction may need to be made to account for the lower DIC:Alkalinity ratio within NFZ soils.

- Critically, such approaches should be further explored in the peer-reviewed literature and applied in ‘method intercomparison studies’ in real-world deployment systems where quantification is approached through solid, aqueous, and gas phase sampling (e.g., deploying both endmembers of the NFZ term balance–Section 5.4.1.1 and Section 5.4.1.2). This continued exploration will help support the development of tools to constrain the impact of non-carbonic acids from readily-available measurements (e.g., Dietzen and Rosing, 2023).

8.4 Cation Sorption

The adsorption of cations onto soil particle surfaces (e.g., clay minerals, organic matter, mineral oxides) plays a crucial role in regulating cation availability for uptake by plants and other soil organisms, as well as their storage in and transport through the soil column (Weil and Brady, 2016). Cation exchange processes are also fundamental to understanding the temporal evolution of carbon dioxide removal for ERW deployments. Cation sorption can act as a transient alkalinity sink; when base cations exchange for acidic cations on exchange sites (e.g., H^+, Al^{3+}), the addition of acidic cations to the soil solution will reduce alkalinity and pH and drive CO_2 evasion, reducing CDR efficiency.

As base cation concentrations in the soil solution decrease through time (e.g., due to continued net infiltration of water out of equilibrium with the soil solution), or the soil begins to re-acidify, these base cations can eventually re-enter the soil solution and drive CDR. The magnitude of potential base cation uptake by exchange reactions will be strongly dependent on soil conditions; cation uptake and associated lag time between alkalinity release through feedstock dissolution and export from the NFZ will be highest in high cation exchange capacity (CEC), low base saturation (often acidic) soils (e.g., Kanzaki et al., 2024).

Many ERW experiments have reported findings of increased exchangeable pools of base cations in soils treated with silicate minerals (e.g., Amann et al., 2020; Dietzen and Rosing, 2023; Kelland et al., 2020; Ten Berge et al., 2012). A planted mesocosm study using a basalt feedstock reported an increase in the exchangeable pool of soil Mg, but no significant change in the pool of exchangeable Ca, and detected no significant changes in leachate Si, Mg, or Ca, which suggests that the base cations released by weathering were retained either on soil exchange sites or in plant biomass (Kelland et al., 2020). A different planted mesocosm study using dunite (>90% olivine) saw ~13x lower Mg^{2+} concentrations in the outflow of a 26 centimeter pot experiment than measured in the surface layer over a year-long study, even in a relatively low CEC soil (8.6 meq/100 g dry soil) (Amann et al., 2020). A series of soil column studies investigating olivine dissolution at different temperatures demonstrated temperature-dependent cation exchange behavior, with Mg^{2+} much more strongly retained in the soil column at 32°C than 19°C (Iff et al., 2024; Renforth et al., 2015).

ERW interventions can also increase the cation exchange capacity of soils. In a downflow soil column experiment, the release of base cations from olivine and wollastonite dissolution increased the base saturation of the soil, and also almost doubled the soil's CEC (Te Pas et al., 2023). Soil CEC has also been shown to substantially increase in studies that applied basalt to highly weathered soils (Anda et al., 2015, 2013), a potential agronomic co-benefit (Te Pas et al., 2023). This increase in soil CEC after silicate weathering is likely due to the increase in soil pH and resultant deprotonation of soil functional groups, alongside potential formation of secondary mineral phases (Anda et al., 2015; MacBride, 1994; Te Pas et al., 2023). Such feedbacks are important to consider, as the creation of new sorption sites in the soil profile may lead to longer lag times in realizing CDR.

Base cation removal from solution in the NFZ due to cation sorption should be quantified and accounted for in netCDR quantification (Eq. 5.4.1.2.1–NFZ term balance).

8.4.1 Guidance for quantifying cation sorption in the NFZ

The actions required to quantify the impact of cation sorption will depend on the measurement approach being used to quantify netCDR:

- If $CO_2e_{NFZ, RP}$ is constrained by the time-integrated alkalinity flux at or beyond the end of the NFZ (e.g., monitoring of tile drainage, deep lysimeters, or catchment drainage waters), any alkalinity loss from cation exchange processes has already been accounted for, and no direct measurement of the exchangeable fraction is required.

- If feedstock dissolution is constrained independently and netCDR in the NFZ is calculated as the sum of potential CDR driven by feedstock dissolution and the change in carbon/alkalinity sources and sinks in the soil profile, changes to the stock of base cations in the exchangeable fraction in the NFZ should be monitored at each reporting period ($CO_2e_{Sorption, RP}$).
    - Cation exchange capacity and base saturation or exchangeable acidity should be quantified using established methods. There are several different extraction techniques (for example, see Dietzen and Rosing (2023) for a comparison of ammonium nitrate and ammonium acetate extractions in an ERW context); in the future, it could be beneficial for the ERW community to develop common standards of practice for extraction methods to allow for field-wide data inter-comparability.

8.5 Secondary Carbonate Formation

Secondary carbonate formation in the soil profile and downstream systems can represent a stable (and measurable) store of atmospheric CO_2 for ERW deployments with non-carbonate feedstocks. That said, the potential for carbonate formation must be considered in the netCDR calculation of all ERW deployments, as secondary carbonate formation reduces (and for carbonate feedstocks, negates) potential CDR by removing cations and carbonate alkalinity from solution:

$$Ca^{2+}(aq) + 2HCO_3^{-}(aq) \leftrightarrow CaCO_3(s) + CO_2 + H_2O \qquad (Eq.\ 2.1.2.1)$$

Carbonate formed as the result of an ERW deployment can thus represent both CO_2 removed from the (soil) atmosphere–there is a mole of CO_2 incorporated in the mineral lattice–*and* a decrease in the overall efficiency of CDR relative to a scenario where CO_2 removed is stored as DIC in a long residence time reservoir (groundwater or the ocean). Similarly to DIC in the NFZ that is counted towards netCDR in the term balance (Section 5.4.1), secondary carbonates that form in the NFZ are also considered CDR that is generated, although they may be vulnerable to dissolution and weathering. In particular, weathering by non-carbonic acids would be of concern (see Section 8.3).

Constraining the magnitude of net carbonate precipitation in the NFZ (as well as downstream of the weathering site–Section 9) is thus required in a thorough accounting of netCDR associated with an ERW deployment. However, not all combinations of feedstock, soil conditions, and microclimates will be conducive to net carbonate accumulation in the soil profile. Here, we first lay the groundwork for understanding and predicting when secondary carbonation formation is likely to occur within the NFZ (or deeper portions of the soil profile) before outlining recommended criteria for determining when the potential for secondary carbonate precipitation in the soil profile can be safely assumed to be negligible. We then provide recommendations for how the impact of potential secondary carbonate formation on netCDR can be quantified for deployments where it must be considered as part of the term balance ($CO_2e_{Secondary\ Carbonates,\ RP}$).

8.5.1 Controls on pedogenic carbonate formation

As with all secondary phase formation, the accumulation or loss of carbonate minerals from the soil profile is a question of thermodynamics and kinetics. The accumulation of secondary carbonate minerals will be fundamentally dictated by the mineral saturation state, which means that to first order, pedogenic carbonate formation is a function of cation supply, soil CO_2 dynamics and pH, temperature, and the all-important soil water balance (Breecker et al., 2009). In soils, plant roots and microorganisms primarily impact the formation of pedogenic carbonates via respiration and CO_2 generation, however, soil organisms may also directly contribute to the production of pedogenic carbonates by forming carbonates as part of their skeleton or glands (see (Zamanian et al., 2016) and references within). Pedogenic carbonates will often go through multiple cycles of precipitation and dissolution in response to fluctuating soil conditions (Breecker et al., 2009; Huth et al., 2019). Carbonate precipitation tends to be favored during warmer, drier intervals, as net evaporation increases aqueous cation activity and higher temperatures reduce carbonate mineral solubility (as a general rule, both Ca^{2+} and Mg^{2+} carbonates are retrograde soluble (Bénézeth et al., 2011; Plummer and Busenberg, 1982)). In turn, carbonate dissolution is favored under cooler, wetter conditions, particularly when this coincides with periods of high soil respiration and CO_2 concentrations (Licht et al., 2022). In ERW deployments, the temporal dynamics of feedstock dissolution (which requires sufficient water and will be favored under high pCO_2 conditions) will further impact variations in carbonate saturation state through space and time.

The most significant accumulations of soil inorganic carbon occur in dry environments (Plaza et al., 2018), though pedogenic carbonates are common throughout temperate regions. Pedogenic carbonate formation and persistence in the soil profile is generally thought to be rare in wetter environments–meta-analyses suggest that soil carbonates are unlikely to form when mean annual precipitation exceeds 1000 mm/yr (Retallack, 2005; Zamanian et al., 2016)–though there is some evidence for persistent pedogenic carbonates in high annual rainfall environments with strongly monsoonal climates (e.g., Licht et al., 2022; van der Kaars and Dam, 1997).

Kinetics can also exert a strong control on carbonate mineral formation in natural systems. From the perspective of ERW quantification, kinetics inform two key considerations: what minerals are likely to form and should thus be of primary concern, and at what saturation states is substantial precipitation likely to occur? For geochemical calculations, it is recommended that practitioners consider the precipitation and dissolution of calcite as the primary carbonate phase. Calcite is the most thermodynamically stable $CaCO_3$ polymorph under Earth surface conditions; although some aragonite has been observed in calcareous horizons (Watts, 1980), calcite with varying levels of Mg substitution is the most commonly formed carbonate phase in soil systems (Lorenz and Lal, 2018). At ambient temperatures, the formation of Mg-carbonates is kinetically limited (Power et al., 2019, 2017) due to the strong hydration and slow desolvation rates of Mg^{2+} (Helm and Merbach, 1999), although the very high Mg concentrations expected from dissolution of Mg-rich feedstocks and the potential for biologically induced precipitation (McCutcheon et al., 2019) could allow for the precipitation of Mg-carbonates in some systems.

Secondly, carbonate precipitation will only occur in soil solutions that are oversaturated with respect to the carbonate phase. However, carbonate precipitation will not necessarily occur at equilibrium (and indeed, seldom does in the complicated aqueous solutions characteristic of soil porewaters). Soil solutions are often observed to be substantially oversaturated with respect to calcite, and it is well-known that inhibitors of calcite growth (e.g., Mg^{2+}, PO_4^{3-}, organic molecules, etc.) can prevent substantial carbonate precipitation in low supersaturation solutions (Davis et al., 2000; Dobberschütz et al., 2018; Dove and Hochella, 1993; Hoch et al., 2000; Inskeep and Bloom, 1986; Lin et al., 2005; Mucci and Morse, 1983). The saturation state with respect to $CaCO_3$ can be expressed as:

$$\Omega = \frac{IAP}{K_{sp}} = \frac{\{Ca^{2+}\}\{CO_3^{\ 2-}\}}{K_{sp}} \qquad \text{Eq. 8.5.1.1}$$

Where IAP is the ion activity product, K_{sp} is the solubility product constant, and $\{Ca^{2+}\}$ and $\{CO_3^{\ 2-}\}$ are the aqueous ion activities of Ca^{2+} and CO_3^{2-}, respectively. Saturation states are also commonly expressed as saturation indices (SI), where $SI = log_{10}\Omega$. Inskeep and Bloom (1986) report the maintenance of oversaturations ranging from SI = 0.4-0.7 in (calcareous) soil solutions, even after seeding the solutions with calcite. Suarez (1977) similarly recommends using a ion activity product of $10^{-7.95}$ as the threshold where $CaCO_3$ precipitation occurs based on observations from soil solutions and the drainage waters of irrigated calcareous agricultural fields; taking the K_{sp} of calcite to be $10^{-8.48}$ (Plummer and Busenberg, 1982), this equates to SI = 0.53. Recent work considering the potential for secondary carbonate precipitation in rivers due to ERW deployments assume a saturation state threshold of SI = 1.0 (Harrington et al., 2023; Knapp and Tipper, 2022). It is thus reasonable to assume that substantial secondary carbonate formation will not occur until a saturation state threshold substantially higher than SI = 0 is reached; as such, we recommend SI = 1.0 as the upper limit of that threshold.

Finally, it is important to note that unlike soil organic carbon, soil inorganic carbon tends to accumulate deeper in the soil profile (Kim et al., 2020; Lorenz and Lal, 2018; Retallack, 2005). In an ERW context, Khalidy et al. (2024, 2023) demonstrated carbonate accumulation in response to wollastonite deployment was not limited to surficial layers containing the feedstock amendment. Monitoring for soil carbonate formation within the near-surface weathering zone will not be sufficient to capture carbonate formation that has a meaningful impact on netCDR; in the very least, the entirety of the NFZ must be considered, and accumulation of carbonate deeper in the soil profile and throughout the lower vadose zone will be an important component of better understanding the FFZ carbon balance moving forward (Section 9.2).

8.5.2 Approaches to monitoring and accounting for potential soil carbonate formation in netCDR quantification

Broadly, there are five approaches to account for (potential) secondary carbonate formation in the soil profile in netCDR quantification ($CO_2e_{Secondary\ Carbonates,\ RP}$):

1) The decline in CDR efficiency due to carbonate formation may already be conservatively captured by the feedstock dissolution measurement (Section 8.2) or monitoring of the integrated weathering flux (Section 8.1). In this case, carbonate formation does not need to be considered independently in the NFZ term balance (Eq. 5.4.1.1.1), though it may be to account for carbon stored in the carbonate lattice.

   Specifically:

   - soil profile (e.g., monitoring of tile drainage, deep lysimeters, or catchment drainage If $CO_2e_{NFZ,\ RP}$ is quantified by measuring the time-integrated alkalinity flux at the base of the waters), the decline in NFZ CDR due any carbonate formation will already be *conservatively* accounted for.

   - If $CO_2e_{Feedstock\ Dissolution,\ RP}$ is quantified by approaches that span the entirety of the NFZ (e.g., by solid-phase measurements of [mobile]/[immobile] elements), the decrease in netCDR due to carbonate precipitation in the soil profile *may* already be conservatively accounted for. This will be the case if the base cations incorporated into carbonate minerals are partitioned into the ‘unweathered’ phase by the measurement technique. Importantly, for solid-phase mass balance approaches, care must be taken to ensure that carbonate phases are not removed during any pretreatment steps (e.g., via ammonium acetate extractions or an acid rinse) such that precipitated carbonates are still considered part of the solid or unweathered phase.

   - If $CO_2e_{Feedstock\ Dissolution,\ RP}$ or the integrated weathering flux is quantified in shallow portions of the soil profile but not the entirety of the NFZ, the alkalinity removed from solution by any carbonate precipitation *within the measurement depth horizon* is already captured by the empirical measurement. However, the potential for carbonate precipitation from the measurement depth through the end of the NFZ must be additionally accounted for.

   - In all cases described here, this would provide a *conservative* estimate of netCDR and not account for the CO_2 stored in any secondary carbonates formed. The additional CDR associated with CO_2 stored as carbonate minerals may be accounted for via direct quantification of SIC stocks (Section 8.5.3).

2) Carbonate formation in the soil profile can be directly monitored through measurements of how soil inorganic carbon stocks evolve through time relative to a business as usual plot. Guidance for the quantification of SIC stocks is provided in Section 8.5.3.

3) As models improve, carbonate accumulation throughout the soil profile (including deeper soils and into the lower vadose zone) could eventually be estimated through geochemical modeling, parameterized by site-specific soil physiochemical and hydrologic characteristics as well as climatic forcing.

    - While the first-order controls on pedogenic carbonate formation are well understood, predictive modeling of pedogenic carbonate accumulation in the soil profile remains challenging; process-based models must accurately capture soil water dynamics, fluctuating pCO_2 and pH driven by biological processes, and may need to incorporate more nuanced mechanisms and controls on carbonate mineral formation (e.g., interactions with inhibitors) than are currently used in most models. In the future, well-validated models may be able to simulate soil processes with sufficient accuracy to move to a largely model-based quantification approach (Section 8.10); however, the assessment of Working Groups 2 and 4 is that reactive transport or other NFZ models should not currently be relied upon to predict soil carbonate accumulation in the NFZ.

    - Future R&D priorities should include gathering long-term (multi-annual) datasets of SIC accumulation in ERW contexts, including measurements of deeper soils. These datasets are required to develop validated modeling frameworks that can predict pedogenic carbonate formation over annual to decadal timescales to the requisite degree of certainty.

4) Under some circumstances, soil carbonate formation may be justifiably assumed to be negligible based on the combination of feedstock, soil conditions, and climatic conditions that characterize a deployment. In this case, potential carbonate formation would not need to be considered as part of the NFZ term balance. This is explored in detail below (Section 8.5.2.1).

5) On the other hand, in systems where there is a high probability of carbonate formation, it may be justified to assume that all alkalinity released from the feedstock forms a carbonate either within the soil profile or downstream and adjust the CDR efficiency accordingly. Notably, this assumes that there is not substantial formation of secondary phases with a lower cation:carbon stoichiometry than carbonates (e.g., some clays), but assuming stoichiometric carbonate precipitation is likely a justifiable assumption at this stage of the field.

8.5.2.1 Under what conditions could pedogenic carbonate formation be assumed to be negligible?

Here, we consider what suites of conditions would either indicate there is a high probability of soil carbonate formation (and thus negligible carbonate formation should *not* be assumed), or indicate that there is a low likelihood of meaningful carbonate accumulation in the soil profile as the result of an ERW deployment.

8.5.2.1.1 Conditions that would indicate a high probability of carbonate formation

- If the soil contains calcic horizons, contains pedogenic evidence of carbonate accumulation, or if the baseline soil inorganic carbon content is high (e.g., > 0.5 wt %), the probability of secondary carbonate formation associated with an ERW deployment should be considered **high**. This criterion applies across all feedstocks used for ERW.
    - Elevated baseline soil inorganic carbon content is interpreted to be indicative of either active pedogenic carbonate formation or situations where there is a high probability that porewaters are near saturation with respect to $CaCO_3$ phases. In the case of high annual infiltration rates,

    it may be possible to prevent unduly triggering more robust quantification in the case of soils with high SIC contents due to calcareous parent materials or significant deposition of calcareous materials where there is a low probability that any carbonates formed will persist long enough to represent a long-term sink of alkalinity in the NFZ. Example metrics that could be used to delineate sufficiently high infiltration rates include an aridity index substantially > 1 (also considering water added via irrigation). However, this should be approached cautiously. As discussed above, persistent pedogenic carbonates have been observed in tropical, high annual rainfall soils with strong monsoonal climates (e.g., Licht et al., 2022; van der Kaars and Dam, 1997). This suggests additional care may be warranted when considering soil systems that are seasonally dry, even with high annual infiltration rates.

    - This condition applies to all alkaline feedstocks, not just Ca-rich feedstocks, as if there is evidence of active pedogenic carbonate formation or soils buffered by $CaCO_3$, the changes induced to the soil carbonate system by the ERW intervention could drive additional $CaCO_3$ formation whether or not the feedstock is Ca-rich. Mg-rich feedstocks can also make Ca more bio-available e.g., via ion exchange which would also alter the $CaCO_3$ saturation state.

- A high probability of pedogenic carbonate formation should also be assumed for fast-weathering feedstocks prone to direct mineral carbonation, for example wollastonite (Haque et al., 2020; Khalidy et al., 2024, 2023; Wood et al., 2023) and silicate assemblages or alkaline wastes with high hydroxide content (Gras et al., 2017; Sanna et al., 2014).

- Broadly, soil conditions that lead to persistently or seasonally elevated carbonate saturation states (explored more below) should be considered to yield a high probability of pedogenic carbonate formation.

8.5.2.1.2 Justifying assumed negligible carbonate formation in the soil profile

Given the current lack of robustly validated models capable of simulating pedogenic carbonate accumulation over annual to decadal timescales, the assessment of the joint market practitioner-working group session assigned to this topic was that for near-term deployments, any justification that (persistent) soil carbonate formation is likely to be negligible for a given deployment would need to be based on saturation state arguments informed by empirical measurements.

One such approach is outlined here. Notably, in some instances, the measurements required to sufficiently justify that carbonate formation is likely negligible may be more onerous than pursuing direct quantification of carbonate formation (e.g., through monitoring of soil inorganic carbon stocks–Section 8.5.3).

As a default, practitioners should produce an estimate of baseline $CaCO_3$ (calcite) saturation state and a ‘deployment’ saturation state–specifically considering how the porewater pH, DIC, and [Ca] are likely to evolve as a result of the deployment. Practitioners could justify that $CaCO_3$ formation is likely to be negligible based on consideration of the predicted range in soil porewater $CaCO_3$ saturation states throughout the NFZ:

- If the baseline calcite saturation index ($SI = \log_{10}(\{Ca^{2+}\}\{CO_3^{2-}\}/K_{sp})$) is greater than 0 in any region of the soil profile **and** the feedstock contains non-negligible Ca (e.g., > 5 wt% CaO), carbonate formation *cannot* be assumed to be negligible.

- If the calcite saturation index at the evolved pH, DIC, and [Ca] predicted for the deployment is greater than 1 in any region of the soil profile, carbonate formation *cannot* be assumed to be negligible regardless of feedstock used.

- Otherwise, a practitioner may argue that carbonate precipitation in the NFZ is likely to be negligible and thus does not need to be constrained as part of netCDR quantification.

Calculations of saturation index should be performed with direct measurements of at least 2 components of the carbonate system (e.g., pH and DIC) and major ion concentrations from deployment soils, considering the entirety of the NFZ. Direct measurements of porewater are recommended (e.g., using water collected via rhizons or lysimeters, where care has been taken to prevent or properly account for CO_2 degassing).

Variation in porewater saturation state through time is a serious complicating factor when considering carbonate saturation state. Fluctuations in soil water content, pCO_2, and temperature can drive significant fluctuations in carbonate saturation state seasonally (Breecker et al., 2009) and in response to precipitation or irrigation (Gallagher and Breecker, 2020). Ideally, any justification for a negligible probability of carbonate formation would be based on a robust time series of aqueous phase measurements, with sampling designed to capture representative variations in water content and pCO_2 through time in the system of interest. Calcite saturation state calculations should be performed for a representative suite of conditions (e.g., considering different seasonal or wet/dry season conditions, in addition to the average annual water content), and the highest calcite saturation states should be considered.

8.5.3 Constraining pedogenic carbonate formation in cases where direct quantification is required

As with quantifying changes in soil organic carbon stocks in response to a change in land use, quantifying changes in soil inorganic carbon content and stocks in response to ERW interventions is complicated by baseline spatial heterogeneity and the fact that even small changes to the soil inorganic carbon pool could represent meaningful changes to netCDR in the NFZ. For example, assuming a bulk density of 1.4g/cm^3, even a change of 0.1 wt % $CaCO_3$ over the top 50 centimeters of the soil column equates to 3.1 ton CO_2/ha stored as $CaCO_3$, with an equivalent reduction in CDR efficiency due to alkalinity removal from solution. High-precision measurements and high spatial density sampling may be required to meaningfully constrain reductions in CDR efficiency and carbon stored due to secondary carbonate formation. We provide high-level guidelines for empirically measuring carbonate formation in the soil profile here:

- The change in soil inorganic carbon (SIC) stock should be quantified both relative to the initial baseline and relative to a Business As Usual (BAU) plot (Section 5.5.3.1).

- The addition of agricultural lime could significantly complicate the assessment of SIC changes induced by the ERW deployment–at least in the upper portions of the soil profile, as shallow soils may contain undissolved carbonate amendments. This may be commonly encountered in BAU plots in regions where liming is a common commercial practice; it is also possible that ag-lime will continue to be deployed on treatment plots alongside other alkaline feedstocks. In these cases, it is recommended that SIC stock measurements focus on soil depths below the surface soil layer into which the liming agent is mixed. An alternative option could be to quantify SIC changes relative to the project baseline in cases where there is a difference in carbonate inputs between the treatment and BAU plot; in this case, it would be particularly important for successive SIC monitoring to occur at a similar time of year.

- As is the case for soil organic carbon, practitioners must be cognizant of baseline variability in SIC and implications for sample density required to achieve the requisite level of precision in quantifying changes in SIC stocks. The following guidelines are recommended:
    - SIC measurements should be taken at a similar time of year, in both the BAU and treatment plots. Note: both the total inorganic carbon content and bulk density must be constrained.
    - The baseline spatial variability in SIC concentration and analytical precision of the measurement technique must be considered in calculating the sample density required (e.g., Section 7.4.1.1).
    - The analytical precision required also should be considered when selecting a measurement method (Campbell et al., 2023); while high-precision measurements of inorganic carbon content are possible through techniques like coulometry (Power et al., 2020), uncertainty due to small-scale sample heterogeneity can still be challenging to overcome.
    - Uncertainty in the SIC stock quantification should be explicitly quantified and accounted for in the overall netCDR quantification (Section 5.6).

A final important consideration is the durability of any carbonates formed within the soil profile. In many environments, cycles of carbonate dissolution-reprecipitation will occur, and carbonates may be leached from the NFZ into deeper soils or groundwater. As further developed in Section 9.1.1, carbonic acid weathering of pedogenic carbonates has the potential to drive net additional CDR if the alkalinity produced remains in solution; strong acid weathering of the carbonate would lead to immediate evasion of the stored CO_2 while also neutralizing 2 moles of acidity in the soil system (Section 8.3). Reductions in SIC stocks between reporting periods should be interpreted with consideration of potential strong acid weathering.

8.6 Secondary Silicate and Other Secondary Phase Formation

The non-carbonate products of incongruent weathering reactions can also substantially impact the efficacy and CDR efficiency of ERW deployments. Of primary concern are secondary silicate minerals (e.g., clays and amorphous Si) and Fe/Al oxy-hydroxides, though other secondary phases–for example, Ca-phosphates (Hayder et al., 2019; Wood et al., 2023)–can be formed in specific systems.

Secondary mineral formation can both play a role in maintaining solution disequilibrium (Harrington et al., 2023; Maher et al., 2009; Schuiling et al., 2011), thereby facilitating faster and sustained dissolution and, on the other hand, acting as an overall limit to dissolution by preventing access to unreacted material (Daval et al., 2011; Maher et al., 2016; Oelkers et al., 2018). The precipitation of secondary minerals can also reduce CDR efficiency by removing base cations from solution or generating acidity; weathering products can be removed from solution via sorption (Bourg and Sposito, 2011), co-precipitation (Leckie et al., 1980), or as a stoichiometric constituent of a mineral phase (Sposito, 2016).

Considering secondary silicate formation specifically: while the absolute magnitude of terrestrial secondary silicate formation remains poorly constrained, estimates based on the global Si isotope budget suggest that a substantial proportion of dissolved Si released through silicate weathering may be cycled through terrestrial secondary silicate minerals (Rahman and Trower, 2023). In any case, it is well-established that secondary clay formation is a fundamental component of soil formation and evolution (Pogge Von Strandmann et al., 2021a; Ryu et al., 2014; Wilson, 1999). Authigenic clay formation in marine sediments via ‘reverse weathering’ reactions is also thought to be quantitatively important for global cation and alkalinity budgets (Dunlea et al., 2017; Isson and Planavsky, 2018; Loucaides et al., 2010; Michalopoulos and Aller, 2004, 1995a; Rahman, 2019).

Secondary silicate phases can also form quickly, and their formation may be spatially and temporally separated from the initial weathering reaction. Column experiments of basalt weathering show evidence of clay formation within hours to days (Pogge Von Strandmann et al., 2021b, 2019); substantial secondary clay formation was interpreted from the Mg isotope composition of well waters at the CarbFix injection site on a timescale of days (Oelkers et al., 2019); and incubation experiments probing olivine dissolution dynamics in seawater solutions have documented the formation of Mg-silicate phases over a timescale of 100 days (Fuhr et al., 2022; Rigopoulos et al., 2018). The translocation of clay minerals from dissolution in upper soil horizons to accumulation in deeper horizons is also a quintessential pattern in soil formation (Maher et al., 2009; Weil and Brady, 2016), which emphasizes the fact that monitoring for secondary silicate formation within the shallow weathering zone of ERW deployments will often not be sufficient to capture potential alkalinity loss via this pathway. The probability of substantial secondary silicate formation (particularly secondary silicate minerals with high cation:Si or Al ratios) is higher in systems with long fluid residence times, such as poorly drained soils and along groundwater flow paths with extended timescales of fluid-rock interaction (Dellinger et al., 2015; Pogge von Strandmann et al., 2023; Wilson, 1999).

8.6.1 Monitoring and explicitly accounting for the CDR impact of secondary phase formation

For ERW deployments utilizing silicate feedstocks, the consensus assessment of Working Group 2 was that, unlike secondary carbonate formation, it is difficult to identify regimes where secondary silicate or Fe/Al oxy-hydroxide could be assumed to be fully negligible. The impact of potential secondary phase formation should thus ideally be accounted for in netCDR quantification ($CO_2e_{Secondary\ Silicates,\ RP}$). As with most NFZ alkalinity loss pathways, the extent to which the impact of secondary phase formation on

$CDR_{NFZ, RP}$ is captured by measurements of the integrated weathering flux (Section 8.1) or feedstock dissolution (Section 8.2) will depend on the details of those measurements:

- If $CO_2e_{NFZ, RP}$ is effectively quantified by measuring the time-integrated alkalinity flux at the base of the soil profile (e.g., monitoring of tile drainage, deep lysimeters, or catchment drainage waters), the decline in NFZ CDR due any secondary phase formation will already be accounted for.

- If $CO_2e_{Feedstock\ Dissolution, RP}$ is quantified by approaches that span the entirety of the NFZ (e.g., by solid-phase measurements of mobile/immobile elements), the decrease in netCDR due to secondary phase formation in the soil profile *may* already be conservatively accounted for (specifically, if the base cations incorporated into secondary phases are partitioned into the 'unweathered' phase by the measurement technique).

- If $CO_2e_{Feedstock\ Dissolution, RP}$ or the integrated weathering flux is quantified in shallow portions of the soil profile but not the entirety of the NFZ, the alkalinity removed from solution by any secondary phase formation within the measurement depth horizon is already captured by the empirical measurement. However, the potential for declines in CDR efficiency due to secondary phase formation from the measurement depth through the end of the NFZ should be additionally accounted for.

If the decline in CDR efficiency due to secondary phase formation is not already captured by measurements of feedstock dissolution or the integrated weathering flux, potential quantification options depend on the secondary phase of interest.

8.6.1.1 Fe and Al oxy-hydroxides

The formation of Fe and Al oxy-hydroxides alone may not lead to a decline in CDR efficiency, as long as Fe or Al are not being considered to potentially drive CDR. While acidity will be produced through Fe^{3+} and Al^{3+} hydrolysis, as a general rule, that production of acidity will simply balance the acidity consumed during the feedstock dissolution that mobilized those cations (though for any dissolved-phase Al under circumneutral to basic pH, the hydrolysis of $Al(OH)_3^0$ to $Al(OH)_4^-$ will produce acidity and reduce CDR efficiency (Povar and Rusu, 2012; Renforth, 2019)). Metal oxy-hydroxide formation can, however, reduce CDR efficiency through base cation sorption (reflected in $CO_2e_{Sorption, RP}$, Section 8.4) or co-precipitation of base cations, including the successive cation enrichment of meta-stable Fe and Al oxy-hydroxides. CDR may also be reduced when OH^- generated during feedstock dissolution substitutes for organic ligands on organic-Al complexes and therefore does not increase DIC. The high point of zero charge of Fe and Al oxy-hydroxides (Kosmulski, 2016) also means they can provide anion exchange capacity in circumneutral and acidic soil solutions, though it has not yet been demonstrated that carbonate or bicarbonate uptake via sorption to metal oxides would represent a meaningful carbon flux in the cropland soil systems relevant to ERW deployments (Mendez and Hiemstra, 2019).

Pedogenic Fe and Al oxy-hydroxides and associated base cation content can be assessed using a variety of extraction methods (see Rennert (2018) for a review). It is recommended that such characterizations are pursued in an R&D capacity for near-term deployments.

8.6.1.2 Secondary silicates

Direct quantification of newly formed secondary clays, e.g., via quantitative XRD (Zhou et al., 2018), could be extremely challenging, particularly over the short timescales of reporting periods and given that the secondary phases most likely to form rapidly in the field are non-crystalline or short-range order phases that cannot be identified via XRD (Bonatotzky et al., 2021; Parfitt, 2009). The detection and quantification of such short-range order phases (both silicates and Fe/Al oxy-hydroxides) should be considered a key research priority, particularly given their importance to soil organic matter stabilization (Chevallier et al., 2019; Kleber et al., 2015; Rasmussen et al., 2018). Looking forward, there is potential to capture secondary silicate formation in reactive transport models (Section 8.10), but substantially more calibration and validation of post-dissolution cation dynamics is required before such models can be used to capture netCDR with high confidence.

Building an improved predictive understanding of the timing and magnitude of secondary silicate formation in both the soil profile and along the long fluid residence time flow paths of the lower vadose zone and groundwater systems (Section 9.2) should be considered a key R&D priority. In a research context, isotope fractionation can be a particularly powerful tool for tracking and inferring secondary silicate formation; lithium (Chapela et al., 2022; Golla et al., 2021; Pistiner and Henderson, 2003; Pogge Von Strandmann et al., 2021b, 2021a), magnesium (Oelkers et al., 2019; Pogge von Strandmann et al., 2008; Ryu et al., 2016; Teng et al., 2010; Tipper et al., 2006; Wimpenny et al., 2014), and silicon isotopes (Z. Li et al., 2020; Pogge von Strandmann et al., 2012; Vienne et al., 2023) can all be used to inform the extent of clay formation in the field and provide empirical constraints for validating reaction-transport models. Solid-state NMR (nuclear magnetic resonance) has also been used to quantify the relative abundance of primary to secondary silicates (based on inferred Al and Si coordination, e.g., Hiradate (2004)).

8.6.1 Call to action: Quantitatively consider the outcome of different pathways of incongruency

Given the challenges associated with direct quantification of secondary silicate phases, it is not recommended that early-stage commercial deployments be required to independently constrain NFZ alkalinity loss through secondary silicate formation.

However, the potential for secondary phase formation and the implications of different potential incongruent weathering pathways should not be ignored. One option to constrain the ‘worst case scenario’ potential impact of secondary phase formation is to consider the implications of different representative secondary phase products on the overall cation and proton balance, informed by the deployment context. The key question is: what secondary phases are likely to form in a given system, and what is the cation stoichiometry of those phases?

The ultimate impact on the net carbon balance of different incongruent weathering pathways (e.g., forming a kaolinite or smectite with an assumed compositional range) could be estimated through the development of a stoichiometric matrix (Morel and Hering, 1993), and assuming those net reactions occur (e.g., balancing on Al). This would yield a maximally conservative estimate of the reduction in CDR efficiency due to secondary phase formation, notably including the potential for secondary phase formation in downstream systems. There will be high uncertainty in this estimate given uncertainty in the Si:cation or Al:cation stoichiometry of potential secondary phases in addition to the general classes of material that will be formed. Nonetheless, starting to acknowledge openly that some fraction of netCDR can and likely will be undone by the formation of secondary (silicate) phases, and placing bounds on that potential through stoichiometric arguments, could be a good place to start.

8.7 Alkalinity Loss due to Biomass Uptake

Plants retrieve nutrients from the soil solution, including base cations such as Ca^{2+}, Mg^{2+}, K^+, and Na^+ (Clarkson and Hanson, 1980). The removal of these cations from the soil solution–generally accompanied by a release of protons to maintain charge balance within the plant–'undoes' any CDR that was being driven by the base cations in solution or equivalently drives CO_2 evasion. No net charge can cross the soil-root boundary, so any excess cation or anion uptake by the plant is stoichiometrically matched by H^+ or OH^- release (Fried and Shapiro, 1961). Analogously, properly attributing the removal of base cations from the soil system via biomass uptake is critical for cation accounting approaches to weathering quantification; cations incorporated into biomass will be removed from the NFZ but not contribute to CDR. Accounting for base cation uptake into plant biomass is thus important for a holistic accounting of netCDR.

There was consensus amongst Working Group 2 that, while the development of sufficiently robust predictive frameworks to estimate element-specific plant uptake for different crop types under different growing conditions is a good goal for the ERW community to work towards, sufficient data (or in the very least sufficient synthesized data) does not yet exist. There are several controls on plant nutrient uptake that could potentially be affected by an ERW deployment, such as the presence of biotic and abiotic stressors, competition between plants and soil microorganisms for available nutrients in the rhizosphere, and the presence of soil enzymes that control the availability of nutrients to the plant's roots (Naeem et al., 2017). Because of the complex interactions between plants, soils, and microbes, as well as their various controls on plant nutrient uptake, it is not a trivial task to accurately predict the amount of cations that will be taken up by a given crop in a deployment area. Significantly more data on how base cation uptake varies across crop types and as a function of growth rate, growing conditions, soil enzyme and microbial activity, and soil chemistry (pH, base cation concentrations, nutrient ratios, etc.) is needed to produce such a predictive understanding, although existing compilations of net cation uptake by plant roots may provide a good starting point (e.g., Espeleta et al., 2017 and references therein).

There are a few direct measurements of plant base cation uptake from ERW field trials, but there is still relatively little certainty about how different crops will respond to increased nutrient availability provided by feedstock dissolution. A 4-year study conducted in a Midwestern U.S. corn and miscanthus cropping system treated with 50 t ha^{-1} of basalt per year showed that 4.5% of base cations released via weathering were taken up by the maize plants, whereas only 1.1% were taken up by miscanthus plants in the neighboring experimental plots (Kantola et al., 2023). Research in the Hubbard Brook experimental watershed, an acidified (base-poor) forested catchment where a one-time 3.8 t ha^{-1} wollastonite treatment was applied, showed a 7.55% greater export of Ca from the surficial Oa horizon than in the Bh horizon, which they concluded was due to plant uptake of Ca from the Oa horizon and/or the lateral flow of soil water (Shao et al 2016). In a field trial examining the effects of a 50 t h^{-1} application of felsic glacial rock flour on potato and corn growth in Denmark, results showed no differences in soil K availability between the treatment and control, which led to the conclusion that any K released via rock flour dissolution was taken up by crops (Gunnarsen et al., 2023). It is clear from these studies that the amount of cation uptake varies widely by element and across different crop types and conditions.

Another consideration as ERW deployments expand is the relationship between base cation uptake and increases in carbon stored as standing biomass, and the implications for holistic carbon accounting. For perennial cropping and forestry systems, while increased growth and standing biomass will lead to alkalinity losses via nutrient uptake, it will also lead to increased carbon stored as biomass (Taylor et al., 2021). Although this increased carbon sequestration from additional biomass growth should not be considered equivalent to the CO_2 removed by geochemical reactions in an ERW deployment, this scenario highlights the need to navigate between different carbon quantification and crediting regimes (e.g., soil organic carbon, forest biomass, and ERW) to avoid overcounting while providing a more holistic accounting of the overall carbon balance.

Similar considerations are relevant to the question of what components of plant biomass should be monitored for base cation uptake, given that some base cations will be incorporated into biomass that is ultimately left on the field. Should base cation uptake into such biomass (e.g., roots or biomass that is not collected during harvesting) be considered as reducing the CDR efficiency as well? Consider the case of base cations incorporated into the root system of annual crops. Such belowground biomass is commonly left on the field after harvesting, and thus not removed from the soil system. However, the base cations will not be returned to the aqueous phase until the biomass decomposes, which for fine roots will likely occur on a continuum of months to years (See et al., 2019; Zhang and Wang, 2015). Base cation uptake into biomass that is not removed from fields may thus represent a transient alkalinity sink with a variable time lag. We recommend that practitioners focus on quantifying the magnitude of base cation uptake into biomass that is *removed* from the field for netCDR quantification, but to consider base cation incorporation into below-ground biomass and biomass that is returned to the field in research studies.

8.7.1 Guidance for quantifying base cation uptake by biomass

The approach for constraining plant uptake ($CO_2e_{Biomass\ Uptake,\ RP}$, Eq. 5.4.1.2.1) will depend on the measurement technique being used to quantify netCDR:

- If $CO_2e_{NFZ,\ RP}$ is constrained by the time-integrated alkalinity flux at or beyond the end of the NFZ (e.g., monitoring of tile drainage, deep lysimeters, or catchment drainage waters), then the alkalinity loss from plant uptake has already been accounted for and no direct measurement of base cation content of biomass is required.
- If feedstock dissolution is constrained independently and $CO_2e_{NFZ,\ RP}$ is calculated as the sum of potential CDR driven by feedstock dissolution and the change in carbon/alkalinity sources and sinks in the soil profile, plant uptake should be estimated through direct measurements of the base cation content of relevant biomass. This also applies to shallow measurements of the integrated weathering flux (Section 8.1); if measurements of dissolved weathering products do not extend to the shallower of the maximum rooting depth for the crop type and the depth of the NFZ (Section 4), plant uptake should also be estimated through direct measurements of the base cation content of relevant biomass.
    - For **annual crops**, this should be informed by direct measurement of the total base cation content of harvested biomass (including all relevant portions of the plant), coupled with an estimate of the total biomass removed from the field. All base cations considered as potential drivers of CDR must be measured, alongside the carbon content of the biomass. Comparable measurements should be made on the BAU plot to quantify counterfactual base cation uptake ($CO_2e_{Biomass\ Uptake,\ RP}$ in the counterfactual scenario calculated as $CO_2e_{CF\ NFZ,\ RP}$).
    - For **perennial crops** or in agroforestry systems, this should be informed by direct measurement of the total base cation content in new growth over the reporting period, coupled with an estimate of net new biomass (Battles et al., 2014). Comparable measurements of new biomass growth should be made on the BAU plot to quantify counterfactual base cation uptake ($CO_2e_{Biomass\ Uptake,\ RP}$ in the counterfactual scenario).

8.8 Changes to the Net Organic Carbon Balance

The inorganic carbon uptake flux of most ERW deployments will be dwarfed by the magnitude of CO_2 uptake by primary productivity and release through respiration; these organic fluxes will often be an order of magnitude or more higher than the inorganic CDR flux in agricultural systems (Kantola et al., 2023; Kutsch et al., 2010). Small changes in the balance between photosynthesis and respiration, or a destabilization of existing soil organic carbon stocks, could substantially reduce or completely negate CO_2 uptake by an ERW deployment. The evidence base for how shifts in soil biogeochemistry and physical conditions due to ERW deployments can influence different aspects of soil organic carbon cycling (productivity, respiration, stabilization, or destabilization of existing organic carbon stocks) is just emerging. The consensus opinion of Working Group 2 was that our understanding of a given ERW intervention's potential impact on soil organic carbon stocks and the net organic carbon balance is nascent, and we do not yet have enough data and sufficient predictive understanding of the underlying mechanistic drivers of interactions between SOC and ERW to consider the potential for SOC mobilization resulting from an ERW deployment to be sufficiently de-risked. The consensus opinion of the Working Group was that, at this stage of our understanding, some monitoring of soil organic carbon stocks is required in the near term.

Observations thus far have demonstrated variable responses of SOC to alkaline feedstock addition in field trials, mesocosm studies, and laboratory experiments (Almaraz, 2023; Buss et al., 2023; Pihlap et al., 2024; Sokol et al., 2024). There are multiple pathways by which an ERW intervention could lead to net stabilization and accumulation of SOC; the release of multivalent cations and formation of secondary minerals can lead to SOC stabilization chemically through organo-mineral associations and physically by aggregate formation (Rasmussen et al., 2018; Slessarev et al., 2022; Te Pas et al., 2023; Torn et al., 1997). A recent incubation experiment showed that the addition of basalt increased the stabilization of soil organic matter from the release of Ca, Mg, and formation of secondary minerals, although this stabilization was partially counteracted by the addition of wheat plants to the soil experiment (Buss et al., 2023). However, other field trials have shown decreases in SOC content in the top 0-10 centimeters of soil relative to a control plot following silicate rock amendment (Almaraz, 2023; Sokol et al., 2024).

Meta-analyses investigating the impact of liming on SOC stocks have highlighted the differential response of soil carbon inputs and outputs to agricultural lime addition (Holland et al., 2018; Paradelo et al., 2015; Rowley et al., 2018). It has been found in many studies that the pH increase from liming can increase microbial respiration, which results in CO_2 losses, but that those losses can be offset by increased carbon inputs courtesy of improved productivity and SOC stabilization over longer timescales (Paradelo et al., 2015).

There are some soil conditions that are at particularly high risk for SOC loss resulting from an ERW deployment. These areas are predicted to be of high-risk because of pH-dependent mechanisms such as the disruption of organo-mineral and organo-metal bonds, or an increase in microbial activity and respiration due to an increase in soil pH (Kleber et al., 2015; Y. Li et al., 2020; Rousk et al., 2009). Given that a relatively small percent change in SOC stocks–even just in surface soils (10-20 centimeter depth)–can be large enough to entirely negate or surpass the carbon captured through inorganic geochemical reactions of an ERW deployment, there is a need to guard against potential SOC losses resulting from ERW deployments. Note that accounting for the accrual of SOC as the result of an ERW deployment is outside the scope of this document because carbon stored as soil organic carbon has a substantially different permanence profile than that of ERW and therefore should not be bundled within the same accounting framework (Brander et al., 2021; Manning et al., 2024).

Given the current state of understanding about the potential impact of an ERW deployment on the net organic carbon balance (inputs versus respiration), it is difficult to say whether a given deployment will have a negligible risk of SOC loss. At the same time, robustly monitoring commercial deployments for changes in soil organic carbon stocks would be expensive and operationally challenging. A two-fold approach is thus recommended here:

- First, deployments should not be undertaken under conditions that have been deemed at 'high risk of substantial SOC loss' (Section 8.8.1), until sufficient evidence has been generated to de-risk the impact of an ERW intervention on organic carbon cycling in such systems.
- Second, for deployments not considered 'high risk', monitoring of bulk SOC stocks should be implemented on a representative sub-plot within the deployment area (randomly selected, representing 10% of the total deployment area) and corresponding 'business as usual' or negative control plot.

We do not recommend that any changes to SOC stocks be directly incorporated into netCDR quantification for commercial ERW deployments at this time. Instead, SOC monitoring data should be transparently reported in a timely manner, and this data should be used to regularly assess whether changes are needed in how the ERW community monitors and accounts for any changes to the net organic carbon balance due to ERW interventions, and guards against significant organic carbon loss (including transient losses).

8.8.1 Criteria that represent a 'high risk of substantial SOC loss'

The consensus assessment of Working Group 2 and a joint Working Group-Market Practitioner convening was that deployments not be undertaken under conditions considered to be at a high risk of substantial SOC loss outside of a research context.

Table 3: High risk of SOC loss. Criteria that would identify a deployment as being at 'high risk of substantial SOC loss'

Criteria identifying a deployment as 'high risk of substantial SOC loss'	Justification for the criteria
Organic soils: peatlands (histosols) or forest soils with acid organic horizons	Increasing soil pH in acidic soils can increase rates of microbial respiration (Rousk et al., 2009). A meta-analysis of studies investigating the effect of liming on SOC stocks found that several trials observed increased respiration in limed soils compared to non-limed ones (Holland et al., 2018; Paradelo et al., 2015). However, changes in SOC stocks reflect the balance between carbon inputs and outputs. Although the pH increase from liming soils can increase microbial respiration on short-term timescales, liming can also stimulate biomass production, thereby increasing long-term SOM accumulation (Fornara et al., 2011; Holland et al., 2018) In acidic peat soils in particular, increasing pH has been demonstrated to increase levels of the enzyme phenol oxidase, which can increase both peat decomposition and DOC export (Kang et al., 2018; Klemme et al., 2022). Other studies surveyed below demonstrate a soil pH-microbial respiration relationship in studies of liming forest soils: Forest–Podzol: The liming of acidic forest soils results in an initial pulse of

	respiration, and the mean residence time of soil C tends to decrease with an increasing dose of lime (Persson et al., 2021). Forest–Podzol: A highly acidic forest soil in Quebec received a 50 Mg/ha dolomitic lime dose in 1994 and 15 years later exhibited a 20-30% decrease in organic matter relative to a control (Moore et al., 2012). Forest–Podzol: Results from liming a forest soil in Sweden with 9 t ha^{-1} of CaCO$_3$ showed long-term decreases (40 year time horizon) in C pools (Persson et al., 1995). Forest–Podzol (increase in DOC): An acidified Norwegian forest soil was limed in with 3 t h^{-1} in 1994 and showed a small increase in TOC when compared to a reference plot (Hindar et al., 2003) Forest–Cambic Arenosol: A Berlin urban forest limed at 6.1 t ha^{-1} showed a sharp decrease in SOC after one year, which is attributed to an increase in microbial respiration (Marschner and Waldemar Wilczynski, 1991). The high risk of SOC destabilization, driven by increased pH in organic soils such as peat or forest soils with acidic organic horizons, leads to the current recommendation that deployments should not be undertaken in these areas.
Organic-rich agricultural soils (>5 wt% OC in the top 10cm, with caution advised above 3 wt% OC content)	A soil with a bulk density of 1g/cm^3 and 5 wt% SOC contains ~50 tonnes of organic C per ha in the upper 10 cm. A loss of even 5% of that SOC stock is equivalent to 9.2 t CO$_2$$^{-1}$ ha^{-1}, which would represent most, if not all, of the total potential inorganic CDR of a typical ERW deployment (e.g., 20t ha^{-1} basalt application). Because of this risk of SOC losses entirely offsetting a deployment's CDR, early commercial deployments should avoid sites with organic-rich top soils. Although 5% is the threshold proposed here, we recognize that there are potential risks of SOC loss in soils with OC contents lower than 5%. To first order, the higher the OC content of a soil, the higher the potential for significant SOC losses. Therefore, in soils with 3-5% OC content, caution is strongly advised when undertaking an ERW deployment.
Soil classified as either acid Andosol (e.g., alu-andic Andosol) or Umbrisol	Increasing the pH of Andosols and Umbrisols can lead to increased soil respiration. Any site where commercial soil pH modification (e.g., liming) is a current practice should be evaluated on a case by case basis and the risk of SOC loss (compared to the counterfactual scenario) should still be strongly considered on these sites. Alkalinization of Andosols (mineral soils with a high organic C concentration) could disrupt the organic matter association with both Al^{3+} and short-range order Al constituents, leading to increased soil respiration (Y. Li et al., 2020). Takahashi et al. (2006) report results from a field trial investigating the effects of liming an Andosol, in which they found that the 1-2 unit pH increase from liming significantly reduced organically complexed Al. Forster et al. (2021) investigated the influence of a ~0.5 unit pH increase from liming on a grassland Umbrisol, where liming was found to "enhance conditions relating to OM decomposition".
Soil with either an "andic" or "umbric" qualifier	The mechanism at play here is the same as described above in Li et al. (2020).

Before a deployment begins, the deployment area should be surveyed to determine if any of these characteristics apply. Commercial deployments should not be undertaken under such conditions until further research de-risks the possibility of significant SOC destabilization/loss. Once an ERW deployment has occurred, there is little that can be done to mitigate SOC destabilization after the fact.

8.8.1.1 Consideration of changes in agronomic practices

It is also recommended that operators monitor for potential changes in SOC stocks if an ERW deployment leads to an increase in tillage, or a change in cover cropping or irrigation practices. Because of the high potential for increased tillage to negatively impact SOC stocks (Follett and Schimel, 1989; Haddaway et al., 2017; Havlin et al., 1990; Salinas-Garcia et al., 1997), any deployment that leads to increased tillage should monitor for changes in SOC stocks. If other agronomic practices are changed as a result of an ERW deployment, such as cover cropping practices or irrigation (e.g., a shift from rain-fed to irrigation due to an ERW intervention), monitoring for SOC stock changes relative to the counterfactual practice implemented in a BAU plot is also recommended.

8.8.2 SOC monitoring should be undertaken on a subcomponent of all deployments

Potential SOC losses should be considered for all deployments, even those that are not identified as ‘high risk’, until a sufficient evidence base has been built to sufficiently de-risk SOC destabilization pathways as a result of ERW deployments. SOC monitoring is thus still recommended for deployments not identified as high-risk, both to further the community’s understanding of ERW-SOC interactions and to flag any site characteristics that indicate a high risk for SOC loss that are not currently considered high risk criteria. However, robustly monitoring the entirety of every deployment could be prohibitive from an operational and cost perspective given field-level variability in SOC content. The monitoring recommendations in this section aim to ensure that the requisite data is being gathered to regularly update a synthesized understanding of ERW-SOC interactions–with a particular emphasis on constraining situations in which substantial SOC loss may occur–and amend the recommendations accordingly.

For deployments that do not fall into the high-risk category, monitoring of bulk SOC stocks is strongly recommended on an area representing 10% of the acreage of each deployment, as well as on a corresponding Business As Usual (BAU) plot.

Selecting a deployment area for monitoring:
The area targeted for SOC monitoring should be randomly selected from amongst the control-treatment block pairs of a deployment (Section 7.3); it is recommended that SOC measurements are made on approximately 10% of the total deployment.

Guidance for monitoring:
Designing a monitoring plan to capture potential SOC losses is complicated by the underlying temporal fluctuations of SOC stocks and potential time evolution on ERW-SOC interactions. Not only are SOC stocks variable through time in natural systems, but the response to an ERW deployment is likely also variable through time. Established SOC monitoring protocols (generally measuring for SOC accrual, not loss) often require baseline measurements and measurements 5 years in the future (BCarbon, 2022; Ebert et al., 2020). However, because the aim of these recommendations is to guard against SOC loss rather than to track SOC accrual, monitoring once every 5 years could mean that SOC loss occurring on shorter time scales is overlooked, and critically, data to inform our understanding of potential near-term SOC loss would not be available for many years. Therefore, it is recommended that SOC stock measurements are performed at each reporting period as a default, or at a minimum once every 2 years to ensure no major SOC losses are occurring as a result of the ERW deployment. Baseline SOC content and bulk density

measurements should be taken before the spreading event in both the treatment and control areas. The randomly selected control-treatment subplots should be sampled at the same time of year to minimize the influence of seasonal variability in the SOC stock measurement.

It is recommended that monitoring should continue for a *minimum* of 10 years. At that 10 year point, if SOC stocks have not significantly declined (see Section 8.8.3 for definition of significance) relative to the BAU plot, monitoring is still recommended for the duration of the project, but should be considered of lower importance than monitoring in the initial 10 years. The recommendation of a 10 year monitoring window applies each time a spreading event occurs, even if re-applying to the same deployment area.

8.8.3 What counts as a "significant loss"?

A significant loss is defined as a statistically significant decline in SOC stocks between the treatment and BAU plot, with sampling that allows for a minimum detectable difference of 15% of the total potential inorganic CDR of the ERW deployment (Section 6.2.2).

8.8.4 Incorporation of SOC loss into netCDR

Regular monitoring and transparent reporting of changes to bulk SOC stocks are thus strongly recommended for a subset of fields under management. However, it is recommended that changes to SOC stocks be reported separately from quantified (inorganic) netCDR, instead of attempting to incorporate any measured SOC losses into netCDR calculations at this stage. Rather, this monitoring data should form the basis of datasets used to regularly assess the risk of SOC mobilization due to ERW interventions, and whether changes in practice should be implemented or requirements for SOC monitoring in commercial deployments should be re-evaluated.

One substantial challenge with incorporating changes in SOC stocks into ERW netCDR calculations is the potential mismatch between the complex temporal dynamics of SOC and the timing of ERW credit generation. It is entirely possible that short-term losses in SOC could be balanced out by a longer-term accrual of SOC or increased biomass in perennial systems. Therefore, future incorporation of SOC losses into the netCDR quantification should be flexible to this type of time-dependent SOC response. For example, any credits withheld or negated due to a measured decline in SOC stocks early in the project should theoretically be allowed to be reissued if SOC stocks return to baseline levels over the project lifetime (i.e., dictated by the dynamic baseline of the BAU plot).

8.8.5 SOC Monitoring Recommendations

Monitoring should follow an established SOC monitoring protocol that has the following characteristics:

- Uses empirical measurement techniques based directly on soil sampling, rather than relying on any use of models to quantify SOC stocks.
- Required measurement is bulk SOC stocks (rather than any specific soil carbon pool).
- Robust direct sampling requirements that account for potentially high baseline spatial variability in bulk SOC stocks, and require uncertainty quantification through a confidence interval.
- Requires SOC measurements on a BAU plot to establish a dynamic baseline. Changes in bulk SOC stocks for the ERW deployment are evaluated relative to this BAU plot.
- Bulk SOC stocks must be measured for the entire depth of the NFZ.

Note: SOC stock quantification calculations should account for the dilution effect of adding feedstock with very-low-to-negligible organic carbon content. The assumptions used to make this correction should be documented and reported.

Examples of protocols with SOC stock measurement requirements that adhere to these characteristics include the Australia Soil Carbon Credits Methodology (2018) and the BCarbon Soil Carbon Protocol (2022).

The SOC crediting community has established protocols that have been put in place to directly monitor changes in SOC in agricultural systems. Utilizing the direct monitoring requirements established in these protocols allows the ERW community to not "reinvent the wheel", but rather rely on the MRV expertise and experience of the SOC community.

8.8.6 Call to action: Regular re-evaluation of recommendations and requirements for commercial deployments

Given the current evidence base for ERW-SOC interactions, regular re-assessment of emergent learnings will be needed. Meta-analyses should be regularly conducted that incorporate both new understanding from the academic literature (drawing across lab, mesocosm, and field trial data) and findings from commercial deployments (Section 8.11). The outcomes of such meta-analyses would dictate whether the recommendations for SOC monitoring, reporting, and incorporation into netCDR quantification described here need to be updated (e.g., via updates to the conditions considered to be at "high risk for SOC loss", recommended changes in practice, or suggested monitoring requirements). Specifically, findings that point to significant SOC loss in certain regions, environments, or soil conditions in a meta-analysis should trigger an expedited re-evaluation and potential update of the recommendations put forth in this document (Section 8.11).

8.8.7 Future research priorities

This section contains preliminary recommendations on the outlook and R&D path forward to build a better predictive understanding of SOC-ERW interactions. Suggested near-term areas of focus include:

- Incorporation of ERW interventions into models of SOC dynamics–e.g., building on the CORPSE (Carbon, Organisms, Rhizosphere, and Protection in the Soil Environment) framework (Sulman et al., 2014). Measurement approaches, particularly for long-term monitoring sites, should consider data needed for model parameterization and model-data comparison.
- Probing the microbial community response to ERW interventions.
- Understanding the biological, mineralogical, and chemical effects of ERW on different pools of SOC.
- Investigating the evolution of mineral-organic and Ca-bridging SOC stabilization pathways across different ERW deployment contexts.

8.9 Potential Changes to Other Greenhouse Gas Emissions

The biogeochemical changes induced by alkaline feedstock addition can also impact the production and consumption of non-CO_2 greenhouse gasses, principally CH_4 and N_2O. For pH-sensitive nitrogen cycling in particular, initial mesocosm and modeling studies are consistent with silicate addition tending to decrease N_2O emissions (Blanc-Betes et al., 2021; Chiaravalloti et al., 2023; Val Martin et al., 2023), but the nitrogen cycle response to a given deployment can be context-dependent, nuanced, and complex (e.g., Nadeem et al., 2020; Poblador et al., 2024). A recent meta-analysis of the impact of liming on soil greenhouse gas fluxes reported significant declines in N_2O emissions, no significant effect on CH_4 uptake in well-aerated agricultural soils, and a decline in CH_4 emissions from rice paddy soils (H.-M. Zhang et al., 2022).

An important immediate consideration is whether reductions in non-CO_2 greenhouse gas emissions should be considered in netCDR of an ERW deployment. The consensus opinion of Working Group 2 was that, as with increases in soil organic carbon stocks or avoided emissions associated with counterfactual ag-lime or fertilizer input use, any decreased N_2O or CH_4 emissions resulting from ERW deployments should not be considered in the netCDR calculation. Such emissions reductions should absolutely be quantified and tracked as a part of holistic accounting of the net greenhouse gas balance of an ERW deployment; crediting these emissions reductions may also be pursued as part of a fit-for-purpose monitoring and crediting scheme. The Working Group concluded that any *required* monitoring should focus on protecting against potential downside risks of non-negligible increases in other greenhouse gas emissions due to an ERW deployment. Building a broader predictive understanding of potential feedback between ERW interventions and non-CO_2 greenhouse gas fluxes in different environments should remain a key R&D priority and be subject to regular meta-analyses (Section 8.11)

8.9.1 Recommendations for monitoring and path forward

The consensus opinion of the Working Group was that no direct monitoring for changes in non-CO_2 greenhouse gas emissions should be required for commercial deployments as default practice at this stage of the ERW pathway.

However, better understanding interactions between ERW interventions and soil N_2O emissions and CH_4 production in methanogenic systems is a key R&D area for both commercial deployments and academic studies. Focus areas should include expanded monitoring of N_2O and CH_4 fluxes following ERW deployments under a range of soil and environmental conditions–including both field and mesocosm studies (e.g., Chiaravalloti et al., 2023)–and model development (e.g., Val Martin et al., 2023).

8.10 Modeling the Near-Field Zone: Validation and Uncertainty Quantification

Geochemical modeling of ERW in soil systems is a critical tool for understanding and interpreting the soil processes at play. In general, there are two endmember types of models used for simulating ERW dynamics in the soil profile.

- Process-based models, such as reactive transport models (RTMs), computationally simulate relevant soil physics and chemical processes in ERW in the NFZ, including feedstock dissolution and cation transport and storage within the soil profile (Beerling et al., 2020; Deng et al., 2023; Kanzaki et al., 2023a, 2022; Kelland et al., 2020; Lewis et al., 2021; Mayer et al., 2002). Integrated soil models have also been developed, which couple field hydrology with biogeochemical dynamics (Bertagni et al., 2024; Cipolla et al., 2021).

- Data-driven models, e.g., ‘black-box’ machine learning models, can be trained on large amounts of empirical data from ERW deployments, without directly representing the physical and chemical processes in the soil.

Looking to the future, it is highly likely that these soil models will eventually need to be a central component of CDR quantification as ERW reaches greater scale, such that monitoring and verification can become less reliant on high density measurement and sampling for every deployment. However, given the early stage of the application of such models to ERW contexts and the need for stronger frameworks and datasets for calibration and validation, there is currently strong consensus in the community that soil models should not be used today in place of direct measurements and empirical constraints to quantify CDR. In an informal poll of the 100+ in-person attendees of the ERW24 conference in April 2024 (including ERW academics, market practitioners, and other key stakeholders), none of the attendees indicated they believed that models could reliably be used today for CDR quantification in ERW.

Thus, there is a strong need for the development of third-party, impartial systems for model validation and uncertainty analysis, such that we can evaluate the predictive skill and sensitivity of ERW models, and understand how and when they can play an increasing role in robust CDR quantification. The goal of this section is to outline the needs and considerations for a robust model validation system, along with a call to action for the community in the coming few years.

8.10.1 High level components of a model evaluation framework

The process of model validation aims to determine whether a model’s description, parameterization, or prediction of the underlying hydrologic and biogeochemical processes in ERW systems sufficiently match reality. This can most rigorously be done by comparing model predictions to empirical data from real soil systems. Given the complexity and heterogeneity of soil systems, a model may have greater predictive skill for a particular subset of deployment environments than others (e.g., particular soil types or field hydrologies), and a system for model validation should be able to reflect this system-specific nuance.

A broader system for model evaluation should also explicitly set out to characterize two distinct forms of uncertainty:

- **Structural uncertainty,** representing uncertainty around whether the computational implementation of physical and chemical processes within a model accurately represents the behavior of a soil system.

- **Parametric uncertainty,** representing uncertainty in the model output that is caused by uncertainty in the input parameters, including those used to represent the initial state of the soil system for modeling runs. This may arise due to measurement error, sampling uncertainty, or coarse estimates being used given insufficient data about the system.

In the following sections, we discuss four core components of a model evaluation framework that includes both a process for model validation and guidelines for characterizing uncertainty for model application in a specific project. These include:

1. Shared expectations and structure for **model documentation**.

2. A **benchmarking system** for data-model validation.

3. Robust and inclusive ERW **model intercomparison** efforts.

4. A shared pipeline for **multivariate sensitivity analyses** and quantification of parametric uncertainty.

It is important to note that these goals of model validation and uncertainty analysis are just as important in the context of the reactive transport, river, and ocean models being developed to track downstream processes (Section 9); for simplicity and to focus the calls to action, only soil models are discussed here.

8.10.2 Represented processes and shared documentation structure

There is a wide array of interconnected geochemical processes that NFZ models for ERW will likely attempt to implement, and each process has a range of possible implementations of varying complexity. Potentially relevant processes might include, for example, mineral dissolution and particle size distribution tracking, cation exchange and secondary site processes, and soil mixing (e.g., bioturbation and tillage), amongst many others.

One early step that the ERW modeling community should take in order to increase the legibility of published NFZ models and facilitate greater ease of mutual understanding and intercomparison is to develop a common structured format and set of expectations for model documentation. Such a format could be developed iteratively and by community consensus, and be designed to highlight important assumptions, details of model spin up, initialization, and parameterization, and process implementation decisions that may otherwise be hard to interpret.

The shared documentation format would include a structured means of describing the ERW scenario being simulated in any particular model run. The model tuning process should also be described in a structured way—this could include an articulation of which parameters are being tuned with particular data sets versus which parameters are fixed, and should also include an articulation of the assumed prior distribution of important model parameters. The process used for model spin-up and initialization can also be complex—the agricultural soils being modeled are often not in steady-state due to many decades of intensive human management, and so a common way of articulating the datasets used and the assumptions and decisions made to do spin-up may be helpful.

Geochemical processes may be represented in models in a variety of ways, so developing means of categorizing these different types of implementations, or structuring the discussion of how each is represented and parameterized into clear documentation sections, could help elucidate the nuances and limitations of each model. Relatedly, beginning to standardize around a common set of core model input and output variables will likely be helpful when creating community goods for model validation, intercomparison, and sensitivity analysis.

8.10.3 Benchmarking for ERW

There is an established literature describing benchmarks for geochemical reactive transport codes comparing model results for a range of subsurface applications (e.g., acid rock drainage and the dynamics of subsurface CO_2 storage) to known analytical solutions or to lab or field data (Mayer et al., 2015; Poonoosamy et al., 2021; Steefel et al., 2015). However, even where models that have been previously benchmarked for other applications are being used to simulate ERW, there is a strong case for the development of ERW-specific benchmarks, to evaluate the predictive skill of a range of models in this unique context. Some examples of ways in which application in ERW contexts might require novel model development and benchmarking compared to existing geochemical RTMs include:

- The context of a managed application of solid (reactive) feedstock with known particle size distributions.
- The centrality of cation exchange processes to ERW dynamics, which may require nuanced parameterization.
- The need to parameterize linkages between organic carbon cycling and evolving aqueous chemistry and soil mineralogy.
- The need to couple geochemical models with agronomic and land surface modeling frameworks (e.g., interactions with plant roots, biomass growth, and land management practices).

A good analogy the ERW modeling community can learn from is the International Land Model Benchmarking (ILAMB) System, an systematic and widely-used open source benchmarking tool which assesses the relative performance of large-scale land models across a standardized series of diagnostic tests and compiled public datasets (Collier et al., 2018). Each model's performance is evaluated for a series of variables (e.g., gross primary production, evapotranspiration, surface relative humidity) in a series of graphical, diagnostics-like contour maps and Taylor diagrams, as well as quantitative metrics (e.g., bias, root-mean-square error, mean for the entire time period, interannual coefficient of variation) that are aggregated into a single scalar score for each variable. Relevant datasets are assigned a score with respect to each variable that represents data quality, based on relevance, level of certainty, and the spatial and temporal scale of the data, and this score is used to weight the dataset's importance in the overall model evaluation process (Collier et al., 2018). The ILAMB open software package generates a series of hierarchical web pages that make using the system and reviewing diagnostic results straightforward.

8.10.3.1 Data-model comparison needs

The development of an open-source benchmarking system for enhanced rock weathering models is a critical near-term need for the modeling community. To enable this, there is a clear need for comprehensive, shared community datasets for use in both model development efforts and as part of such benchmarking systems. One approach could be to generate a series of high-resolution, public datasets at newly-established sentinel field sites, representing both feedstock dissolution and carbon and cation dynamics as the weathering flux transits the soil profile, extending into deeper soils. These sentinel sites could be established across distinct regions, field conditions, and with a variety of feedstock mineralogies, allowing for model predictive skill to be tested and compared across heterogeneous soil conditions. A shared suite of well-articulated model run scenarios and boundary conditions could be developed, and much like ILAMB, the benchmarking system could include a scoring method and a set of common diagnostic metrics across a core set of variables of interest.

By scoring model performance separately for each variable of interest, we can also accelerate the inclusion of models as an increasingly important component of MRV systems for commercial deployments—rather than waiting until models can simulate the entire system to be able use them in commercial ERW quantification, simulations can begin to replace direct measurements for the particular components of the system where process-based understanding is sufficiently validated. For example, by separately scoring a model's performance of dissolution kinetics from its implementation of post-dissolution reactive transport in the soil column, the ERW community can potentially move more quickly towards reducing the need for deep soil measurements in the medium-term, even if silicate dissolution cannot yet be modeled with sufficient accuracy at that time.

8.10.3.2 Model intercomparison

Model intercomparison projects are another important component of a robust validation and benchmarking system, which can play an important role in the near-term even before ERW sentinel sites and data-model benchmarking systems develop. Model intercomparison provides a means of evaluating structural uncertainty—dispersion between models in a key diagnostic result can help evaluate the accuracy and/or uncertainty of underlying parameterizations. For example, differences between well-established IPCC-class climate models have been a key tool for climate model validation (Arias et al., 2021). At least initially, we expect to observe significant spread in ERW model predictions, and so finding these sources of misalignment and uncertainty across models can inform iterative model improvement.

Initial efforts for ERW model intercomparison have begun (e.g., RockMIP, Taylor et al., 2023), but greater efforts are needed to develop the infrastructure for ongoing intercomparison with a higher degree of inclusion of both academic and private-sector models. This could include creating a shared set of model scenarios and boundary conditions for spin-up, a list of parameters to vary and ranges to vary them over, and infrastructure and documentation to automate and streamline the process of including additional models.

8.10.4 Sensitivity analysis and model uncertainty quantification

When using a NFZ model to predict ERW outcomes and quantify carbon removal at a particular field site, measured or estimated site-specific baseline data must be provided to initialize the model. Meteorological variables can be estimated using local weather stations at granular temporal resolution, while variables representing soil baseline conditions (e.g., initial buffering capacity, soil hydrology and infiltration) may need to be measured at field scale or even sub-field scale, depending on the degree of site heterogeneity.

In order to understand the response of model output to each input variable, and the degree to which uncertainty in the value of each parameter affects key model outputs, sensitivity analyses should be performed that vary a range of potentially important parameters (e.g., the initial reactive surface area of the feedstock, kinetic coefficients for mineral dissolution, cation exchange capacity, soil porosity). Given the complex interactions between these variables, a multivariate sensitivity analysis is likely needed–for example, using inclusive stochastic methods. Parametric uncertainty for the model's full quantification of netCDR (or any other scalar output variable) can be determined through a similar process, using Monte Carlo simulations over the distribution of each input parameter to derive a probability distribution for the output variable.

It may also be helpful to collectively drive towards a shared, automated system for running the same multivariate sensitivity analyses and assessments of parametric uncertainty across both process-based and machine learning ERW models. While the parameters that matter most for driving model output will be different depending on model implementation, the shared platform could vary model inputs for a common set of agreed upon parameters that will likely be present and important in a majority of models.

An example of such a system is the Predictive Ecosystem Analyzer (PEcAn) project, which provides a wrapper platform for ecosystem and vegetation models with a series of built-in modules for sensitivity analysis, data-model validation, and an accessible web interface with visualization tools for tracking model runs (LeBauer et al., 2013). To use the platform, a new model only needs to convert its inputs and outputs to the common standards used within PEcAn. A similar platform for ERW models could be a very high value community good to develop in the coming years, which would support all of the above goals (benchmarking, model intercomparison, and sensitivity and uncertainty analysis).

8.11 Call to Action: Regularly Occurring Meta-Analyses

Due to the frequent release of new findings in areas relevant to NFZ quantification, we recommend that meta-analyses be regularly conducted to ensure that quantification of all fluxes are being accounted for using the most up-to-date science available. These meta-analyses would incorporate new findings on topics addressed throughout this section (e.g., ERW-SOC interactions, secondary phase formation, etc.) and form the basis for a re-evaluation of quantification methods proposed in this document.

9 Components of the Far-Field Zone Term Balance

The NFZ encompasses the initial weathering of alkaline feedstocks in the soil column and the generation of CDR. At this stage of quantification science and practice, the NFZ is an area where direct empirical measurements are required to monitor feedstock dissolution and the transport of weathering products through–and storage in–the soil profile. The FFZ encompasses much larger spatial scales and longer time horizons over which to consider both reactions and transport of weathering products, and as such, represents a more significant monitoring challenge. In many cases it will be challenging, if not impossible, to measure discernible changes in downstream fluxes of weathering products due to ERW deployments until ERW is deployed at scale. In large river basins such as the Mississippi, large-scale, decades-long application of rock powders have already been demonstrated to lead to measurable alkalinity export to downstream systems (Raymond et al., 2008), but tracking the influence of an individual deployment on a timescale of years presents a much more formidable challenge.

Irrespective of the monitoring challenge, once the weathering flux has been exported from the NFZ, there are a number of reactions that can lead to net carbon loss (and in some systems, gain) as the weathering products are transported to a durable storage reservoir. The carbon and cation dynamics that need to be considered, and the potential magnitude of impact on netCDR through time, will depend on the flow path and the environment that the weathering flux is transported through. We begin this section with a discussion of the possible durable storage reservoirs for carbon removed through ERW in a given deployment, and associated considerations for the spatial scope of the FFZ. We then provide a detailed discussion of the reactive transport processes and residence times within different compartments of the FFZ, including the lower vadose zone, groundwater, surface water, and marine systems. Finally, we conclude with recommendations for how to incorporate the cation and carbon fluxes through each of these compartments of the FFZ into overall netCDR.

9.1 Defining the Scope of the Far-Field Zone: Where is carbon being durably stored?

There are two primary durable storage pathways for CO_2 removed through ERW: (1) storage as a carbonate mineral in soils or downstream systems; and (2) storage as dissolved inorganic carbon (DIC) in a long residence time reservoir. Importantly, carbonate minerals can only represent durable storage for non-carbonate feedstocks. Consideration of potential changes to the net carbon balance due to interactions in the FFZ thus first requires defining the durable storage reservoir—is the storage reservoir assumed to be a carbonate mineral? If not, is the deployment draining into a sufficiently long residence time groundwater system to forgo further consideration of carbon exchange in terrestrial surface water systems and the ocean? What documentation or justification would be required to demonstrate that the waters draining from a deployment site will be stored in a sufficiently long residence time groundwater system? If waters draining from a deployment site are ultimately transported to the ocean, what is the most probable path they take to get there (Section 9.1.4), and what reactions will occur along the way?

The durability of removed CO_2 ultimately exists as a probability distribution of residence times in a given reservoir. However, residence time is commonly reported as a single number once the carbon enters that reservoir, and this has also been adopted by the CDR industry in setting thresholds for acceptable CDR durability. Although there is no set durability requirement for CDR projects, some buyers and credit issuers are coalescing around the assumption that high-durability carbon removal requires demonstrating the CO_2 removed reaches a reservoir with a mean storage lifetime of >1000 years (Frontier, 2024; Isometric, 2024; Microsoft, 2024). We adopt that assumption here. Reductions in alkalinity and other fluxes that decrease the CO_2 removed in the FFZ within this durability time horizon are considered CO_2 losses or declines in CDR efficiency, and therefore should be subtracted from netCDR. The value of and role for 'temporary' (i.e., lower durability) carbon removal is incredibly important as a broader societal, climate, and CDR strategy consideration, but is beyond the scope of this document (Balmford et al., 2023; Cullenward et al., 2020; Matthews et al., 2023; Parisa et al., 2022).

9.1.1 Storage in carbonate minerals

Depending on the storage location, CO_2 incorporated into carbonate minerals can either be relatively labile or effectively permanently stored for geologic timescales (10^4-10^9 years). The carbon stored in carbonate minerals can be liberated by two primary mechanisms: thermal degradation and mineral dissolution. Thermal degradation is generally not applicable for the systems of interest here–temperatures in excess of 450°C and 600°C are required to *directly* liberate CO_2 from calcite (Karunadasa et al., 2019; Rodriguez-Navarro et al., 2009) and magnesite (Tian et al., 2014), respectively. The primary concern for carbonates formed in the soil profile and along downstream flow paths is the potential for subsequent dissolution of the carbonate mineral and export of weathering products.

Pedogenic carbonates formed in wetter climate regions may only be stored for relatively short durations–on a continuum from undergoing seasonal dissolution/reprecipitation cycles (Breecker et al., 2009; Domínguez-Villar et al., 2022; Huth et al., 2019) to stable for a timescale of years to decades (though there is some evidence for long-lived pedogenic carbonates formed in strongly monsoonal climates with high annual precipitation rates (Licht et al., 2022; van der Kaars and Dam, 1997)). Substantial accumulation of soil inorganic carbon over long timescales is far more common in dry ecosystems (Plaza et al., 2018); pedogenic carbon formation in dryland calcareous soils may be stable for time horizons of 10^2-10^5 years (Gocke et al., 2012; Kim et al., 2020; Mayer et al., 1988; Wang et al., 1996), dependent on land use practice. Increases in the soil water balance due to agricultural practices have been demonstrated to substantially increase SIC loss from both rain-fed and irrigated dryland agricultural soils (Kim et al., 2020).

The potential for subsequent strong acid weathering of carbonates formed in agricultural soils is of particular relevance to understanding the net carbon impact of subsequent carbonate dissolution. Subsequent carbonic acid weathering of the carbonate mineral has the potential to drive net additional CDR if the alkalinity produced remains in solution; strong acid weathering of the carbonate would lead to immediate evasion of the stored CO_2 while also neutralizing 2 moles of acidity in the soil system (Section 8.3).

For feedstocks and deployment environments where there is a high probability of significant carbonate formation, and pedogenic carbonates in particular are considered a primary storage pathway, practitioners should be cognizant of risks to the long-term durability of NFZ carbonates and associated implications for netCDR. Practitioners should provide justification for how subsequent dissolution and potential for strong acid weathering–particularly as a result of future land management decisions–are considered in FFZ carbon accounting. There may be project locations where crediting the pedogenic carbonate generated will be sufficiently conservative to forgo further consideration of carbon dynamics in downstream systems.

Carbonate formation in the open ocean should represent durable storage; subsequent dissolution of carbonate phases in the surface ocean would generate DIC that is also considered durably stored. Carbonate minerals formed within, or transferred to, marine sediments below the aerobic respiration zone will be stored effectively permanently for geologic timescales (10^4-10^9 years; anaerobic respiration reactions generate alkalinity).

9.1.2 Storage in long residence time groundwater systems

Groundwater residence times can vary from timescales of days to millenia regionally (Gleeson et al., 2016; Kessler and Harvey, 2001; Sprenger et al., 2019). When discussing the potential to demonstrate durable storage of weathering products in a long residence time groundwater system, Working Group 3 emphasized that it is not sufficient to demonstrate that water from the deployment field is infiltrating the ground somewhere, as many local groundwater systems have very short residence times. In order to argue for long-lived groundwater storage, it must be clearly demonstrated that fluids infiltrating through soils of a deployment predominantly drain into a flow path that has a mean residence time in excess of the durability threshold.

The Working Group highlighted that groundwater flow paths and associated residence times will be dependent on basin topography and geologic structure (Freeze, R.A. Cherry, J.A., 1979), and concluded that in the absence of extensive data, the best way to infer and provide evidence of drainage into a long residence time flow path would be groundwater flow models. There are national-scale models that have been used to estimate groundwater flow residence times for large watersheds (e.g., ParFlow (Jones and Woodward, 2001) and GSFLOW (Markstrom et al., 2008)), but local models would likely be needed to inform individual ERW deployments (e.g., Zhou and Li, 2011). In the absence of a validated regional groundwater flow model, it is recommended that long-term storage in the ocean be assumed, meaning that practitioners should assume that weathering products exported from the deployment site are transported through surface water systems of the drainage catchment.

In considering groundwater storage of cations and DIC from an ERW deployment, practitioners must also be cognizant of current and potential future utilization of that groundwater resource. In some locations field irrigation is also carried out with shallow groundwater, meaning that the weathering products in the groundwater could be re-distributed over farmland multiple times. Deeper (i.e., older) groundwater resources can also be utilized for irrigation (Siebert et al., 2010), which in some cases can represent a CO_2 source to the atmosphere (Ortiz et al., 2022; Wood and Hyndman, 2017). For completeness, practitioners should consider and provide support as to why groundwater is unlikely to be returned to the surface by anthropogenic groundwater pumping within the durability timescale.

9.1.3 Storage in other freshwater systems

Some deployment contexts may also need to consider long residence time freshwater systems as part of the FFZ (e.g., lacustrine systems). At this time, the potential storage of carbon in such systems should be considered on a site-by-site basis. Practitioners should consider the residence time of water and DIC in the water body of interest (including any stratification) in determining whether it represents a viable durable storage reservoir.

9.1.4 Storage in the ocean

The residence time of bicarbonate in the whole ocean is $>10^5$ years, making this a durable storage reservoir over human timescales and far exceeding current durability thresholds for crediting (Middelburg et al., 2020; Renforth and Henderson, 2017). Potential carbon losses in the surface ocean that should be considered in netCDR quantification are further discussed in Section 9.4.

9.1.5 Identifying the probable transport path through the Far-Field Zone

There are numerous tools and frameworks that can be used to delineate watershed boundaries and to model fluid transport at the catchment and watershed scale. We provide high-level guidance here for predicting the flow path of weathering products exported from deployment fields, but encourage transparent reporting of assumptions made and models used for any ERW deployment.

- The data products in HydroSHEDs (Lehner et al., 2008) and Hydrography90m (Amatulli et al., 2022) can be used to identify catchment boundaries and river networks for evaluating likely surface water flow.
- Shallow groundwater flow may be inferred from local topography, supplemented with knowledge of underlying geology and aquifer characteristics (Winter et al., 1998). For a more advanced understanding, groundwater modeling tools including ParFlow (Jones and Woodward, 2001), MODFLOW (Hughes et al., 2017), and GSFLOW (Markstrom et al., 2008) may also be useful.
- It should be noted that not all flow paths leading to long-term storage in the ocean will travel through a surface water system; weathering products can also enter the ocean through submarine groundwater discharge (Taniguchi et al., 2019; Zhou et al., 2019). If a groundwater flow path that terminates as submarine groundwater discharge can be justified for a given deployment, potential carbon dynamics in river/stream systems need not be considered.

9.2 Lower Vadose Zone and Groundwater Systems

Once weathering products and associated DIC are exported out of the NFZ into deeper regions of the soil profile and groundwater systems, the fluid, mineral, organic, and biotic interactions that constitute the components of the NFZ term balance continue to operate (Li et al., 2017; Moravec and Chorover, 2020). While the impact of CO_2 production or consumption processes at depth in the critical zone—for example, CO_2 degassing due to carbonate mineral formation—may not be immediately felt by the atmosphere, the impact of any net alkalinity loss does matter for CDR quantification once the modified water mass returns to a surface water system.

In many ecosystems, deep vadose zones can extend for many meters into the subsurface and are significant for water availability, water quality, and landscape formation. Processes in the deep vadose zone may modulate the delivery of ERW-derived alkalinity to downstream systems and impact overall CDR efficiency. For example, soil layers, weathering, and parent rock heterogeneity can result in complex porosity and permeability changes with depth leading to variable fluid transit time and potentially impacting the timescale of weathering product export to downstream systems (e.g., Wu et al., 2023). Understanding reactive transport through the lower vadose zone and along groundwater flow paths is needed to quantitatively constrain carbon and alkalinity fluxes of both counterfactual and deployment scenarios. The flux of weathering products exported from ERW deployments could impact the rates of natural weathering reactions (Brantley et al., 2013; Zhu et al., 2004) including the timing and extent of strong acid generation (e.g., by pyrite oxidation, Winnick et al., 2017), impacting the acid/base balance of catchment drainage waters relative to the counterfactual (Brantley et al., 2013; Zhu et al., 2004). In addition, clay or other secondary phase formation (Golla et al., 2024) could lead to a reduction in CDR efficiency due to base cation uptake and sorption (Iff et al., 2024; Krause et al., 2023; Oelkers et al., 2019).

Methods to determine and quantify deep vadose zone processes are improving with advances in isotope chemistry (e.g., Golla et al., 2021; Soulet et al., 2021), innovative well design (e.g., Rimon et al., 2011; Tokunaga et al., 2016), and reactive transport models (e.g., Li et al., 2017; Wen et al., 2022). Our understanding of deep vadose zones has progressed significantly in recent years due to large-scale research initiatives such as the Critical Zone Observatory network (Brantley et al., 2017; Gaillardet et al., 2018; Riebe et al., 2017; Wilson et al., 2018). However, questions of how the weathering flux from an ERW deployment will impact baseline weathering rates and natural alkalinity generation, and to what extent secondary mineral formation along the long fluid residence time flow paths of the lower vadose zone and groundwater systems could impact CDR efficiency in different deployment contexts, remain largely unexplored.

The consensus assessment of the Working Group was that it is not currently feasible to require monitoring or modeling of processes occurring in the deep vadose zone and along groundwater flow paths in commercial ERW deployments. Considering ERW interventions in the context of models that simulate relevant critical zone biogeochemical processes (e.g., ion exchange, mineral dissolution and precipitation, and redox reactions) should instead be a key R&D priority for the ERW community. In addition, undertaking deep vadose zone monitoring or installing groundwater monitoring wells in a select subset of commercial deployments, where applicable and feasible, is recommended. This would be undertaken in a research capacity and funded independently of carbon crediting activities. Such monitoring would be highly beneficial from an R&D perspective, would assist in understanding the need for a counterfactual assessment in projects underlain by a deep vadose zone, and would support efforts to develop models that simulate relevant critical zone biogeochemical processes.

9.3 Surface Water Systems

When the weathering products from an ERW deployment enter a surface water system (either directly through surface run-off or via groundwater discharge), reactions can occur that either lead to net loss of carbon and a decline in CDR efficiency, or lead to net additional downstream CDR. There are multiple pathways by which net additional CDR can be driven in downstream surface water systems, including:

- The titration of acidity from low-pH soils prevents subsequent CO_2 degassing in downstream systems relative to the counterfactual scenario (Section 8.3). Considering this from a cation perspective, the base cations released by weathering in low-pH soils, where limited CDR is generated in the NFZ, can be charge-balanced by DIC in higher pH downstream systems. Analogously, base cations released through strong acid weathering reactions (e.g., nitric or sulfuric acid) can be charge-balanced by bicarbonate and carbonate if the counter-ions (e.g., NO_3^- or SO_4^{2-}) are removed from solution by subsequent reactions downstream.
- Increasing alkalinity levels and pH in the receiving waters of ERW deployments could reduce existing levels of CO_2 degassing due to carbonate buffering, particularly in low order streams (Stets et al., 2017). Importantly, this will not always be the case, so it will be critically important to consider this in the context of the specific deployment environment.

At the current stage of ERW pathway development, it is recommended that commercial actors err on the side of conservative accounting and only incorporate net losses from downstream systems in netCDR ($CO_2e_{Net\,Loss,\,Surface\,Water,\,RP}$, Eq. 5.4.2.1). Future development of catchment-scale models capable of simulating the site-specific proton, alkalinity, and carbon balance as a function of time for a counterfactual and deployment scenario could ultimately allow project developers to relax this assumption and credit net additional CDR in downstream systems.

We begin by providing an overview of the fluxes identified by the Working Group that should be considered in a fully comprehensive analysis of the potential net carbon impact of an ERW deployment in downstream surface water systems. Significant uncertainty remains in our mechanistic understanding and ability to confidently predict how the export of weathering products from ERW deployments–particularly when undertaken at significant regional or global scales–will impact downstream carbon budgets. We thus hone in on the most well-understood fluxes for which it is possible to produce conservative loss estimates for a given surface water system, and provide a suite of practical recommendations for capturing potential carbon losses in downstream surface water systems for near-term deployments in a site-specific manner.

9.3.1 Fluxes that should be considered in surface water systems

The Working Group identified the following carbon system fluxes as potential components of a comprehensive analysis of the net carbon impact of an ERW deployment in downstream surface water systems:

- Outgassing caused by DIC system equilibration (Zhang et al., 2024).
- Carbonate mineral burial (Harrington et al., 2023; Knapp and Tipper, 2022).
- Changes to organic matter respiration and metabolic activity in stream/river systems, including the influence on aquatic vegetation that directly takes up bicarbonate (Brandrud, 2002; Iversen et al., 2019; Kaijser et al., 2021; Klemme et al., 2022; Maavara et al., 2023).
- Authigenic clay formation and reverse weathering (Michalopoulos and Aller, 1995b; Rahman, 2019).
- Bedrock interaction with solution and changes to counterfactual alkalinity generation (Bach, 2024).
- Changes to nutrient export and nitrogen cycling (Rosi-Marshall et al., 2016).

Our present ability to track and model these fluxes in a predictive manner is nascent. In discussing how and if each of the fluxes articulated above should be included in a process-based quantification of downstream evasion, the Working Group was broadly aligned that the community needed to start with a sensitivity analysis to better determine what processes are likely to lead to large downstream losses. Notably, at present, only outgassing due to DIC system equilibration and the potential for carbonate mineral precipitation during the transport of weathering products through surface water pathways have been considered in the literature in an ERW-specific context. Understanding how changes in DIC, alkalinity, and individual element fluxes associated with ERW deployments could modify many of these carbon system fluxes remains at the cutting edge of ERW science.

The Working Group's assessment of both the importance of–and our ability to–currently capture potential carbon and alkalinity loss pathways in quantitative models is as follows:

Outgassing caused by DIC system equilibration.

- It is not clear that this would be a large net loss pathway under most circumstances. However, it is tractable to model in cases where regional-scale river network, hydrology, and stream chemistry data exist (e.g., Zhang et al., 2024). The Working Group noted that losses could be important regionally, and were aligned that it should be considered in netCDR quantification. This is discussed in further detail in Section 9.3.2.1.

Carbonate mineral burial.

- The Working Group emphasized that the net alkalinity loss due to carbonate *burial* is what matters–considering carbonate precipitation without the potential for carbonate dissolution in sediments may provide an overly conservative estimate of loss. That said, the likelihood of carbonate precipitation in a given catchment and relatively conservative constraints on potential carbonate precipitation can be generated using process-based models (Harrington et al., 2023; Knapp and Tipper, 2022), and the potential impacts of carbonate burial should be considered in netCDR quantification. This is discussed in further detail in Section 9.3.2.2.

Changes to organic matter respiration and metabolic activity in the surface water system, including the influence on aquatic vegetation that directly takes up bicarbonate.

- Changes to downstream pH, alkalinity, and nutrient concentrations could lead to changes in biogeochemical cycling that destabilize organic carbon reservoirs or change the relative balance between carbon fixation and respiration in catchment waters. Klemme et al. (2022) consider this in detail for the case of tropical peat systems, using established relationships between pH and peat decomposition and downstream dissolved organic carbon (DOC) decomposition in (acidic) peat-draining rivers, to predict potential changes in CO_2 emissions due to the organic carbon cycle response to hypothetical ERW deployment in tropical peat systems. They demonstrate that the total carbon uptake for ERW deployments could be substantially reduced, or even completely offset, by shifts in organic carbon cycling in these low-pH peatland environments.

- Many aquatic plants also directly utilize bicarbonate in addition to CO_2 for photosynthesis (Iversen et al., 2019). Shifts in the bicarbonate and CO_2 concentrations of downstream waters could alter freshwater plant species compositions, as has been observed in limed lakes and river systems (Brandrud, 2002; Iversen et al., 2019; Kaijser et al., 2021). The net carbon impact of such potential shifts in community structure remains to be determined.

- The overall assessment from the Working Group is that such organic carbon fluxes could potentially be quite important, but in general, we do not yet have sufficient constraints to predict the impact of an ERW deployment in a generalized manner. This should be a key research priority as we look ahead to large-scale ERW deployments that have the potential to drive significant shifts in downstream aqueous chemistry. This could, for example, be an important component of understanding potential interactions between large-scale ERW and coastal blue carbon interventions pursued for either carbon sequestration or broader ecosystem service aims (Fakhraee et al., 2023; Hilmi et al., 2021).

- In the interim, a precautionary approach akin to that recommended for minimizing the risk of soil organic carbon destabilization (Section 8.8.1) is recommended: ERW deployments should be avoided in systems where there is a known feedback that could lead to substantial organic carbon destabilization until further research sufficiently de-risks that loss pathway, including tropical peatland systems (Klemme et al., 2022).

Authigenic clay formation / reverse weathering.

- While authigenic clay formation could occur in terrestrial surface water systems, the shorter fluid residence times and higher water:rock ratios relative to groundwater systems and (marginal) marine sediments likely decreases the potential magnitude of alkalinity loss due to secondary silicate formation in surface water systems. We consider the potential for changes to rates of authigenic clay formation to meaningfully reduce the CDR efficiency of ERW deployments in more detail in the context of marine systems (Section 9.4.1).

Bedrock interaction with solution and changes to counterfactual alkalinity generation.

- As ERW is brought to scale, it is possible that deployments will alter the alkalinity produced by natural weathering reactions (e.g., Bach, 2024). This would apply across environments in the FFZ, and is discussed in more detail throughout Section 9. Quantitatively interrogating potential changes to counterfactual alkalinity generation in river and stream systems would require robustly validated reactive-transport modeling frameworks that include fluid-mineral interactions of bedload particles and underlying bedrock.

Changes to nutrient fluxes and nitrogen cycling.

- While changes to nutrient export and cycling (Morgan, 1987; Rosi-Marshall et al., 2016; Wyatt and Stevenson, 2010) are important components of understanding the holistic impact of ERW deployments on downstream aquatic ecosystems–alongside other potential impacts such as increased turbidity due to feedstock runoff (Bilotta and Brazier, 2008)–this is outside the immediate scope of this document.

9.3.2 Recommended approach for constraining downstream evasion from surface water systems in early deployments

Drawing from this assessment, the recommendation from the Working Group is to place particular emphasis on potential outgassing losses due to carbonate system equilibration and carbonate mineral precipitation and burial in netCDR quantification at this time. In considering the specific guidance for how to implement this for a given deployment, a serious operational complication is the significant asymmetries in data availability, particularly high-spatial and temporal resolution aqueous chemistry data, across geographic regions (Hartmann et al., 2019, 2014). There was consensus within the Working Group that it is not currently realistic to require practitioners to utilize process-based models that incorporate the flow characteristics and chemistry of the entire river network system to produce estimates of potential carbon loss. Two primary reasons underpinned this assessment: (1) this may place undue burden on practitioners working in data-poor regions, and (2) regardless of data richness, the parameterization of relevant processes is still nascent and sufficiently validated process-based models simply do not yet exist.

At the same time, there was strong consensus within the Working Group that setting a single conservative loss estimate to be used across all deployments is not a workable approach and would entail making largely unconstrained assumptions (e.g., some catchments draining limestone lithologies will be far more saturated with respect to calcium carbonate than others).

The following recommendations aim to develop a ‘minimum viable product’ approach that accounts for both potential carbonate precipitation and outgassing due to DIC equilibration. However, this should not be considered a long-term solution. Moving forward, R&D efforts should build towards improved process-based frameworks for explicitly modeling the fluxes discussed in Section 9.3.1, new data products for the validation of predictive modeling frameworks, and open-source community tools that enable the generation of catchment-specific conservative loss estimates that would account for the relative vulnerability of a given catchment to downstream loss (but may not require the level of data necessary to parameterize process-based models for all systems).

9.3.2.1 Estimating potential degassing due to carbonate system equilibration

The influence of pH (and pCO_2 or another carbonate system parameter) on d[DIC]/d[alkalinity] can be calculated from carbonate speciation calculations like those demonstrated in Bertagni and Porporato (2022) and Zeebe and Wolf-Gladrow (2001). A key question is *where* operators should be required to constrain potential evasion: for example, with substantial changes in pH as the weathering flux makes its way downstream. The carbonic acid system will be continuously re-equilibrating as the weathering flux mixes into other water masses and travels downstream. In many cases, outgassing could very well be transient, with CO_2 taken back up when the water mass mixes with higher pH, more highly buffered water mass downstream.

The Working Group discussed whether it would be sufficient to only consider carbonate system equilibration in the large river systems that a deployment catchment is ultimately draining into. While this may be sufficient in some systems, there was not consensus that this approach could be taken across the board, as an acute degassing event may or may not be followed by complete re-equilibration in a better-buffered system downstream (gas exchange can be rate limiting). The highest probability of realizing substantial shifts in pH or DIC occurs at mixing or confluence zones where the waters of multiple rivers combine. However, it would be operationally infeasible to require sampling or pre-existing data for every confluence point along a river system that could be 100's of kilometers long.

It is thus recommended that project developers assess potential net CO_2 loss due to carbonate system re-equilibration at two points: in the immediate discharge zone (i.e., the surface water system the weathering flux from a deployment is draining into), and in the major river system of the deployment catchment (i.e., the highest order segment in the deployment catchment). Project developers must thus identify the most proximal continuous surface water system (i.e., not ephemeral or intermittent stream) along the predicted flow path (Section 9.1.4), as well as the major river system for the drainage catchment.

At a minimum, the potential magnitude of outgassing should be calculated using an empirically-informed estimate of *average annual pH* in the immediate discharge zone and along the major river system, either through measurements by the practitioner or established databases. It is likely necessary to go a step further to measure pH on a sub-annual timescale in order to determine seasonal dynamics, either with sample grabs or sensors, rather than only utilizing average annual pH. This should be coupled with either direct measurements of temperature and DIC/pCO_2, or a conservative estimate of carbonate system parameters in the two spatial areas of interest (i.e., the immediate discharge zone and the major river system). To produce a conservative estimate of potential CO_2 loss, it should be assumed that the water fully equilibrates with the atmosphere–e.g., that gas transfer is not kinetically limited. Practitioners are encouraged to gather the data needed to run process-based models that examine gas exchange along the full river network/transport pathway (e.g., Zhang et al., 2024); in this case, full air-water CO_2 equilibration need not be assumed.

Operators should estimate losses due to outgassing in both systems–the immediate discharge basin and major downstream river system. For maximally conservative accounting, whichever loss is larger should be used in the netCDR quantification. This may represent an overly conservative accounting in some systems, specifically in cases where initial offgassing is likely to be (partially) offset by subsequent re-equilibration downstream. In this case, practitioners should be able to justify likely re-equilibration in the downstream system based on considerations of the fluid residence time and kinetics of gas exchange.

A note on data availability and monitoring requirements. It is difficult to provide generalized guidance on the absolute length and time scales over which monitoring would be required to properly characterize the aqueous chemistry and flow characteristics of the proximal surface water system or major river system. Practitioners should propose and justify a monitoring plan if existing data for relevant streams in the drainage system are not available. As a general rule, it would be beneficial to have data collected over at least one full hydrological year to capture seasonal dynamics. It is also important to consider whether measurements–including those in regional and global databases–are taken during baseflow versus stormflow, as it is well-documented that event statistics can have major impacts on solute fluxes across scales in catchments (Godsey et al., 2009; Hall, 1970; Knapp et al., 2020; Moatar et al., 2017), with the result that the average annual pH and alkalinity may not be representative of the water chemistry when most of the weathering products are moving through the system.

9.3.2.2 Estimating carbon loss due to carbonate precipitation and burial in surface water systems

Analyses of the carrying capacity of rivers to transport weathering products from ERW deployments have focused on constraining the saturation state with respect to carbonate minerals along river segments of interest (Harrington et al., 2023; Knapp and Tipper, 2022; Zhang et al., 2022). This remains the recommended approach for determining whether there is a high probability of non-negligible carbonate precipitation along the downstream flow path—operators should specifically consider the saturation state with respect to calcite in discharge waters and downstream river segments. It is well-established that the presence of inhibitors (e.g., Mg^{2+}, PO_4^{3-}, organic molecules, etc.) can prevent substantial carbonate precipitation in low supersaturation solutions (Davis et al., 2000; Dobberschütz et al., 2018; Dove and Hochella, 1993; Hoch et al., 2000; Inskeep and Bloom, 1986; Lin et al., 2005; Mucci and Morse, 1983). It is thus recommended that a threshold saturation state of SI = 1 with respect to calcite (saturation index, $SI = \log_{10}(\{Ca^{2+}\}\{CO_3^{2-}\}/K_{sp})$) is used to define when precipitation may occur (Section 8.5, also see (Harrington et al., 2023) and references therein).

Importantly, carbonate precipitation is not the full story. While it is well-documented that authigenic carbonate precipitation can remove substantial fractions of the total dissolved Ca^{2+} load in carbonate-rich catchments (Chen et al., 2022; Erlanger et al., 2021; Grosbois et al., 2001; Li et al., 2023; Zavadlav et al., 2017), subsequent carbonate dissolution often returns that alkalinity to surface waters (Müller et al., 2022). Carbonate produced in rivers can subsequently dissolve in riverine sediments (Rousseau et al., 2019; Striegl et al., 2007) or as the base load is transported down system; carbonate dissolution in marginal marine sediments is also widespread and extremely well-documented (e.g., Aller, 1982; Fakhraee et al., 2023; Santos et al., 2019); detrital carbonate dissolution driven by eutrophication-related bottom water acidification is increasingly common (Abril et al., 2003; Nesbitt and Mucci, 2021; Shen et al., 2019); and substantial dissolution of biogenic carbonates in otherwise supersaturated portions of the shallow water column has been documented (Subhas et al., 2022; Ziveri et al., 2023).

Given the current state of predictive models of riverine (carbonate) biogeochemistry, it is recommended that practitioners utilize conservative accounting, and thus consider carbonate precipitation without subsequent dissolution. The following recommendations follow this simplified, ‘precipitation only’ framing. Future work developing process-based frameworks for assessing the vulnerability of different catchments to downstream carbon loss during transport through surface water systems should consider the probability of subsequent dissolution of carbonates predicted to precipitate from solution.

At a minimum, operators should calculate a *baseline* calcite saturation state and a *‘max’* saturation state that accounts for the weathering flux resulting from the deployment for the *immediate discharge basin*. If the saturation state is above the SI = 1 threshold for either the baseline or post-weathering states, the operator should calculate an estimate of total carbonate precipitation (e.g., using a model like that developed in (Harrington et al., 2023)) and account for that downstream carbonate precipitation in the netCDR for the deployment. It is recommended that operators consider the carbonate saturation state of a representative time series throughout the year (and, if needed, directly measure pH, major ions, and DIC)–e.g., capturing both dry and wet season dynamics if applicable.

Ideally, operators should also calculate the saturation state along the complete flow path of the weathering flux (from the field to the ocean), and similarly look to quantify the net impact of carbonate formation on netCDR *if* the SI = 1 threshold is surpassed anywhere along the flow path. There was consensus within Working Group 3 that a lack of aqueous chemistry and hydrologic data for constructing complete river networks in some deployment regions represents a major challenge. Given the current magnitude of ERW deployments and the potential for significant uncertainty in aqueous chemistry and carbonate saturation state at the time when the bulk of weathering products are being exported from deployments–aqueous chemistry will often be derived from sparse spatial and temporal sampling, including biases towards base flow (Section 9.3.2.1)–we recommend any sampling of discharge waters focus on proximal systems. Specifically, if sufficient data does not exist in the deployment region, constraining potential carbonate precipitation only in the immediate discharge basin should be considered sufficient *if* the practitioner can demonstrate the subsequent flow path does not pass through catchments where the underlying bedrock lithology is dominated by carbonate phases. Opportunities for practitioners working in data-poor regions to draw analogies to other catchments with better representation in global databases (e.g., GLORICH (Hartmann et al., 2019, 2014)) that have similar underlying bedrock lithology and land use characteristics in order to produce first-order estimates of saturation state should also be explored in early-stage deployment and R&D efforts.

9.3.3 Guidance for robust use of models to capture carbon dynamics in surface water systems

The recommended outlook for the development of model benchmarking and calibration/validation systems for soil models utilized in an ERW context is discussed in Section 8.10. The development of publicly available, benchmarked models that have been developed and/or validated by the broader scientific community would also be of high utility for downstream ecosystems (groundwater, surface water, and the ocean). In the absence of a widely accepted benchmarking system for models of surface water systems and a process for rigorously validating new models, here we provide high-level guidance on what should be considered sufficiently rigorous models of inorganic carbon dynamics in downstream surface water systems for use in netCDR quantification and crediting.

The Working Group recommended the following suite of basic requirements for models of downstream surface water processes, and emphasized that these should be coupled with a critical assessment of model use during the quantification and verification process:

- Model structure and function should be clearly documented, and ideally publicly available. Data inputs and sources should also be clearly identified and documented, including the spatial and temporal resolution of data streams.
- For process-based models, at a minimum, carbonic acid system speciation, air-water gas exchange, and carbonate mineral precipitation should be considered. Ideally, carbonate dissolution would also be considered. The model should therefore track major ion concentrations and carbonate system parameters, allowing for the calculation of mineral saturation indices. Any carbonate-system model would need to be coupled to a hydrological model to capture the influence of fluid flow (residence time, mixing, dilution, etc.).
- While validating models of downstream surface water processes remains challenging, practitioners should demonstrate, at a minimum, the model's ability to reconstruct relevant background fluctuations (e.g., spatial and temporal fluctuations in carbonate system parameters).
- Model uncertainty should be characterized, and the approach to characterizing uncertainty should be documented.

9.4 Marine Systems

Many of the fluxes and biogeochemical interactions discussed for terrestrial downstream systems continue to operate once weathering-derived alkalinity enters the ocean through riverine input or submarine groundwater discharge. In the following section, we provide an assessment of these fluxes in coastal and open ocean ecosystems, focusing on prioritizing what needs to be considered for near-term ERW deployments ($CO_2e_{Net\ Loss,\ Oceans,\ RP}$, Eq. 5.4.2.1) versus what should be considered R&D priorities moving forward.

9.4.1 Fluxes that should be considered in marine systems

When weathering-derived alkalinity enters the ocean, there will often be CO_2 evasion due to carbonic acid system equilibration when two water masses with differing carbonate chemistry mix together (Kanzaki et al., 2023b; Renforth and Henderson, 2017). There was strong consensus amongst the Working Group that this loss pathway can be tractably constrained in a conservative manner, and should thus be incorporated into current netCDR quantification (Section 9.4.2).

There was less consensus on a tractable near-term path forward for two other categories of potentially impactful carbon and alkalinity feedbacks resulting from ERW deployments: feedbacks associated with short time horizon (years to decades) changes to surface ocean chemistry and associated carbon export, and changes to diagenetic reactions in shallow marine sediments. Both of these categories encompass very active areas of research, and their potential impact on the net carbon balance of ERW deployments should not be ignored, particularly as we consider deployments at regionally and globally impactful scale. However, there was consensus across Working Group 3 that project developers should not be required to explicitly incorporate potential losses due to these pathways in near-term deployments. We discuss both categories in a forward-looking capacity here. We separately consider the question of accounting for the decline in CDR efficiency due to marine carbonate burial over long timescales in Section 9.4.3.

9.4.1.1 Feedbacks associated with short time horizon changes to surface ocean chemistry

Over timescales comparable to the project lifetime, increased biogenic calcification relative to the counterfactual (Bach et al., 2019; Gately et al., 2023; Gore et al., 2019; Paul et al., 2024; Renforth and Henderson, 2017), could remove alkalinity from the surface ocean and reduce CDR efficiency. Shifts in pelagic community structure (e.g., the relative dominance of diatoms versus calcifiers) with increased Si flux into coastal waters, or fertilization effects of trace element addition, could also lead to shifts in the biological carbon pump (Bach et al., 2019; Köhler et al., 2013). For ERW deployments, this is most likely to occur in the coastal ocean, where any changes to alkalinity, major ion, dissolved Si, and trace element concentrations as the result of accelerated weathering will be highest. However, at the current scale of ERW deployments, the magnitude of ocean chemistry change due to an individual deployment will be exceedingly de-minimis; we thus recommend that individual deployments need not consider potential changes in carbon export due to shifts in surface ocean chemistry at this time. As deployments scale and our understanding of the biogeochemical feedbacks associated with altered alkalinity, Si, alkaline earth, and trace element export from terrestrial systems improves (Bach et al., 2019), the net impact of ERW deployments on coastal and shallow-ocean carbon fluxes could be interrogated with the same biogeochemical models used to evaluate outgassing due to carbonic acid system equilibration in the surface ocean (Section 9.4.2).

9.4.1.2 Changes to the net carbon balance due to reactions in marine sediments

The coastal waters augmented with weathering products from ERW deployments will also be in contact with marine sediments. A holistic accounting of the net carbon cycle impact of large-scale ERW deployments would thus also consider shifts in biogeochemical cycling in marine sediments–particularly changes in the alkalinity flux relative to the counterfactual baseline.

As with shifts in biocalcification, increased carbonate saturation state can lead to alkalinity loss due to inorganic carbonate precipitation in sediments, where sediment particles can serve as nuclei for precipitation (Fuhr et al., 2022; Hartmann et al., 2023; Moras et al., 2022). The potential for meaningful increases in sedimentary carbonate precipitation is much lower for ERW deployments than for direct application of alkaline materials in marine environments, and the ocean alkalinity enhancement research community is actively researching saturation state thresholds that could trigger substantial carbonate precipitation for different alkalinity addition pathways (e.g., direct mineral addition versus alkaline solutions of different alkalinity:DIC ratios (Hartmann et al., 2023)).

Another potential sedimentary alkalinity sink is authigenic clay formation through ‘reverse weathering’ reactions (Loucaides et al., 2010; Michalopoulos and Aller, 2004, 1995a; Rahman, 2019). Coastal environments like deltas and estuaries can be hot spots of rapid authigenic clay formation, and reactive Si is often the limiting factor for clay formation (Michalopoulos and Aller, 2004). That said, diatom frustules are the source of reactive Si for most marine reverse weathering, and reverse weathering reactions will occur in systems that are very strongly pore-fluid-buffered relative to overlaying water. Shifts in pelagic community structure–e.g., the calcifier:diatom ratio of overlying waters–may be more likely to drive changes to the magnitude of the reverse weathering flux. Overall, the potential magnitude of reductions in CDR efficiency due to authigenic clay formation in marine environments and timescale over which that reduction in efficiency would be incurred remains poorly understood.

Finally, as introduced in Section 9.3, marine sediments can also be significant sources of alkalinity: for example, due to anaerobic respiration and carbonate dissolution (Aller, 1982; Fakhraee et al., 2023; Krumins et al., 2013; Middelburg et al., 2020). Shifts in the alkalinity and carbonate saturation state of overlying waters of shallow marine and marginal marine sediments could decrease the natural or counterfactual baseline alkalinity flux, thereby decreasing net additional CDR (Bach, 2024). This question of potential changes to counterfactual baseline alkalinity fluxes due to various forms of open-system alkalinity enhancement should be a focus of continued R&D in the coming years.

9.4.2 Constraining CO_2 evasion due to carbonic acid system equilibration in the surface ocean

The potential reduction in CDR efficiency due to carbonic acid system equilibration in the surface ocean should be incorporated into netCDR quantification. At a minimum, practitioners should derive a conservative assumption of evasion from carbonic acid system equilibration by considering the thermodynamic storage efficiency as a worst-case scenario, assuming complete equilibration with atmospheric CO_2 at representative temperature, salinity, and current atmospheric pCO_2 (Renforth and Henderson, 2017; Zeebe and Wolf-Gladrow, 2001).

To move away from this worst-case scenario assessment, practitioners could run a region-specific coastal biogeochemistry model (e.g., Zhang and Xue, 2022), incorporating the assumptions used to assess potential losses in surface water systems (Section 9.3) as alkalinity and DIC inputs to the coastal ocean. Uncertainty would need to be quantified through model ensembles in which key parameter values are stochastically varied. Moving forward, we encourage further consideration of the impacts of the weathering products produced by ERW deployments using coastal biogeochemical and diagenetic models.

Importantly, there was consensus amongst the Working Group that using a single generalized loss estimate–for example, derived from early studies utilizing Earth System models to interrogate the stability of ocean carbon storage following large-scale ERW deployment (Kanzaki et al., 2023b)–is not appropriate at this stage of the field. In particular, more research is needed to determine whether results from relatively coarsely gridded Earth Systems Models continue to hold with more finely resolved models.

9.4.3 Potential netCDR losses due to ocean carbonate burial over long timescales

Over very long (10^4-10^5 year) timescales, half of the CDR efficiency from silicate weathering, and all of the CDR efficiency from carbonate weathering, will be lost to marine carbonate burial (Ridgwell and Zeebe, 2005). This 100,000 year time constant integrates over a continuum of response times, so longer timescale carbonate burial should not be disregarded as a flux that impacts the ultimate efficiency of ERW deployments out of hand. But whether ERW project developers at the current state and scale of the pathway should need to account for this remains an open question.

While scale-dependent arguments can be made (e.g., the magnitude of global ocean alkalinity change is negligibly small at current scales of deployment), early modeling work has shown relative scale independence in the long-term storage efficiency of CDR stored as DIC in global oceans (Kanzaki et al., 2023b). An alternative line of argument hinges on the fact that anthropogenic CO_2 emissions and associated ocean acidification have meaningfully reduced the carbonate saturation state of global oceans (Feely et al., 2004; Jiang et al., 2023). It can be argued that the substantial environmental co-benefit of increasing marine carbonate saturation state should not be penalized–and thus marine carbonate production and burial should not be considered to reduce the efficiency of CDR–until saturation states equivalent to the pre-anthropogenic baseline have been achieved. The challenge with this argument is that the counterfactual baseline of a given CDR deployment is not pre-anthropogenic conditions, but instead the counterfactual of inaction and an ocean system responding rapidly to decades of CO_2 and heat uptake. An alternative framing is that reductions in CDR efficiency due to long-duration marine carbonate burial should be recognized as a real component of the (long duration) carbon balance of ERW deployments. However, we should also value the co-benefits of CDR pathways and deployments for the utility they bring to the world, independent of carbon outcome.

Overall, we recommend that at the current scale of the ERW pathway, reductions in CDR efficiency due to long-timescale carbonate burial should not be incorporated in netCDR calculations. Looking forward to ERW deployment at regionally and globally impactful scales, the community will need tools with which to confidently assess the long-term stability of CDR stored as DIC in the global oceans. We consider this to be a cross-pathway R&D priority that should not be the responsibility of individual practitioners today. Notably, this is an area of overlap with the research and tool development needs of the Ocean Alkalinity Enhancement community, and as such, we strongly recommend that cross-pathway collaborations are undertaken accordingly.

10 Quantification of Life Cycle Emissions

In addition to carbon and cation fluxes in the **Near-Field Zone** and **Far-Field Zone**, **life cycle emissions** are the third category of greenhouse gas fluxes that must be accounted for in project-level netCDR quantification. Life cycle emissions can take place both prior to the deployment ("upstream" emissions) and throughout the project lifetime. Practitioners should produce a life cycle assessment (LCA) per the system boundaries defined below that follows the general LCA guidelines described in ISO 14040 and ISO 14044 standards. High-level recommendations for best practices, specifically targeting substantive decisions specific to ERW deployments discussed by Working Group 5, are outlined here.

10.1 System Boundaries

For a given deployment, the system boundaries of *upstream* life cycle greenhouse gas emissions must include:

- Operations required for extracting the feedstock, including fuels, electricity, water, and other material and equipment inputs.
- Operations required for any processing of the feedstock–for example, comminution to achieve the desired particle size (crushing, grinding, milling)–including fuels, electricity, water, and other material and equipment inputs.
- Operations required for handling, loading, transportation, and storage of the feedstock, including fuels, electricity, water, and other material and equipment inputs.
- Operations required for spreading the feedstock and incorporating the feedstock into soil, including fuels, electricity, water, and other material and equipment inputs.

When byproducts or waste streams are used as feedstock for ERW deployments, the LCA subgroup of Working Group 5 recommended following ISO 14044 standards and to clearly document underlying data, assumptions, and calculations. Extraction of the feedstock could be considered 'burden-free' if there is neither economic value nor economic use associated with the material. In cases where the feedstock material does have a value or use, it is recommended for practitioners to either use the "system expansion" approach or apply allocations appropriately (Langhorst et al., 2022). When using the "system expansion" approach, practitioners should transparently show how they define the expanded and substituted systems (e.g., the life cycle emissions associated with the alternative uses or end of life treatment of the feedstock materials), articulate what inputs and output flows are being accounted for, and document underlying data and calculations. If burdens are allocated, practitioners should clearly indicate how the burdens are allocated (whether by mass, energy, market value), provide the inventory of input and output flows, and document underlying data and calculations. Moving forward, we encourage more LCA case studies that work towards a better collective understanding of the implications that ERW deployments at scale may have on the mining and mine waste management patterns of key feedstock materials.

The system boundaries of *ongoing* life cycle greenhouse gas emissions must include operations that are specifically tied to the maintenance of treatment and control plots (inclusive of BAU and negative control plots) that would not have occurred in the absence of ERW deployment operations. Emissions associated with ancillary site activities (e.g., the instantiation and maintenance of research plots not required for netCDR quantification) can be excluded from the system boundary. In addition, the Working Group recommended that emissions associated with ongoing measurement, monitoring, and verification (e.g., traveling to site, sampling, analysis, model simulations) be excluded from the system boundary. Because ERW is still in early phases of deployment, direct, frequent, and redundant measurements are necessary to reduce uncertainty. As such, inclusion of emissions associated with monitoring and verification could disincentivize the high-density field measurements required to develop more robust MRV approaches. This recommendation was intended to encourage the collection and analysis of more data from direct and redundant MRV, and was explicitly not a recommendation for crediting activities. It is still strongly recommended that practitioners continue to closely track emissions associated with ongoing MRV activities for the purpose of carbon crediting, tracking comprehensive organizational emissions, and gathering data on the emissions intensity of different monitoring and verification system design choices (e.g., to inform the decision of whether to locate lab facilities near clusters of deployment sites or to ship refrigerated samples over long distances) for the benefit of the field.

Reiterating what was discussed in Section 5.5.4.2, any counterfactual life cycle emissions in excess of deployment life cycle emissions represent avoided emissions which must be accounted for separately from the netCDR quantification. The consensus assessment of the Working Group was that such avoided emissions due to the displacement of agronomic pH control and fertilization practices cannot yet reliably be estimated. It is recommended that practitioners gather data and track such avoided emissions on a project level, both for avoided emissions accounting purposes, and for helping the field to work towards a better collective understanding of the implications that ERW deployments at scale may have on wider shifts of agronomic practices.

11 Table of Acronyms

ATE - Average Treatment Effect
BAU - Business As Usual
CDR - Carbon Dioxide Removal
CEC - Cation Exchange Capacity
DIC - Dissolved Inorganic Carbon
DOC - Dissolved Organic Carbon
ERW - Enhanced Rock Weathering
FFZ - Far Field Zone
HSRA - Health and Safety Risk Assessment
LCA - Life Cycle Assessment
MRV - Measurement, Reporting, and Verification
NFZ - Near Field Zone
NMR - Nuclear Magnetic Resonance
PPE - Personal Protective Equipment
PSD - Particle Size Distribution
R&D - Research and Development
RCS - Respirable Crystalline Silica
RP - Reporting Period
RTM - Reactive Transport Model
SIC - Soil Inorganic Carbon
SOC - Soil Organic Carbon
XRD - X-Ray Diffraction

12 List of Equations

Equation 2.1.1:

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad (Eq.\ 2.1.1)$$

Equation 2.1.2:

$$K_H = \frac{CO_2(aq)}{CO_2(g)} \qquad (Eq.\ 2.1.2)$$

Equation 2.1.3:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \leftrightarrow 2H^+(aq) + CO_3^{2-}(aq) \qquad (Eq.\ 2.1.3)$$

Equation 2.1.4:

$$DIC \ = \ [H_2CO_3]^* + [HCO_3^-] + [CO_3^{2-}] \qquad (Eq.\ 2.1.4)$$

Equation 2.1.5:

$$\begin{array}{r} Mg_2SiO_4(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + H_4SiO_4(aq) \\ 4H_2CO_3(aq) \rightarrow 4H^+(aq) + 4HCO_3^-(aq) \\ + \quad 4CO_2(g) + 4H_2O \rightarrow 4H_2CO_3(aq) \\ \hline Mg_2SiO_4(s) + 4CO_2(g) + 4H_2O \rightarrow 2Mg^{2+}(aq) + 4HCO_3^-(aq) + H_4SiO_4(aq) \end{array} \ (Eq.\ 2.1.5)$$

Equation 2.1.1.1:

$$\begin{aligned} A_T = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] \\ & + [NH_3] + [HS^-] + \ldots - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots \qquad (Eq.\ 2.1.1.1) \end{aligned}$$

Equation 2.1.1.2:

$$\begin{aligned} TA_{ec} = {} & [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] + \ldots - [Cl^-] - [Br^-] - [NO_3^-] \\ & - \ldots TPO_4 + TNH_3 - 2TSO_4 - THF - THNO_2 \qquad (Eq.\ 2.1.1.2) \end{aligned}$$

Equation 2.1.2.1:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \leftrightarrow CaCO_3(s) + CO_2 + H_2O \qquad (Eq.\ 2.1.2.1)$$

Equation 5.2.1:

$$CDR_{Net,\,RP} = CO_2e_{NFZ,\,RP} + CO_2e_{FFZ,\,RP} - CO_2e_{LCA\ emissions,\,RP} \qquad (Eq.\ 5.2.1)$$

Equation 5.2.2:

$$CO_2e_{NFZ,\,RP} \ = \ CO_2e_{Treatment\ NFZ,\,RP} - CO_2e_{CF\ NFZ,\,RP} \qquad (Eq.\ 5.2.2)$$

Equation 5.2.3:

$$CO_2e_{FFZ,\,RP} \ = \ CO_2e_{Treatment\ FFZ,\,RP} - CO_2e_{CF\ FFZ,\,RP} \qquad (Eq.\ 5.2.3)$$

Equation 5.2.4:

$$CO_2e_{LCA\ emissions,\ RP} = CO_2e_{Treatment\ LCA\ emissions,\ RP} - CO_2e_{CF\ LCA\ emissions,\ RP} \quad (Eq.\ 5.2.4)$$

Equation 5.4.1.1.1:

$$CO_2e_{NFZ,\ RP} = \sum_{time} DIC_{Export,\ RP} + \sum_{volume} DIC_{NFZ,\ RP} - \sum_{volume} DIC_{NFZ,\ Prev\ RP} + CO_2e_{Secondary\ Carbonates,\ RP} \quad (Eq.\ 5.4.1.1.1)$$

Equation 5.4.1.2.1:

$$CO_2e_{NFZ,\ RP} = CO_2e_{Feedstock\ Dissolution,\ RP} - CO_2e_{Biomass\ Uptake,\ RP} - CO_2e_{pH\ and\ Non-Carbonic\ Acid\ Weathering,\ RP} - CO_2e_{Sorption,\ RP} - CO_2e_{Secondary\ Carbonates,\ RP} - CO_2e_{Secondary\ Silicates,\ RP} \quad (Eq.\ 5.4.1.2.1)$$

Equation 5.4.2.1:

$$CO_2e_{FFZ,\ RP} = CO_2e_{Groundwater,\ RP} + CO_2e_{Surface\ Water,\ RP} + CO_2e_{Oceans,\ RP} \quad (Eq.\ 5.4.2.1)$$

Equation 7.5.2.1:

$$DIC_{Export} = \int_{time} c(t)\, q(t)\, dt \quad (Eq.\ 7.5.2.1)$$

Equation 8.5.1.1:

$$\Omega = \frac{IAP}{K_{sp}} = \frac{\{Ca^{2+}\}\{CO_3^{\ 2-}\}}{K_{sp}} \quad (Eq.\ 8.5.1.1)$$

13 References

Abril, G., Etcheber, H., Delille, B., Frankignoulle, M., Borges, A., 2003. Carbonate dissolution in the turbid and eutrophic Loire estuary. Mar. Ecol. Prog. Ser. 259, 129–138. https://doi.org/10.3354/meps259129

Alberta Environment and Protected Areas, 2023. Quantification Protocol for Agricultural Nitrous Oxide Emission Reductions.

Alfieri, J.G., Kustas, W.P., Anderson, M.C., 2018. A Brief Overview of Approaches for Measuring Evapotranspiration, in: Hatfield, J.L., Sivakumar, M.V.K., Prueger, J.H. (Eds.), Agronomy Monographs. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Inc., Madison, WI, USA, pp. 109–127. https://doi.org/10.2134/agronmonogr60.2016.0034

Allen, R., Pereira, L., Raes, D., Smith, M., 1998. Crop evapotranspiration - Guidelines for computing crop water requirements, in: FAO Irrigation and Drainage Paper 56. FAO - Food and Agriculture Organization of the United Nations, Rome.

Aller, R.C., 1982. Carbonate Dissolution in Nearshore Terrigenous Muds: The Role of Physical and Biological Reworking. J. Geol. 90, 79–95. https://doi.org/10.1086/628652

Almaraz, M., 2023. Short term response of soil carbon to enhanced weathering field trials in an agroecosystem. Presented at the AGU23, San Francisco, CA.

Almaraz, M., Bingham, N.L., Holzer, I.O., Geoghegan, E.K., Goertzen, H., Sohng, J., Houlton, B.Z., 2022. Methods for determining the CO2 removal capacity of enhanced weathering in agronomic settings. Front. Clim. 4, 970429. https://doi.org/10.3389/fclim.2022.970429

Amann, T., Hartmann, J., 2022. Carbon Accounting for Enhanced Weathering. Front. Clim. 4, 849948. https://doi.org/10.3389/fclim.2022.849948

Amann, T., Hartmann, J., Struyf, E., De Oliveira Garcia, W., Fischer, E.K., Janssens, I., Meire, P., Schoelynck, J., 2020. Enhanced Weathering and related element fluxes – a cropland mesocosm approach. Biogeosciences 17, 103–119. https://doi.org/10.5194/bg-17-103-2020

Amatulli, G., Garcia Marquez, J., Sethi, T., Kiesel, J., Grigoropoulou, A., Üblacker, M.M., Shen, L.Q., Domisch, S., 2022. Hydrography90m: a new high-resolution global hydrographic dataset. Earth Syst. Sci. Data 14, 4525–4550. https://doi.org/10.5194/essd-14-4525-2022

Anda, M., Shamshuddin, J., Fauziah, C.I., 2015. Improving chemical properties of a highly weathered soil using finely ground basalt rocks. CATENA 124, 147–161. https://doi.org/10.1016/j.catena.2014.09.012

Anda, M., Shamshuddin, J., Fauziah, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11. https://doi.org/10.1016/j.still.2013.04.005

Andrews, J.A., Schlesinger, W.H., 2001. Soil CO2 dynamics, acidification, and chemical weathering in a temperate forest with experimental CO2 enrichment. Glob. Biogeochem. Cycles 15, 149–162. https://doi.org/10.1029/2000GB001278

Andrews, M.G., Jacobson, A.D., 2017. The radiogenic and stable Sr isotope geochemistry of basalt weathering in Iceland: Role of hydrothermal calcite and implications for long-term climate regulation. Geochim. Cosmochim. Acta 215, 247–262. https://doi.org/10.1016/j.gca.2017.08.012

Angert, A., Yakir, D., Rodeghiero, M., Preisler, Y., Davidson, E.A., Weiner, T., 2015. Using O<sub>2</sub> to study the relationships between soil CO<sub>2</sub> efflux and soil respiration. Biogeosciences 12, 2089–2099. https://doi.org/10.5194/bg-12-2089-2015

Apostolakis, A., Schöning, I., Klaus, V.H., Michalzik, B., Bischoff, W.-A., Boeddinghaus, R.S., Bolliger, R., Fischer, M., Hölzel, N., Kandeler, E., Kleinebecker, T., Manning, P., Marhan, S., Neyret, M., Oelmann, Y., Prati, D., Van Kleunen, M., Schwarz, A., Schurig, E., Schrumpf, M., 2022. Direct and plant community mediated effects of management intensity on annual nutrient leaching risk in temperate grasslands. Nutr. Cycl. Agroecosystems 123, 83–104. https://doi.org/10.1007/s10705-022-10209-1

Arias, P.A., Bellouin, N., Coppola, E., Jones, R.G., Krinner, G., Marotzke, J., Naik, V., Palmer, M.D., Plattner, G.-K., Rogelj, J., Rojas, M., Sillmann, J., Storelvmo, T., Thorne, P.W., Trewin, B., Achuta Rao, K., Adhikary, B., Allan, R.P., Armour, K., Bala, G., Barimalala, R., Berger, S., Canadell, J.G., Cassou, C., Cherchi, A., Collins, W.D., Connors, S.L., Corti, S., Cruz, F., Dentener, F.J., Dereczynski, C., Di Luca, A., Diongue Niang, A., Doblas-Reyes, F.J., Dosio, A., Douville, H., Engelbrecht, F., Eyring, V., Fischer, E., Forster, P., Fox-Kemper, B., Fuglestvedt, J.S., Fyfe, J.C., Gillett, N.P., Goldfarb, L., Gorodetskaya, I., Gutierrez, J.M., Hamdi, R., Hawkins, E., Hewitt, H.T., Hope, P., Islam, A.S., Jones, C., Kaufman, D.S., Kopp, R.E., Kosaka, Y., Kossin, J., Krakovska, S., Lee, J.-Y., Li, J., Mauritsen, T., Maycock, T.K., Meinshausen, M., Min, S.-K., Monteiro, P.M.S., Ngo-Duc, T., Otto, F., Pinto, I., Pirani, A., Raghavan, K., Ranasinghe, R., Ruane, A.C., Ruiz, L., Sallée, J.-B., Samset, B.H., Sathyendranath, S., Seneviratne, S.I., Sörensson, A.A., Szopa, S., Takayabu, I., Tréguier, A.-M., van den Hurk, B., Vautard, R., von Schuckmann, K., Zaehle, S., Zhang, X., Zickfeld, K., 2021. Technical Summary. Clim. Change 2021 Phys. Sci. Basis Contrib. Work. Group Sixth Assess. Rep. Intergov. Panel Clim. Change. https://doi.org/10.1017/9781009157896.002

Australia Soil Carbon Credits Methodology, 2018.

Bach, L.T., 2024. The additionality problem of ocean alkalinity enhancement. Biogeosciences 21, 261–277. https://doi.org/10.5194/bg-21-261-2024

Bach, L.T., Gill, S.J., Rickaby, R.E.M., Gore, S., Renforth, P., 2019. CO2 Removal With Enhanced Weathering and Ocean Alkalinity Enhancement: Potential Risks and Co-benefits for Marine Pelagic Ecosystems. Front. Clim. 1. https://doi.org/10.3389/fclim.2019.00007

Baldocchi, D.D., 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. Glob. Change Biol. 9, 479–492. https://doi.org/10.1046/j.1365-2486.2003.00629.x

Balmford, A., Keshav, S., Venmans, F., Coomes, D., Groom, B., Madhavapeddy, A., Swinfield, T., 2023. Realizing the social value of impermanent carbon credits. Nat. Clim. Change 13, 1172–1178. https://doi.org/10.1038/s41558-023-01815-0

Battles, J.J., Fahey, T.J., Driscoll, C.T., Blum, J.D., Johnson, C.E., 2014. Restoring Soil Calcium Reverses Forest Decline. Environ. Sci. Technol. Lett. 1, 15–19. https://doi.org/10.1021/ez400033d

BCarbon Soil Carbon Protocol, 2022.

Beerling, D.J., Kantzas, E.P., Lomas, M.R., Wade, P., Eufrasio, R.M., Renforth, P., Sarkar, B., Andrews, M.G., James, R.H., Pearce, C.R., Mercure, J.-F., Pollitt, H., Holden, P.B., Edwards, N.R., Khanna, M., Koh, L., Quegan, S., Pidgeon, N.F., Janssens, I.A., Hansen, J., Banwart, S.A., 2020. Potential for large-scale CO2 removal via enhanced rock weathering with croplands. Nature 583, 242–248. https://doi.org/10.1038/s41586-020-2448-9

Beerling, D.J., Kantzas, E.P., Martin, M.V., Lomas, M.R., Zhang, S., Kanzaki, Y., Reinhard, C.T., Planavsky, N.J., Eufrasio, R.M., Renforth, P., Mecure, J.-F., Pollitt, H., Edwards, N.R., Koh, L., Epihov, D.Z., Wolf, A., Pidgeon, N.F., Banwart, S.A., 2024. Transforming U.S. agriculture with crushed rock for CO2 sequestration and increased production. PNAS.

Beerling, D.J., Leake, J.R., Long, S.P., Scholes, J.D., Ton, J., Nelson, P.N., Bird, M., Kantzas, E., Taylor, L.L., Sarkar, B., Kelland, M., DeLucia, E., Kantola, I., Müller, C., Rau, G., Hansen, J., 2018. Farming with crops and rocks to address global climate, food and soil security. Nat. Plants 4, 138–147. https://doi.org/10.1038/s41477-018-0108-y

Belmont, E., Friedmann, J., Potts, M., Sanchez, D., Hartley, R., Khan, S., Schaper, A., 2022. Bio-oil Sequestration: Prototype Protocol for Measurement, Reporting, & Verification.

Bénézeth, P., Saldi, G.D., Dandurand, J.-L., Schott, J., 2011. Experimental determination of the solubility product of magnesite at 50 to 200 °C. Chem. Geol. 286, 21–31. https://doi.org/10.1016/j.chemgeo.2011.04.016

Bertagni, M., Porporato, A., 2022. Carbon capture efficiency of natural water alkalinization. Sci. Total Environ.

Bertagni, M.B., Calabrese, S., Cipolla, G., Noto, L.V., Porporato, A.M., 2024. Advancing Enhanced Weathering Modeling in Soils: Systematic Comparison and Validation with Experimental Data. https://doi.org/10.22541/essoar.170559500.09183720/v1

Bhatia, P., Cummis, C., Brown, A., Rich, D., Draucker, L., Lahd, H., 2011. Corporate Value Chain (Scope 3) Accounting and Reporting Standard.

Bilotta, G., Brazier, R., 2008. Understanding the Influence of Suspended Solids on Water Quality and Aquatic Biota. Water Res. 42, 2849–61. https://doi.org/10.1016/j.watres.2008.03.018

Blanc-Betes, E., Kantola, I.B., Gomez-Casanovas, N., Hartman, M.D., Parton, W.J., Lewis, A.L., Beerling, D.J., DeLucia, E.H., 2021. In silico assessment of the potential of basalt amendments to reduce N2O emissions from bioenergy crops. GCB Bioenergy 13, 224–241. https://doi.org/10.1111/gcbb.12757

Bonatotzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G., 2021. Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland. CATENA 198, 105030. https://doi.org/10.1016/j.catena.2020.105030

Bourg, I., Sposito, G., 2011. Ion exchange phenomena.
Brander, M., Ascui, F., Scott, V., Tett, S., 2021. Carbon accounting for negative emissions technologies. Clim. Policy 21, 699–717. https://doi.org/10.1080/14693062.2021.1878009
Brandrud, T.E., 2002. Effects of liming on aquatic macrophytes, with emphasis on Scandinavia. Aquat. Bot., Acidification and restoration of soft water lakes and their vegetation 73, 395–404. https://doi.org/10.1016/S0304-3770(02)00032-3
Brantley, S.L., Holleran, M.E., Jin, L., Bazilevskaya, E., 2013. Probing deep weathering in the Shale Hills Critical Zone Observatory, Pennsylvania (USA): the hypothesis of nested chemical reaction fronts in the subsurface. Earth Surf. Process. Landf. 38, 1280–1298. https://doi.org/10.1002/esp.3415
Brantley, S.L., Lebedeva, M., 2011. Learning to Read the Chemistry of Regolith to Understand the Critical Zone. Annu. Rev. Earth Planet. Sci. 39, 387–416. https://doi.org/10.1146/annurev-earth-040809-152321
Brantley, S.L., McDowell, W.H., Dietrich, W.E., White, T.S., Kumar, P., Anderson, S.P., Chorover, J., Lohse, K.A., Bales, R.C., Richter, D.D., Grant, G., Gaillardet, J., 2017. Designing a network of critical zone observatories to explore the living skin of the terrestrial Earth. Earth Surf. Dyn. 5, 841–860. https://doi.org/10.5194/esurf-5-841-2017
Breecker, D.O., Sharp, Z.D., McFadden, L.D., 2009. Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA. GSA Bull. 121, 630–640. https://doi.org/10.1130/B26413.1
Brimhall, G.H., Christopher J., L., Ford, C., Bratt, J., Taylor, G., Warin, O., 1991. Quantitative geochemical approach to pedogenesis: importance of parent material reduction, volumetric expansion, and eolian influx in lateritization. Geoderma 51, 51–91. https://doi.org/10.1016/0016-7061(91)90066-3
Brus, D.J., Kempen, B., Rossiter, D., Balwinder-Singh, McDonald, A.J., 2022. Bayesian approach for sample size determination, illustrated with Soil Health Card data of Andhra Pradesh (India). Geoderma 405, 115396. https://doi.org/10.1016/j.geoderma.2021.115396
Buss, W., Hasemer, H., Ferguson, S., Borevitz, J., 2023. Stabilisation of soil organic matter with rock dust partially counteracted by plants. Glob. Change Biol. e17052. https://doi.org/10.1111/gcb.17052
Calabrese, S., Wild, B., Bertagni, M.B., Bourg, I.C., White, C., Aburto, F., Cipolla, G., Noto, L.V., Porporato, A., 2022. Nano- to Global-Scale Uncertainties in Terrestrial Enhanced Weathering. Environ. Sci. Technol. 56, 15261–15272. https://doi.org/10.1021/acs.est.2c03163
Campbell, J., Bastianini, L., Buckman, J., Bullock, L., Foteinis, S., Furey, V., Hamilton, J., Harrington, K., Hawrot, O., Holdship, P., Knapp, W., Maesano, C.N., Mayes, W.M., Von Strandmann, P.P., Reershemius, T., Rosair, G.M., Sturgeon, F., Turvey, C., Wilson, S., Renforth, P., 2023. Measurements in Geochemical Carbon Dioxide Removal. Heriot-Watt University. https://doi.org/10.17861/2GE7-RE08
Cassidy, R., Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. J. Hydrol. 405, 182–193. https://doi.org/10.1016/j.jhydrol.2011.05.020
Chapela, M., Buss, H., Henehan, M., Schuessler, J., McDowell, W., 2022. Secondary Minerals Drive Extreme Lithium Isotope Fractionation During Tropical Weathering. J. Geophys. Res. Earth Surf. 127. https://doi.org/10.1029/2021JF006366
Chay, F., Badgley, G., Martin, K., Freeman, J., Hamman, J., Cullenward, D., 2022. Unpacking ton-year accounting – CarbonPlan. URL https://carbonplan.org/research/ton-year-explainer (accessed 9.16.24).
Chen, B., Li, S.-L., Pogge von Strandmann, P., Wilson, D., Zhong, J., Sun, J., Liu, C.-Q., 2022. Calcium isotopes tracing secondary mineral formation in the high-relief Yalong River Basin, Southeast Tibetan Plateau. Sci. Total Environ. 827, 154315. https://doi.org/10.1016/j.scitotenv.2022.154315
Chevallier, T., Fujisaki, K., Roupsard, O., Guidat, F., Kinoshita, R., de Melo Viginio Filho, E., Lehner, P., Albrecht, A., 2019. Short-range-order minerals as powerful factors explaining deep soil organic carbon stock distribution: the case of a coffee agroforestry plantation on Andosols in Costa Rica. SOIL 5, 315–332. https://doi.org/10.5194/soil-5-315-2019
Chiaravalloti, I., Theunissen, N., Zhang, S., Wang, J., Sun, F., Ahmed, A.A., Pihlap, E., Reinhard, C.T., Planavsky, N.J., 2023. Mitigation of soil nitrous oxide emissions during maize production with basalt amendments. Front. Clim. 5, 1203043. https://doi.org/10.3389/fclim.2023.1203043
Cipolla, G., Calabrese, S., Noto, L.V., Porporato, A., 2021. The role of hydrology on enhanced weathering for carbon sequestration I. Modeling rock-dissolution reactions coupled to plant, soil moisture, and carbon dynamics. Adv. Water Resour. 154, 103934. https://doi.org/10.1016/j.advwatres.2021.103934

Clarkson, D.T., Hanson, J., 1980. The Mineral Nutrition of Higher Plants. Annu. Rev. Plant Physiol.

Clarkson, M., Larkin, C., Swoboda, P., Reershemius, T., Suhrhoff, J., Maesano, C., Campbell, J., 2024. A Review of Measurement for Quantification of Carbon Dioxide Removal by Enhanced Weathering in Soil. Front. Clim. 6. https://doi.org/10.3389/fclim.2024.1345224

Collier, N., Hoffman, F.M., Lawrence, D.M., Keppel-Aleks, G., Koven, C.D., Riley, W.J., Mu, M., Randerson, J.T., 2018. The International Land Model Benchmarking (ILAMB) System: Design, Theory, and Implementation. J. Adv. Model. Earth Syst. 10, 2731–2754. https://doi.org/10.1029/2018MS001354

Cullenward, D., Hamman, J., Freeman, J., 2020. The cost of temporary carbon removal. URL https://carbonplan.org/research/permanence-calculator-explainer (accessed 6.6.24).

Daval, D., Sissmann, O., Menguy, N., Saldi, G.D., Guyot, F., Martinez, I., Corvisier, J., Garcia, B., Machouk, I., Knauss, K.G., Hellmann, R., 2011. Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and elevated *p*CO2. Chem. Geol. 284, 193–209. https://doi.org/10.1016/j.chemgeo.2011.02.021

Davis, K.J., Dove, P.M., De Yoreo, J.J., 2000. The Role of Mg2+ as an Impurity in Calcite Growth. Science 290, 1134–1137. https://doi.org/10.1126/science.290.5494.1134

Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Louvat, P., Dosseto, A., Gorge, C., Alanoca, L., Maurice, L., 2015. Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes. Geochim. Cosmochim. Acta 164, 71–93. https://doi.org/10.1016/j.gca.2015.04.042

Deng, H., Sonnenthal, E., Arora, B., Breunig, H., Brodie, E., Kleber, M., Spycher, N., Nico, P., 2023. The environmental controls on efficiency of enhanced rock weathering in soils. Sci. Rep. 13, 9765. https://doi.org/10.1038/s41598-023-36113-4

Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep Sea Res. Part Oceanogr. Res. Pap. 28, 609–623. https://doi.org/10.1016/0198-0149(81)90121-7

Dietzen, C., Harrison, R., Michelsen-Correa, S., 2018. Effectiveness of enhanced mineral weathering as a carbon sequestration tool and alternative to agricultural lime: An incubation experiment. Int. J. Greenh. Gas Control 74, 251–258. https://doi.org/10.1016/j.ijggc.2018.05.007

Dietzen, C., Rosing, M.T., 2023. Quantification of CO2 uptake by enhanced weathering of silicate minerals applied to acidic soils. Int. J. Greenh. Gas Control 125, 103872. https://doi.org/10.1016/j.ijggc.2023.103872

Dobberschütz, S., Nielsen, M.R., Sand, K.K., Civioc, R., Bovet, N., Stipp, S.L.S., Andersson, M.P., 2018. The mechanisms of crystal growth inhibition by organic and inorganic inhibitors. Nat. Commun. 9, 1578. https://doi.org/10.1038/s41467-018-04022-0

Domínguez-Villar, D., Bensa, A., Švob, M., Krklec, K., 2022. Causes and implications of the seasonal dissolution and precipitation of pedogenic carbonates in soils of karst regions – A thermodynamic model approach. Geoderma 423, 115962. https://doi.org/10.1016/j.geoderma.2022.115962

Dove, P.M., Hochella, M.F., 1993. Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by Scanning Force Microscopy. Geochim. Cosmochim. Acta 57, 705–714. https://doi.org/10.1016/0016-7037(93)90381-6

Dressing, S., 2003. Load Estimation Techniques, in: National Management Measures to Control Nonpoint Source Pollution from Agriculture. EPA, pp. 225–242.

Drever, J.I., Clow, D.W., 2018. Weathering Rates in Catchements, in: Reviews in Mineralogy and Geochemistry. De Gruyter, pp. 463–484. https://doi.org/10.1515/9781501509650-012

Dunlea, A.G., Murray, R.W., Santiago Ramos, D.P., Higgins, J.A., 2017. Cenozoic global cooling and increased seawater Mg/Ca via reduced reverse weathering. Nat. Commun. 8, 844. https://doi.org/10.1038/s41467-017-00853-5

Ebert, C., Osman, S., Raven, H., Remucal, J., Wescott, S., Zavariz, B., 2020. CAR Soil Enrichment Protocol.

Enoch, H.Z., Olesen, J.M., 1993. Plant response to irrigation with water enriched with carbon dioxide. New Phytol. 125, 249–258. https://doi.org/10.1111/j.1469-8137.1993.tb03880.x

Erlanger, E.D., Rugenstein, J.K.C., Bufe, A., Picotti, V., Willett, S.D., 2021. Controls on Physical and Chemical Denudation in a Mixed Carbonate-Siliciclastic Orogen. J. Geophys. Res. Earth Surf. 126, e2021JF006064. https://doi.org/10.1029/2021JF00606410.1002/essoar.10505807.2

Espeleta, J.F., Cardon, Z.G., Mayer, K.U., Neumann, R.B., 2017. Diel plant water use and competitive soil cation exchange interact to enhance NH4+ and K+ availability in the rhizosphere. Plant Soil 414, 33–51. https://doi.org/10.1007/s11104-016-3089-5

Fakhraee, M., Planavsky, N.J., Reinhard, C.T., 2023. Ocean alkalinity enhancement through restoration of blue carbon ecosystems. Nat. Sustain. 6, 1087–1094. https://doi.org/10.1038/s41893-023-01128-2

Fan, Y., Li, H., Miguez-Macho, G., 2013. Global Patterns of Groundwater Table Depth. Science 339, 940–943. https://doi.org/10.1126/science.1229881

Fan, Y., Miguez-Macho, G., Weaver, C.P., Walko, R., Robock, A., 2007. Incorporating water table dynamics in climate modeling: 1. Water table observations and equilibrium water table simulations. J. Geophys. Res. Atmospheres 112. https://doi.org/10.1029/2006JD008111

Fearnside, P.M., Lashof, D.A., Moura-Costa, P., 2000. Accounting for time in Mitigating Global Warming through land-use change and forestry. Mitig. Adapt. Strateg. Glob. Change 5, 239–270. https://doi.org/10.1023/A:1009625122628

Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., Millero, F.J., 2004. Impact of Anthropogenic CO2 on the CaCO3 System in the Oceans. Science 305, 362–366. https://doi.org/10.1126/science.1097329

Fisher, B.A., Rendahl, A.K., Aufdenkampe, A.K., Yoo, K., 2017. Quantifying weathering on variable rocks, an extension of geochemical mass balance: Critical zone and landscape evolution. Earth Surf. Process. Landf. 42, 2457–2468. https://doi.org/10.1002/esp.4212

Follett, R.F., Schimel, D.S., 1989. Effect of Tillage Practices on Microbial Biomass Dynamics. Soil Sci. Soc. Am. J. 53, 1091–1096. https://doi.org/10.2136/sssaj1989.03615995005300040018x

Fornara, D.A., Steinbeiss, S., McNAMARA, N.P., Gleixner, G., Oakley, S., Poulton, P.R., Macdonald, A.J., Bardgett, R.D., 2011. Increases in soil organic carbon sequestration can reduce the global warming potential of long-term liming to permanent grassland: LIMING EFFECTS ON SOIL CARBON SEQUESTRATION. Glob. Change Biol. 17, 1925–1934. https://doi.org/10.1111/j.1365-2486.2010.02328.x

Forster, D., Fraser, M.D., Rowe, R., McNamara, N.P., 2021. Influence of liming and sward management on soil carbon storage by semi-improved upland grasslands. Soil Tillage Res. 212, 105059. https://doi.org/10.1016/j.still.2021.105059

Freeze, R.A. Cherry, J.A., 1979. Groundwater. Prentice-Hall Inc., Englewood Cliffs, New Jersey.

Fried, M., Shapiro, R.E., 1961. Soil-Plant Relationships in Ion Uptake. Annu. Rev. Plant Physiol. 12, 91–112. https://doi.org/10.1146/annurev.pp.12.060161.000515

Friedlingstein, P., O'Sullivan, M., Jones, M.W., Andrew, R.M., Bakker, D.C.E., Hauck, J., Landschützer, P., Le Quéré, C., Luijkx, I.T., Peters, G.P., Peters, W., Pongratz, J., Schwingshackl, C., Sitch, S., Canadell, J.G., Ciais, P., Jackson, R.B., Alin, S.R., Anthoni, P., Barbero, L., Bates, N.R., Becker, M., Bellouin, N., Decharme, B., Bopp, L., Brasika, I.B.M., Cadule, P., Chamberlain, M.A., Chandra, N., Chau, T.-T.-T., Chevallier, F., Chini, L.P., Cronin, M., Dou, X., Enyo, K., Evans, W., Falk, S., Feely, R.A., Feng, L., Ford, D.J., Gasser, T., Ghattas, J., Gkritzalis, T., Grassi, G., Gregor, L., Gruber, N., Gürses, Ö., Harris, I., Hefner, M., Heinke, J., Houghton, R.A., Hurtt, G.C., Iida, Y., Ilyina, T., Jacobson, A.R., Jain, A., Jarníková, T., Jersild, A., Jiang, F., Jin, Z., Joos, F., Kato, E., Keeling, R.F., Kennedy, D., Klein Goldewijk, K., Knauer, J., Korsbakken, J.I., Körtzinger, A., Lan, X., Lefèvre, N., Li, H., Liu, J., Liu, Z., Ma, L., Marland, G., Mayot, N., McGuire, P.C., McKinley, G.A., Meyer, G., Morgan, E.J., Munro, D.R., Nakaoka, S.-I., Niwa, Y., O'Brien, K.M., Olsen, A., Omar, A.M., Ono, T., Paulsen, M., Pierrot, D., Pocock, K., Poulter, B., Powis, C.M., Rehder, G., Resplandy, L., Robertson, E., Rödenbeck, C., Rosan, T.M., Schwinger, J., Séférian, R., Smallman, T.L., Smith, S.M., Sospedra-Alfonso, R., Sun, Q., Sutton, A.J., Sweeney, C., Takao, S., Tans, P.P., Tian, H., Tilbrook, B., Tsujino, H., Tubiello, F., Van Der Werf, G.R., Van Ooijen, E., Wanninkhof, R., Watanabe, M., Wimart-Rousseau, C., Yang, D., Yang, X., Yuan, W., Yue, X., Zaehle, S., Zeng, J., Zheng, B., 2023. Global Carbon Budget 2023. Earth Syst. Sci. Data 15, 5301–5369. https://doi.org/10.5194/essd-15-5301-2023

Frontier, 2024. Frontier Funding Criteria [WWW Document]. URL https://frontierclimate.com/apply (accessed 6.6.24).

Fuhr, M., Geilert, S., Schmidt, M., Liebetrau, V., Vogt, C., Ledwig, B., Wallmann, K., 2022. Kinetics of Olivine Weathering in Seawater: An Experimental Study. Front. Clim. 4. https://doi.org/10.3389/fclim.2022.831587

Gaillardet, J., Braud, I., Hankard, F., Anquetin, S., Bour, O., Dorfliger, N., De Dreuzy, J.R., Galle, S., Galy, C., Gogo, S., Gourcy, L., Habets, F., Laggoun, F., Longuevergne, L., Le Borgne, T., Naaim-Bouvet, F., Nord, G., Simonneaux, V., Six, D., Tallec, T., Valentin, C., Abril, G., Allemand, P., Arènes, A., Arfib, B., Arnaud, L., Arnaud, N., Arnaud, P., Audry, S., Comte, V.B., Batiot, C., Battais, A., Bellot, H., Bernard, E., Bertrand, C., Bessière, H., Binet, S., Bodin, J., Bodin, X., Boithias, L., Bouchez, J., Boudevillain, B., Moussa, I.B., Branger, F., Braun, J.J., Brunet, P., Caceres, B., Calmels, D., Cappelaere, B., Celle-Jeanton, H., Chabaux, F., Chalikakis, K., Champollion, C., Copard, Y., Cotel, C., Davy, P., Deline, P., Delrieu, G., Demarty, J., Dessert, C., Dumont, M., Emblanch, C., Ezzahar, J., Estèves, M., Favier, V., Faucheux, M., Filizola, N., Flammarion, P., Floury, P., Fovet, O., Fournier, M., Francez, A.J., Gandois, L., Gascuel, C., Gayer, E., Genthon, C., Gérard, M.F., Gilbert, D., Gouttevin, I., Grippa, M., Gruau, G., Jardani, A., Jeanneau, L., Join, J.L., Jourde, H., Karbou, F., Labat, D., Lagadeuc, Y., Lajeunesse, E., Lastennet, R., Lavado, W., Lawin, E., Lebel, T., Le Bouteiller, C., Legout, C., Lejeune, Y., Le Meur, E., Le Moigne, N., Lions, J., Lucas, A., Malet, J.P., Marais-Sicre, C., Maréchal, J.C., Marlin, C., Martin, P., Martins, J., Martinez, J.M., Massei, N., Mauclerc, A., Mazzilli, N., Molénat, J., Moreira-Turcq, P., Mougin, E., Morin, S., Ngoupayou, J.N., Panthou, G., Peugeot, C., Picard, G., Pierret, M.C., Porel, G., Probst, A., Probst, J.L., Rabatel, A., Raclot, D., Ravanel, L., Rejiba, F., René, P., Ribolzi, O., Riotte, J., Rivière, A., Robain, H., Ruiz, L., Sanchez-Perez, J.M., Santini, W., Sauvage, S., Schoeneich, P., Seidel, J.L., Sekhar, M., Sengtaheuanghoung, O., Silvera, N., Steinmann, M., Soruco, A., Tallec, G., Thibert, E., Lao, D.V., Vincent, C., Viville, D., Wagnon, P., Zitouna, R., 2018. OZCAR: The French Network of Critical Zone Observatories. Vadose Zone J. 17, 1–24. https://doi.org/10.2136/vzj2018.04.0067

Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chem. Geol. 159, 3–30. https://doi.org/10.1016/S0009-2541(99)00031-5

Gallagher, T.M., Breecker, D.O., 2020. The Obscuring Effects of Calcite Dissolution and Formation on Quantifying Soil Respiration. Glob. Biogeochem. Cycles 34, e2020GB006584. https://doi.org/10.1029/2020GB006584

Gammans, M., Hacker, N., Leckie, C., Sitarska, O., Patel, C., Podgorney, C., 2024. Biomass Feedstock Accounting — Isometric.

Gately, J.A., Kim, S.M., Jin, B., Brzezinski, M.A., Iglesias-Rodriguez, M.D., 2023. Coccolithophores and diatoms resilient to ocean alkalinity enhancement: A glimpse of hope? Sci. Adv. 9, eadg6066. https://doi.org/10.1126/sciadv.adg6066

Gillman, G.P., Burkett, D.C., Coventry, R.J., 2002. Amending highly weathered soils with finely ground basalt rock. Appl. Geochem. 17, 987–1001. https://doi.org/10.1016/S0883-2927(02)00078-1

Gleeson, T., Befus, K.M., Jasechko, S., Luijendijk, E., Cardenas, M.B., 2016. The global volume and distribution of modern groundwater. Nat. Geosci. 9, 161–167. https://doi.org/10.1038/ngeo2590

Gocke, M., Pustovoytov, K., Kuzyakov, Y., 2012. Pedogenic carbonate formation: Recrystallization versus migration—Process rates and periods assessed by 14C labeling. Glob. Biogeochem. Cycles 26. https://doi.org/10.1029/2010GB003871

Godsey, S.E., Kirchner, J.W., Clow, D.W., 2009. Concentration–discharge relationships reflect chemostatic characteristics of US catchments. Hydrol. Process. 23, 1844–1864. https://doi.org/10.1002/hyp.7315

Golla, J.K., Bouchez, J., Kuessner, M.L., Druhan, J.L., 2024. Weathering Incongruence in Mountainous Mediterranean Climates Recorded by Stream Lithium Isotope Ratios. J. Geophys. Res. Earth Surf. 129, e2023JF007359. https://doi.org/10.1029/2023JF007359

Golla, J.K., Kuessner, M.L., Henehan, M.J., Bouchez, J., Rempe, D.M., Druhan, J.L., 2021. The evolution of lithium isotope signatures in fluids draining actively weathering hillslopes. Earth Planet. Sci. Lett. 567, 116988. https://doi.org/10.1016/j.epsl.2021.116988

Gore, S., Renforth, P., Perkins, R., 2019. The potential environmental response to increasing ocean alkalinity for negative emissions. Mitig. Adapt. Strateg. Glob. Change 24, 1191–1211. https://doi.org/10.1007/s11027-018-9830-z

Gras, A., Beaudoin, G., Molson, J., Plante, B., Bussière, B., Lemieux, J.M., Dupont, P.P., 2017. Isotopic evidence of passive mineral carbonation in mine wastes from the Dumont Nickel Project (Abitibi, Quebec). Int. J. Greenh. Gas Control 60, 10–23. https://doi.org/10.1016/j.ijggc.2017.03.002

Grosbois, C., Négrel, P., Grimaud, D., Fouillac, C., 2001. An Overview of Dissolved and Suspended Matter Fluxes in the Loire River Basin: Natural and Anthropogenic Inputs. Aquat. Geochem. 7, 81–105. https://doi.org/10.1023/A:1017518831860

Grunwald, D., Panten, K., Schwarz, A., Bischoff, W., Schittenhelm, S., 2020. Comparison of maize, permanent cup plant and a perennial grass mixture with regard to soil and water protection. GCB Bioenergy 12, 694–705. https://doi.org/10.1111/gcbb.12719

Gunnarsen, K.C., Jensen, L.S., Rosing, M.T., Dietzen, C., 2023. Greenlandic glacial rock flour improves crop yield in organic agricultural production. Nutr. Cycl. Agroecosystems 126, 51–66. https://doi.org/10.1007/s10705-023-10274-0

Haddaway, N.R., Hedlund, K., Jackson, L.E., Kätterer, T., Lugato, E., Thomsen, I.K., Jørgensen, H.B., Isberg, P.-E., 2017. How does tillage intensity affect soil organic carbon? A systematic review. Environ. Evid. 6, 30. https://doi.org/10.1186/s13750-017-0108-9

Hall, F.R., 1970. Dissolved Solids-Discharge Relationships: 1. Mixing Models. Water Resour. Res. 6, 845–850. https://doi.org/10.1029/WR006i003p00845

Hamilton, S.K., Kurzman, A.L., Arango, C., Jin, L., Robertson, G.P., 2007. Evidence for carbon sequestration by agricultural liming: FATE OF CARBON IN AGRICULTURAL LIME. Glob. Biogeochem. Cycles 21, n/a-n/a. https://doi.org/10.1029/2006GB002738

Haque, F., Santos, R.M., Chiang, Y.W., 2020. CO2 sequestration by wollastonite-amended agricultural soils – An Ontario field study. Int. J. Greenh. Gas Control 97, 103017. https://doi.org/10.1016/j.ijggc.2020.103017

Harrington, K.J., Hilton, R.G., Henderson, G.M., 2023. Implications of the Riverine Response to Enhanced Weathering for CO2 removal in the UK. Appl. Geochem. 152, 105643. https://doi.org/10.1016/j.apgeochem.2023.105643

Hartmann, J., Lauerwald, R., Moosdorf, N., 2019. GLORICH - Global river chemistry database. Suppl. Hartmann J Al 2014 Brief Overv. Glob. RIver Chem. Database GLORICH Procedia Earth Planet. Sci. 10 23-27 Httpsdoiorg101016jproeps201408005. https://doi.org/10.1594/PANGAEA.902360

Hartmann, J., Lauerwald, R., Moosdorf, N., 2014. A Brief Overview of the GLObal RIver Chemistry Database, GLORICH. Procedia Earth Planet. Sci. 10, 23–27. https://doi.org/10.1016/j.proeps.2014.08.005

Hartmann, J., Suitner, N., Lim, C., Schneider, J., Marín-Samper, L., Arístegui, J., Renforth, P., Taucher, J., Riebesell, U., 2023. Stability of alkalinity in ocean alkalinity enhancement (OAE) approaches – consequences for durability of CO $_2$ storage. Biogeosciences 20, 781–802. https://doi.org/10.5194/bg-20-781-2023

Hartmann, J., West, A.J., Renforth, P., Köhler, P., De La Rocha, C.L., Wolf-Gladrow, D.A., Dürr, H.H., Scheffran, J., 2013. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification: ENHANCED WEATHERING. Rev. Geophys. 51, 113–149. https://doi.org/10.1002/rog.20004

Havlin, J.L., Kissel, D.E., Maddux, L.D., Claassen, M.M., Long, J.H., 1990. Crop Rotation and Tillage Effects on Soil Organic Carbon and Nitrogen. Soil Sci. Soc. Am. J. 54, 448–452. https://doi.org/10.2136/sssaj1990.03615995005400020026x

Hayder, A., Vanderburgt, S., Santos, R.M., Chiang, Y.W., 2019. Phosphorous runoff risk assessment and its potential management using wollastonite according to geochemical modeling. Open Agric. 4, 787–794. https://doi.org/10.1515/opag-2019-0075

Haynes, W.M. (Ed.), 2014. CRC Handbook of Chemistry and Physics, 95th ed. CRC Press.

Helm, L., Merbach, A.E., 1999. Water exchange on metal ions: experiments and simulations. Coord. Chem. Rev. 187, 151–181. https://doi.org/10.1016/S0010-8545(99)90232-1

Hilmi, N., Chami, R., Sutherland, M.D., Hall-Spencer, J.M., Lebleu, L., Benitez, M.B., Levin, L.A., 2021. The Role of Blue Carbon in Climate Change Mitigation and Carbon Stock Conservation. Front. Clim. 3. https://doi.org/10.3389/fclim.2021.710546

Hilton, R.G., West, A.J., 2020. Mountains, erosion and the carbon cycle. Nat. Rev. Earth Environ. 1, 284–299. https://doi.org/10.1038/s43017-020-0058-6

Hindar, A., Wright, R.F., Nilsen, P., Larssen, T., Høgberget, R., 2003. Effects on stream water chemistry and forest vitality after whole-catchment application of dolomite to a forest ecosystem in southern Norway. For. Ecol. Manag. 180, 509–525. https://doi.org/10.1016/S0378-1127(02)00647-3

Hiradate, S., 2004. Speciation of aluminum in soil environments: Application of NMR technique. Soil Sci. Plant Nutr. 50, 303–314. https://doi.org/10.1080/00380768.2004.10408483

Hoch, A.R., Reddy, M.M., Aiken, G.R., 2000. Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. Geochim. Cosmochim. Acta 64, 61–72. https://doi.org/10.1016/S0016-7037(99)00179-9

Holland, J.E., Bennett, A.E., Newton, A.C., White, P.J., McKenzie, B.M., George, T.S., Pakeman, R.J., Bailey, J.S., Fornara, D.A., Hayes, R.C., 2018. Liming impacts on soils, crops and biodiversity in the UK: A review. Sci. Total Environ. 610–611, 316–332. https://doi.org/10.1016/j.scitotenv.2017.08.020

Holzer, I.O., Nocco, M.A., Houlton, B., 2023. Direct evidence for atmospheric carbon dioxide removal via enhanced weathering in cropland soil. Environ. Res. Commun. https://doi.org/10.1088/2515-7620/acfd89

Hughes, J.D., Langevin, C.D., Banta, E.R., 2017. Documentation for the MODFLOW 6 Framework

(Techniques and Methods), Groundwater Modeling Techniques. US Geological Survey, Reston, VA.

Hurlbert, S.H., 1984. Pseudoreplication and the Design of Ecological Field Experiments. Ecol. Monogr. 54, 187–211. https://doi.org/10.2307/1942661

Huth, T.E., Cerling, T.E., Marchetti, D.W., Bowling, D.R., Ellwein, A.L., Passey, B.H., 2019. Seasonal Bias in Soil Carbonate Formation and Its Implications for Interpreting High-Resolution Paleoarchives: Evidence From Southern Utah. J. Geophys. Res. Biogeosciences 124, 616–632. https://doi.org/10.1029/2018JG004496

Iff, N., Renforth, P., Pogge Von Strandmann, P.A.E., 2024. The dissolution of olivine added to soil at 32°C: the fate of weathering products and its implications for enhanced weathering at different temperatures. Front. Clim. 6, 1252210. https://doi.org/10.3389/fclim.2024.1252210

Imbens, G.W., Rubin, D.B., 2015. Causal Inference for Statistics, Social, and Biomedical Sciences: An Introduction. Cambridge University Press.

Inskeep, W.P., Bloom, P.R., 1986. Calcium Carbonate Supersaturation in Soil Solutions of Calciaquolls. Soil Sci. Soc. Am. J. 50, 1431–1437. https://doi.org/10.2136/sssaj1986.03615995005000060011x

Isometric, 2024. Isometric Standard.

Isson, T.T., Planavsky, N.J., 2018. Reverse weathering as a long-term stabilizer of marine pH and planetary climate. Nature 560, 471–475. https://doi.org/10.1038/s41586-018-0408-4

Iversen, L.L., Winkel, A., Baastrup-Spohr, L., Hinke, A.B., Alahuhta, J., Baattrup-Pedersen, A., Birk, S., Brodersen, P., Chambers, P.A., Ecke, F., Feldmann, T., Gebler, D., Heino, J., Jespersen, T.S., Moe, S.J., Riis, T., Sass, L., Vestergaard, O., Maberly, S.C., Sand-Jensen, K., Pedersen, O., 2019. Catchment properties and the photosynthetic trait composition of freshwater plant communities. Science 366, 878–881. https://doi.org/10.1126/science.aay5945

Jackson, R.B., Canadell, J., Ehleringer, J.R., Mooney, H.A., Sala, O.E., Schulze, E.D., 1996. A global analysis of root distributions for terrestrial biomes. Oecologia 108, 389–411. https://doi.org/10.1007/BF00333714

Jähne, B., Heinz, G., Dietrich, W., 1987. Measurement of the diffusion coefficients of sparingly soluble gases in water. J. Geophys. Res. Oceans 92, 10767–10776. https://doi.org/10.1029/JC092iC10p10767

Jiang, L.-Q., Dunne, J., Carter, B.R., Tjiputra, J.F., Terhaar, J., Sharp, J.D., Olsen, A., Alin, S., Bakker, D.C.E., Feely, R.A., Gattuso, J.-P., Hogan, P., Ilyina, T., Lange, N., Lauvset, S.K., Lewis, E.R., Lovato, T., Palmieri, J., Santana-Falcón, Y., Schwinger, J., Séférian, R., Strand, G., Swart, N., Tanhua, T., Tsujino, H., Wanninkhof, R., Watanabe, M., Yamamoto, A., Ziehn, T., 2023. Global Surface Ocean Acidification Indicators From 1750 to 2100. J. Adv. Model. Earth Syst. 15, e2022MS003563. https://doi.org/10.1029/2022MS003563

Johannes, F., Nadine, M., Eva, S., Mengzhu, X., Daniela, T., 2021. PROJECT BRIEFING #3 AVOIDED AND REMOVED EMISSIONS VERSION #2.

Jones, D.L., 1998. Organic acids in the rhizosphere – a critical review. Plant Soil 205, 25–44. https://doi.org/10.1023/A:1004356007312

Jones, D.L., Dennis, P.G., Owen, A.G., van Hees, P.A.W., 2003. Organic acid behavior in soils – misconceptions and knowledge gaps. Plant Soil 248, 31–41. https://doi.org/10.1023/A:1022304332313

Jones, J.E., Woodward, C.S., 2001. Newton–Krylov-multigrid solvers for large-scale, highly heterogeneous, variably saturated flow problems. Adv. Water Resour. 24, 763–774. https://doi.org/10.1016/S0309-1708(00)00075-0

Kaijser, W., Lorenz, A.W., Birk, S., Hering, D., 2021. The interplay of nutrients, dissolved inorganic carbon and algae in determining macrophyte occurrences in rivers. Sci. Total Environ. 781, 146728. https://doi.org/10.1016/j.scitotenv.2021.146728

Kang, H., Kwon, M.J., Kim, S., Lee, S., Jones, T.G., Johncock, A.C., Haraguchi, A., Freeman, C., 2018. Biologically driven DOC release from peatlands during recovery from acidification. Nat. Commun. 9, 3807. https://doi.org/10.1038/s41467-018-06259-1

Kantola, I.B., Blanc-Betes, E., Masters, M.D., Chang, E., Marklein, A., Moore, C.E., Von Haden, A., Bernacchi, C.J., Wolf, A., Epihov, D.Z., Beerling, D.J., DeLucia, E.H., 2023. Improved net carbon budgets in the US Midwest through direct measured impacts of enhanced weathering. Glob. Change Biol. gcb.16903. https://doi.org/10.1111/gcb.16903

Kanzaki, Y., Chiaravalloti, I., Zhang, S., Planavsky, N.J., Reinhard, C.T., 2023a. In-silico calculation of soil pH by SCEPTER v1.0 (preprint). Biogeosciences. https://doi.org/10.5194/gmd-2023-137

Kanzaki, Y., Planavsky, N., Zhang, S., Jordan, J., Reinhard, C.T., 2024. Soil cation storage as a key control on the timescales of carbon dioxide removal through enhanced weathering. https://doi.org/10.22541/essoar.170960101.14306457/v1

Kanzaki, Y., Planavsky, N.J., Reinhard, C.T., 2023b. New estimates of the storage permanence and ocean co-benefits of enhanced rock weathering. PNAS Nexus 2, pgad059. https://doi.org/10.1093/pnasnexus/pgad059

Kanzaki, Y., Zhang, S., Planavsky, N.J., Reinhard, C.T., 2022. Soil Cycles of Elements simulator for Predicting TERrestrial regulation of greenhouse gases: SCEPTER v0.9. Geosci. Model Dev. 15, 4959–4990. https://doi.org/10.5194/gmd-15-4959-2022

Karunadasa, K.S.P., Manoratne, C.H., Pitawala, H.M.T.G.A., Rajapakse, R.M.G., 2019. Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. J. Phys. Chem. Solids 134, 21–28. https://doi.org/10.1016/j.jpcs.2019.05.023

Kelland, M.E., Wade, P.W., Lewis, A.L., Taylor, L.L., Sarkar, B., Andrews, M.G., Lomas, M.R., Cotton, T.E.A., Kemp, S.J., James, R.H., Pearce, C.R., Hartley, S.E., Hodson, M.E., Leake, J.R., Banwart, S.A., Beerling, D.J., 2020. Increased yield and CO_2 sequestration potential with the C_4 cereal *Sorghum bicolor* cultivated in basaltic rock dust-amended agricultural soil. Glob. Change Biol. 26, 3658–3676. https://doi.org/10.1111/gcb.15089

Kessler, T.J., Harvey, C.F., 2001. The global flux of carbon dioxide into groundwater. Geophys. Res. Lett. 28, 279–282. https://doi.org/10.1029/2000GL011505

Khalidy, R., Chiang, Y.W., Santos, R.M., 2024. Tracking pedogenic carbonate formation and migration in agricultural soils amended with crushed wollastonite ore- Evidence from field trials. https://doi.org/10.21203/rs.3.rs-3851689/v1

Khalidy, R., Chiang, Y.W., Santos, R.M., 2023. Fate and migration of enhanced rock weathering products through soil horizons; implications of irrigation and percolation regimes. CATENA 233, 107524. https://doi.org/10.1016/j.catena.2023.107524

Khalidy, R., Santos, R.M., 2021. The fate of atmospheric carbon sequestrated through weathering in mine tailings. Miner. Eng. 163, 106767. https://doi.org/10.1016/j.mineng.2020.106767

Khan, A., 2024. Quantification Beyond Crediting. Carbon Remov. Stand. Initiat. URL https://www.carbonremovalstandards.org/blog/jurisdiction-level-monitoring-of-enhanced-weathering (accessed 9.23.24).

Kim, J.H., Jobbágy, E.G., Richter, D.D., Trumbore, S.E., Jackson, R.B., 2020. Agricultural acceleration of soil carbonate weathering. Glob. Change Biol. 26, 5988–6002. https://doi.org/10.1111/gcb.15207

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments, in: Advances in Agronomy. Elsevier, pp. 1–140. https://doi.org/10.1016/bs.agron.2014.10.005

Klemme, A., Rixen, T., Müller, M., Notholt, J., Warneke, T., 2022. Destabilization of carbon in tropical peatlands by enhanced weathering. Commun. Earth Environ. 3, 212. https://doi.org/10.1038/s43247-022-00544-0

Knapp, J.L.A., von Freyberg, J., Studer, B., Kiewiet, L., Kirchner, J.W., 2020. Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics. Hydrol. Earth Syst. Sci. 24, 2561–2576. https://doi.org/10.5194/hess-24-2561-2020

Knapp, W.J., Stevenson, E.I., Renforth, P., Ascough, P.L., Knight, A.C.G., Bridgestock, L., Bickle, M.J., Lin, Y., Riley, A.L., Mayes, W.M., Tipper, E.T., 2023. Quantifying CO_2 Removal at Enhanced Weathering Sites: a Multiproxy Approach. Environ. Sci. Technol. 57, 9854–9864. https://doi.org/10.1021/acs.est.3c03757

Knapp, W.J., Tipper, E.T., 2022. The efficacy of enhancing carbonate weathering for carbon dioxide sequestration. Front. Clim. 4, 928215. https://doi.org/10.3389/fclim.2022.928215

Köhler, P., Abrams, J.F., Völker, C., Hauck, J., Wolf-Gladrow, D.A., 2013. Geoengineering impact of open ocean dissolution of olivine on atmospheric CO_2, surface ocean pH and marine biology. Environ. Res. Lett. 8, 014009. https://doi.org/10.1088/1748-9326/8/1/014009

Kosmulski, M., 2016. Isoelectric points and points of zero charge of metal (hydr)oxides: 50 years after Parks' review. Adv. Colloid Interface Sci. 238, 1–61. https://doi.org/10.1016/j.cis.2016.10.005

Krause, A.J., Sluijs, A., Van Der Ploeg, R., Lenton, T.M., Pogge Von Strandmann, P.A.E., 2023. Enhanced clay formation key in sustaining the Middle Eocene Climatic Optimum. Nat. Geosci. 16, 730–738. https://doi.org/10.1038/s41561-023-01234-y

Krumins, V., Gehlen, M., Arndt, S., Van Cappellen, P., Regnier, P., 2013. Dissolved inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates for different shelf environments and sensitivity to global change. Biogeosciences 10, 371–398. https://doi.org/10.5194/bg-10-371-2013

Kutsch, W.L., Aubinet, M., Buchmann, N., Smith, P., Osborne, B., Eugster, W., Wattenbach, M., Schrumpf, M., Schulze, E.D., Tomelleri, E., Ceschia, E., Bernhofer, C., Béziat, P., Carrara, A., Di Tommasi, P., Grünwald, T., Jones, M., Magliulo, V., Marloie, O., Moureaux, C., Olioso, A., Sanz, M.J., Saunders, M., Søgaard, H., Ziegler, W., 2010. The net biome production of full crop rotations in Europe. Agric. Ecosyst. Environ., The carbon balance of European croplands 139, 336–345. https://doi.org/10.1016/j.agee.2010.07.016

Langhorst, T., McCord, S., Zimmermann, A., Müller, L., Cremonese, L., Strunge, T., Wang, Y., Zaragoza, A.V., Wunderlich, J., Marxen, A., Armstrong, K., Buchner, G., Kätelhön, A., Bachmann, M., Sternberg, A., Michailos, S., Naims, H., Winter, B., Roskosch, D., Faber, G., Mangin, C., Olfe-Kräutlein, B., Styring, P., Schomäcker, R., Bardow, A., Sick, V., 2022. Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO2 Utilization (Version 2.0) (Technical Report). Global CO2 Initiative. https://doi.org/10.7302/4190

Larkin, C.S., Andrews, M.G., Pearce, C.R., Yeong, K.L., Beerling, D.J., Bellamy, J., Benedick, S., Freckleton, R.P., Goring-Harford, H., Sadekar, S., James, R.H., 2022. Quantification of CO2 removal in a large-scale enhanced weathering field trial on an oil palm plantation in Sabah, Malaysia. Front. Clim. 4, 959229. https://doi.org/10.3389/fclim.2022.959229

LeBauer, D.S., Wang, D., Richter, K.T., Davidson, C.C., Dietze, M.C., 2013. Facilitating feedbacks between field measurements and ecosystem models. Ecol. Monogr. 83, 133–154. https://doi.org/10.1890/12-0137.1

Leckie, J.O., Benjamin, M.M., Hayes, K., Kaufman, G., Altmann, S., 1980. Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide (No. EPRI-CS-1513). Stanford Univ., CA (USA). Dept. of Civil Engineering. https://doi.org/10.2172/5101674

Lehner, B., Verdin, K., Jarvis, A., 2008. New Global Hydrography Derived From Spaceborne Elevation Data. Eos Trans. Am. Geophys. Union 89, 93–94. https://doi.org/10.1029/2008EO100001

Lewis, A.L., Sarkar, B., Wade, P., Kemp, S.J., Hodson, M.E., Taylor, L.L., Yeong, K.L., Davies, K., Nelson, P.N., Bird, M.I., Kantola, I.B., Masters, M.D., DeLucia, E., Leake, J.R., Banwart, S.A., Beerling, D.J., 2021. Effects of mineralogy, chemistry and physical properties of basalts on carbon capture potential and plant-nutrient element release via enhanced weathering. Appl. Geochem. 132, 105023. https://doi.org/10.1016/j.apgeochem.2021.105023

Li, L., Maher, K., Navarre-Sitchler, A., Druhan, J., Meile, C., Lawrence, C., Moore, J., Perdrial, J., Sullivan, P., Thompson, A., Jin, L., Bolton, E.W., Brantley, S.L., Dietrich, W.E., Mayer, K.U., Steefel, C.I., Valocchi, A., Zachara, J., Kocar, B., Mcintosh, J., Tutolo, B.M., Kumar, M., Sonnenthal, E., Bao, C., Beisman, J., 2017. Expanding the role of reactive transport models in critical zone processes. Earth-Sci. Rev. 165, 280–301. https://doi.org/10.1016/j.earscirev.2016.09.001

Li, S., Li, G.K., Li, W., Chen, Y., Raymo, M.E., Chen, J., 2023. Effects of Secondary Carbonate Precipitation and Dissolution on Changjiang (Yangtze) River Chemistry and Estimates of Silicate Weathering Rates. Glob. Biogeochem. Cycles 37, e2022GB007581. https://doi.org/10.1029/2022GB007581

Li, Y., Wang, T., Camps-Arbestain, M., Suárez-Abelenda, M., Whitby, C.P., 2020. Lime and/or Phosphate Application Affects the Stability of Soil Organic Carbon: Evidence from Changes in Quantity and Chemistry of the Soil Water-Extractable Organic Matter. Environ. Sci. Technol. 54, 13908–13916. https://doi.org/10.1021/acs.est.0c01341

Li, Z., Cornelis, J.-T., Linden, C.V., Van Ranst, E., Delvaux, B., 2020. Neoformed aluminosilicate and phytogenic silica are competitive sinks in the silicon soil–plant cycle. Geoderma 368, 114308. https://doi.org/10.1016/j.geoderma.2020.114308

Licht, A., Kelson, J., Bergel, S., Schauer, A., Petersen, S.V., Capirala, A., Huntington, K.W., Dupont-Nivet, G., Win, Z., Aung, D.W., 2022. Dynamics of Pedogenic Carbonate Growth in the Tropical Domain of Myanmar. Geochem. Geophys. Geosystems 23, e2021GC009929. https://doi.org/10.1029/2021GC009929

Lin, Y.-P., Singer, P.C., Aiken, G.R., 2005. Inhibition of Calcite Precipitation by Natural Organic Material: Kinetics, Mechanism, and Thermodynamics. Environ. Sci. Technol. 39, 6420–6428. https://doi.org/10.1021/es050470z

Lorenz, K., Lal, R., 2018. Soil Carbon Stock, in: Lorenz, K., Lal, R. (Eds.), Carbon Sequestration in Agricultural Ecosystems. Springer International Publishing, Cham, pp. 39–136. https://doi.org/10.1007/978-3-319-92318-5_2

Loucaides, S., Michalopoulos, P., Presti, M., Koning, E., Behrends, T., Van Cappellen, P., 2010.

Seawater-mediated interactions between diatomaceous silica and terrigenous sediments: Results from long-term incubation experiments. Chem. Geol. 270, 68–79. https://doi.org/10.1016/j.chemgeo.2009.11.006

Maavara, T., Brinkerhoff, C., Hosen, J., Aho, K., Logozzo, L., Saiers, J., Stubbins, A., Raymond, P., 2023. Watershed DOC uptake occurs mostly in lakes in the summer and in rivers in the winter. Limnol. Oceanogr. 68, 735–751. https://doi.org/10.1002/lno.12306

MacBride, M.B., 1994. Environmental chemistry of soils. Oxford University Press, New York Oxford.

Maher, K., 2010. The dependence of chemical weathering rates on fluid residence time. Earth Planet. Sci. Lett. 294, 101–110. https://doi.org/10.1016/j.epsl.2010.03.010

Maher, K., Johnson, N.C., Jackson, A., Lammers, L.N., Torchinsky, A.B., Weaver, K.L., Bird, D.K., Brown, G.E., 2016. A spatially resolved surface kinetic model for forsterite dissolution. Geochim. Cosmochim. Acta 174, 313–334. https://doi.org/10.1016/j.gca.2015.11.019

Maher, K., Steefel, C.I., White, A.F., Stonestrom, D.A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. Geochim. Cosmochim. Acta 73, 2804–2831. https://doi.org/10.1016/j.gca.2009.01.030

Manning, D.A.C., De Azevedo, A.C., Zani, C.F., Barneze, A.S., 2024. Soil carbon management and enhanced rock weathering: The separate fates of organic and inorganic carbon. Eur. J. Soil Sci. 75, e13534. https://doi.org/10.1111/ejss.13534

Manning, D.A.C., Theodoro, S.H., 2020. Enabling food security through use of local rocks and minerals. Extr. Ind. Soc. 7, 480–487. https://doi.org/10.1016/j.exis.2018.11.002

Markstrom, S., Niswonger, R., Regan, S., Prudic, D., Barlow, P., 2008. GSFLOW—Coupled Ground-Water and Surface-Water Flow Model Based on the Integration of the Precipitation-Runoff Modeling System (PRMS) and the Modular Ground-Water Flow Model (MODFLOW-2005), in: Chapter 1 of Section D, Ground-Water/Surface-Water, Book 6, Modeling Techniques. U.S. Department of the Interior, U.S. Geological Survey.

Marschner, B., Waldemar Wilczynski, A., 1991. The effect of liming on quantity and chemical composition of soil organic matter in a pine forest in Berlin, Germany. Plant Soil 137, 229–236. https://doi.org/10.1007/BF00011201

Matthews, H.D., Zickfeld, K., Koch, A., Luers, A., 2023. Accounting for the climate benefit of temporary carbon storage in nature. Nat. Commun. 14, 5485. https://doi.org/10.1038/s41467-023-41242-5

Mayer, K.U., Alt-Epping, P., Jacques, D., Arora, B., Steefel, C.I., 2015. Benchmark problems for reactive transport modeling of the generation and attenuation of acid rock drainage. Comput. Geosci. 19, 599–611. https://doi.org/10.1007/s10596-015-9476-9

Mayer, K.U., Frind, E.O., Blowes, D.W., 2002. Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resour. Res. 38, 13-1-13–21. https://doi.org/10.1029/2001WR000862

Mayer, L., McFadden, L.D., Harden, J.W., 1988. Distribution of calcium carbonate in desert soils: A model. Geology 16, 303–306. https://doi.org/10.1130/0091-7613(1988)016<0303:DOCCID>2.3.CO;2

McColl, K.A., 2020. Practical and Theoretical Benefits of an Alternative to the Penman-Monteith Evapotranspiration Equation. Water Resour. Res. 56, e2020WR027106. https://doi.org/10.1029/2020WR027106

McCutcheon, J., Power, I.M., Shuster, J., Harrison, A.L., Dipple, G.M., Southam, G., 2019. Carbon Sequestration in Biogenic Magnesite and Other Magnesium Carbonate Minerals. Environ. Sci. Technol. 53, 3225–3237. https://doi.org/10.1021/acs.est.8b07055

Mendez, J.C., Hiemstra, T., 2019. Carbonate Adsorption to Ferrihydrite: Competitive Interaction with Phosphate for Use in Soil Systems. ACS Earth Space Chem. 3, 129–141. https://doi.org/10.1021/acsearthspacechem.8b00160

Michalopoulos, P., Aller, R.C., 2004. Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. Geochim. Cosmochim. Acta 68, 1061–1085. https://doi.org/10.1016/j.gca.2003.07.018

Michalopoulos, P., Aller, R.C., 1995a. Rapid Clay Mineral Formation in Amazon Delta Sediments: Reverse Weathering and Oceanic Elemental Cycles. Science 270, 614–617. https://doi.org/10.1126/science.270.5236.614

Michalopoulos, P., Aller, R.C., 1995b. Rapid Clay Mineral Formation in Amazon Delta Sediments: Reverse Weathering and Oceanic Elemental Cycles. Science 270, 614–617. https://doi.org/10.1126/science.270.5236.614

Microsoft, 2024. Microsoft Carbon Dioxide Removal Program [WWW Document]. Microsoft Sustain. URL https://www.microsoft.com/en-us/corporate-responsibility/sustainability/carbon-removal-program (accessed 6.6.24).

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

Millar, N., Robertson, P., Diamant, A., 2013. Quantifying N2O Emissions Reductions in Agricultural Crops through Nitrogen Fertilizer Rate Reduction.

Millock, K., 2013. Clean Development Mechanism, in: Encyclopedia of Energy, Natural Resource, and Environmental Economics. Elsevier, pp. 15–21. https://doi.org/10.1016/B978-0-12-375067-9.00127-3

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resour. Res. 53, 1270–1287. https://doi.org/10.1002/2016WR019635

Moatar, F., Meybeck, M., 2005. Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic River Loire. Hydrol. Process. 19, 429–444. https://doi.org/10.1002/hyp.5541

Moldrup, P., Olesen, T., Yamaguchi, T., Schjønning, P., Rolston, D.E., 1999. MODELING DIFFUSION AND REACTION IN SOILS: IX. THE BUCKINGHAM-BURDINE-CAMPBELL EQUATION FOR GAS DIFFUSIVITY IN UNDISTURBED SOIL. Soil Sci. 164, 542.

Monteith, J.L., 1981. Evaporation and surface temperature. Q. J. R. Meteorol. Soc. 107, 1–27. https://doi.org/10.1002/qj.49710745102

Moore, J.-D., Ouimet, R., Duchesne, L., 2012. Soil and sugar maple response 15years after dolomitic lime application. For. Ecol. Manag. 281, 130–139. https://doi.org/10.1016/j.foreco.2012.06.026

Moorhead, J.E., Marek, G.W., Gowda, P.H., Lin, X., Colaizzi, P.D., Evett, S.R., Kutikoff, S., 2019. Evaluation of Evapotranspiration from Eddy Covariance Using Large Weighing Lysimeters. Agronomy 9, 99. https://doi.org/10.3390/agronomy9020099

Moras, C.A., Bach, L.T., Cyronak, T., Joannes-Boyau, R., Schulz, K.G., 2022. Ocean alkalinity enhancement – avoiding runaway $CaCO_3$ precipitation during quick and hydrated lime dissolution. Biogeosciences 19, 3537–3557. https://doi.org/10.5194/bg-19-3537-2022

Moravec, B., Chorover, J., 2020. Critical Zone Biogeochemistry, in: Biogeochemical Cycles. American Geophysical Union (AGU), pp. 131–149. https://doi.org/10.1002/9781119413332.ch6

Morel, F.M., Hering, J.G., 1993. Principles and applications of aquatic chemistry. John Wiley & Sons.

Morgan, M.D., 1987. Impact of nutrient enrichment and alkalinization on periphyton communities in the New Jersey Pine Barrens. Hydrobiologia 144, 233–241. https://doi.org/10.1007/BF00005557

Mucci, A., Morse, J.W., 1983. The incorporation of Mg2+ and Sr2+ into calcite overgrowths: influences of growth rate and solution composition. Geochim. Cosmochim. Acta 47, 217–233. https://doi.org/10.1016/0016-7037(83)90135-7

Müller, G., Börker, J., Sluijs, A., Middelburg, J.J., 2022. Detrital Carbonate Minerals in Earth's Element Cycles. Glob. Biogeochem. Cycles 36, e2021GB007231. https://doi.org/10.1029/2021GB007231

Myklebust, M.C., Hipps, L.E., Ryel, R.J., 2008. Comparison of eddy covariance, chamber, and gradient methods of measuring soil CO2 efflux in an annual semi-arid grass, *Bromus tectorum*. Agric. For. Meteorol. 148, 1894–1907. https://doi.org/10.1016/j.agrformet.2008.06.016

Nadeem, S., Bakken, L.R., Frostegård, Å., Gaby, J.C., Dörsch, P., 2020. Contingent Effects of Liming on N2O-Emissions Driven by Autotrophic Nitrification. Front. Environ. Sci. 8, 598513. https://doi.org/10.3389/fenvs.2020.598513

Naeem, M., Ansari, A.A., Gill, S.S. (Eds.), 2017. Essential Plant Nutrients. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-319-58841-4

Navarre-Sitchler, A., Brantley, S., 2007. Basalt weathering across scales. Earth Planet. Sci. Lett. 261, 321–334. https://doi.org/10.1016/j.epsl.2007.07.010

Navarre-Sitchler, A., Steefel, C.I., Sak, P.B., Brantley, S.L., 2011. A reactive-transport model for weathering rind formation on basalt. Geochim. Cosmochim. Acta 75, 7644–7667. https://doi.org/10.1016/j.gca.2011.09.033

Nesbitt, W.A., Mucci, A., 2021. Direct evidence of sediment carbonate dissolution in response to bottom-water acidification in the Gulf of St. Lawrence, Canada. Can. J. Earth Sci. 58, 84–92. https://doi.org/10.1139/cjes-2020-0020

Neumann, R.B., Polizzotto, M.L., Badruzzaman, A.B.M., Ali, M.A., Zhang, Z., Harvey, C.F., 2009. Hydrology of a groundwater-irrigated rice field in Bangladesh: Seasonal and daily mechanisms of infiltration. Water Resour. Res. 45, 2008WR007542. https://doi.org/10.1029/2008WR007542

Nugent, M.A., Brantley, S.L., Pantano, C.G., Maurice, P.A., 1998. The influence of natural mineral coatings on feldspar weathering. Nature 395, 588–591. https://doi.org/10.1038/26951

Oelkers, E.H., Butcher, R., Pogge Von Strandmann, P.A.E., Schuessler, J.A., Von Blanckenburg, F., Snæbjörnsdóttir, S.Ó., Mesfin, K., Aradóttir, E.S., Gunnarsson, I., Sigfússon, B., Gunnlaugsson, E., Matter, J.M., Stute, M., Gislason, S.R., 2019. Using stable Mg isotope signatures to assess the fate of magnesium during the in situ mineralisation of CO2 and H2S at the CarbFix site in SW-Iceland. Geochim. Cosmochim. Acta 245, 542–555. https://doi.org/10.1016/j.gca.2018.11.011

Oelkers, E.H., Declercq, J., Saldi, G.D., Gislason, S.R., Schott, J., 2018. Olivine dissolution rates: A critical review. Chem. Geol. 500, 1–19. https://doi.org/10.1016/j.chemgeo.2018.10.008

Oh, N.-H., Raymond, P.A., 2006. Contribution of agricultural liming to riverine bicarbonate export and CO $_2$ sequestration in the Ohio River basin: LIMING EFFECTS ON RIVERINE BICARBONATE EXPORT. Glob. Biogeochem. Cycles 20, n/a-n/a. https://doi.org/10.1029/2005GB002565

Ordóñez, R.A., Castellano, M.J., Hatfield, J.L., Helmers, M.J., Licht, M.A., Liebman, M., Dietzel, R., Martinez-Feria, R., Iqbal, J., Puntel, L.A., Córdova, S.C., Togliatti, K., Wright, E.E., Archontoulis, S.V., 2018. Maize and soybean root front velocity and maximum depth in Iowa, USA. Field Crops Res. 215, 122–131. https://doi.org/10.1016/j.fcr.2017.09.003

Ortiz, A.C., Jin, L., Ogrinc, N., Kaye, J., Krajnc, B., Ma, L., 2022. Dryland irrigation increases accumulation rates of pedogenic carbonate and releases soil abiotic CO2. Sci. Rep. 12, 464. https://doi.org/10.1038/s41598-021-04226-3

Paessler, D., Smet, I., Hammes, J.S., Steffens, R., Stöckel, A.A., 2024. Data Deep Dive: Could soil EC sensors or leachate EC measurements be used to monitor enhanced weathering? Insights from several hundred soil EC sensors and several thousand water analyses in three long-term weathering experiments. https://doi.org/10.13140/RG.2.2.11415.79521

Paessler, D., Steffens, R., Hammes, J., Smet, I., 2023. Monitoring CO2 Concentrations in Soil Gas: A Novel MRV Approach for Cropland-Based ERW?

Paradelo, R., Virto, I., Chenu, C., 2015. Net effect of liming on soil organic carbon stocks: A review. Agric. Ecosyst. Environ. 202, 98–107. https://doi.org/10.1016/j.agee.2015.01.005

Parfitt, R.L., 2009. Allophane and imogolite: role in soil biogeochemical processes. Clay Miner. 44, 135–155. https://doi.org/10.1180/claymin.2009.044.1.135

Parisa, Z., Marland, E., Sohngen, B., Marland, G., Jenkins, J., 2022. The time value of carbon storage. For. Policy Econ. 144, 102840. https://doi.org/10.1016/j.forpol.2022.102840

Paul, A.J., Haunost, M., Goldenberg, S.U., Hartmann, J., Sánchez, N., Schneider, J., Suitner, N., Riebesell, U., 2024. Ocean alkalinity enhancement in an open ocean ecosystem: Biogeochemical responses and carbon storage durability. EGUsphere 1–31. https://doi.org/10.5194/egusphere-2024-417

Pavelka, M., Acosta, M., Kiese, R., Altimir, N., Brümmer, C., Crill, P., Darenova, E., Fuß, R., Gielen, B., Graf, A., Klemedtsson, L., Lohila, A., Longdoz, B., Lindroth, A., Nilsson, M., Jiménez, S.M., Merbold, L., Montagnani, L., Peichl, M., Pihlatie, M., Pumpanen, J., Ortiz, P.S., Silvennoinen, H., Skiba, U., Vestin, P., Weslien, P., Janous, D., Kutsch, W., 2018. Standardisation of chamber technique for CO2, N2O and CH4 fluxes measurements from terrestrial ecosystems. Int. Agrophysics 32, 569–587. https://doi.org/10.1515/intag-2017-0045

Perez-Fodich, A., Derry, L.A., 2019. Organic acids and high soil CO2 drive intense chemical weathering of Hawaiian basalts: Insights from reactive transport models. Geochim. Cosmochim. Acta 249, 173–198. https://doi.org/10.1016/j.gca.2019.01.027

Persson, T., Andersson, S., Bergholm, J., Grönqvist, T., Högbom, L., Vegerfors, B., Wirén, A., 2021. Long-Term Impact of Liming on Soil C and N in a Fertile Spruce Forest Ecosystem. Ecosystems 24, 968–987. https://doi.org/10.1007/s10021-020-00563-y

Persson, T., Rudebeck, A., Wir�n, A., 1995. Pools and fluxes of carbon and nitrogen in 40-year-old forest liming experiments in Southern Sweden. Water. Air. Soil Pollut. 85, 901–906. https://doi.org/10.1007/BF00476944

Pett-Ridge, J., Firestone, M.K., 2017. Using stable isotopes to explore root-microbe-mineral interactions in soil. Rhizosphere, New Understanding of Rhizosphere Processes Enabled by Advances in Molecular and Spatially Resolved Techniques 3, 244–253. https://doi.org/10.1016/j.rhisph.2017.04.016

Pihlap, E., Olagaray, N.Y., Klöffel, T., Masters, M.D., Kantola, I.B., Beerling, D.J., 2024. Effects of enhanced mineral weathering on soil structure and organic carbon storage. Presented at the EGU24, Vienna, Austria. https://doi.org/10.5194/egusphere-egu24-10036, 2024.

Pistiner, J.S., Henderson, G.M., 2003. Lithium-isotope fractionation during continental weathering processes. Earth Planet. Sci. Lett. 214, 327–339. https://doi.org/10.1016/S0012-821X(03)00348-0

Plaza, C., Zaccone, C., Sawicka, K., Méndez, A.M., Tarquis, A., Gascó, G., Heuvelink, G.B.M., Schuur, E.A.G., Maestre, F.T., 2018. Soil resources and element stocks in drylands to face global issues. Sci. Rep. 8, 13788. https://doi.org/10.1038/s41598-018-32229-0

Plummer, L.N., Busenberg, E., 1982. The solubilities of calcite, aragonite and vaterite in CO2-H2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO3-CO2-H2O. Geochim. Cosmochim. Acta 46, 1011–1040. https://doi.org/10.1016/0016-7037(82)90056-4

Poblador, S., Le Noir de Carlan, C., Verbruggen, E., Vicca, S., 2024. Enhanced weathering in acid and alkaline agricultural soils: greenhouse gas emissions and soil bacterial communities implications. Presented at the EGU General Assembly 2022, Vienna, Austria. https://doi.org/10.5194/egusphere-egu22-13396

Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P., Gislason, S.R., Sigfússon, B., 2008. The influence of weathering processes on riverine magnesium isotopes in a basaltic terrain. Earth Planet. Sci. Lett. 276, 187–197. https://doi.org/10.1016/j.epsl.2008.09.020

Pogge Von Strandmann, P.A.E., Burton, K.W., Opfergelt, S., Genson, B., Guicharnaud, R.A., Gislason, S.R., 2021a. The lithium isotope response to the variable weathering of soils in Iceland. Geochim. Cosmochim. Acta 313, 55–73. https://doi.org/10.1016/j.gca.2021.08.020

Pogge von Strandmann, P.A.E., Cosford, L.R., Liu, C.-Y., Liu, X., Krause, A.J., Wilson, D.J., He, X., McCoy-West, A.J., Gislason, S.R., Burton, K.W., 2023. Assessing hydrological controls on the lithium isotope weathering tracer. Chem. Geol. 642, 121801. https://doi.org/10.1016/j.chemgeo.2023.121801

Pogge Von Strandmann, P.A.E., Fraser, W.T., Hammond, S.J., Tarbuck, G., Wood, I.G., Oelkers, E.H., Murphy, M.J., 2019. Experimental determination of Li isotope behaviour during basalt weathering. Chem. Geol. 517, 34–43. https://doi.org/10.1016/j.chemgeo.2019.04.020

Pogge von Strandmann, P.A.E., Opfergelt, S., Lai, Y.-J., Sigfússon, B., Gislason, S.R., Burton, K.W., 2012. Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. Earth Planet. Sci. Lett. 339–340, 11–23. https://doi.org/10.1016/j.epsl.2012.05.035

Pogge Von Strandmann, P.A.E., Renforth, P., West, A.J., Murphy, M.J., Luu, T.-H., Henderson, G.M., 2021b. The lithium and magnesium isotope signature of olivine dissolution in soil experiments. Chem. Geol. 560, 120008. https://doi.org/10.1016/j.chemgeo.2020.120008

Poonoosamy, J., Wanner, C., Alt Epping, P., Águila, J.F., Samper, J., Montenegro, L., Xie, M., Su, D., Mayer, K.U., Mäder, U., Van Loon, L.R., Kosakowski, G., 2021. Benchmarking of reactive transport codes for 2D simulations with mineral dissolution–precipitation reactions and feedback on transport parameters. Comput. Geosci. 25, 1337–1358. https://doi.org/10.1007/s10596-018-9793-x

Povar, I., Rusu, V., 2012. Aluminium heterogeneous speciation in natural waters. Can. J. Chem. 90, 326–332. https://doi.org/10.1139/v2012-003

Power, I.M., Dipple, G.M., Bradshaw, P.M.D., Harrison, A.L., 2020. Prospects for CO2 mineralization and enhanced weathering of ultramafic mine tailings from the Baptiste nickel deposit in British Columbia, Canada. Int. J. Greenh. Gas Control 94, 102895. https://doi.org/10.1016/j.ijggc.2019.102895

Power, I.M., Harrison, A.L., Dipple, G.M., Wilson, S., Barker, S.L.L., Fallon, S.J., 2019. Magnesite formation in playa environments near Atlin, British Columbia, Canada. Geochim. Cosmochim. Acta 255, 1–24. https://doi.org/10.1016/j.gca.2019.04.008

Power, I.M., Kenward, P.A., Dipple, G.M., Raudsepp, M., 2017. Room Temperature Magnesite Precipitation. Cryst. Growth Des. 17, 5652–5659. https://doi.org/10.1021/acs.cgd.7b00311

Pullin, H., Bray, A.W., Burke, I.T., Muir, D.D., Sapsford, D.J., Mayes, W.M., Renforth, P., 2019. Atmospheric Carbon Capture Performance of Legacy Iron and Steel Waste. Environ. Sci. Technol. 53, 9502–9511. https://doi.org/10.1021/acs.est.9b01265

Rahman, S., 2019. Reverse Weathering Reactions in Marine Sediments, in: Cochran, J.K., Bokuniewicz, H.J., Yager, P.L. (Eds.), Encyclopedia of Ocean Sciences (Third Edition). Academic Press, Oxford, pp. 216–227. https://doi.org/10.1016/B978-0-12-409548-9.10835-8

Rahman, S., Trower, E.J., 2023. Probing surface Earth reactive silica cycling using stable Si isotopes: Mass balance, fluxes, and deep time implications. Sci. Adv. 9, eadi2440. https://doi.org/10.1126/sciadv.adi2440

Ramos, C.G., Querol, X., Dalmora, A.C., De Jesus Pires, K.C., Schneider, I.A.H., Oliveira, L.F.S., Kautzmann, R.M., 2017. Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer. J. Clean. Prod. 142, 2700–2706. https://doi.org/10.1016/j.jclepro.2016.11.006

Ramsey, M.H., Argyraki, A., Thompson, M., 1995. Estimation of sampling bias between different sampling protocols on contaminated land. Analyst 120, 1353–1356. https://doi.org/10.1039/AN9952001353

Rasmussen, C., Throckmorton, H., Liles, G., Heckman, K., Meding, S., Horwath, W., 2018. Controls on Soil Organic Carbon Partitioning and Stabilization in the California Sierra Nevada. Soil Syst. 2, 41. https://doi.org/10.3390/soilsystems2030041

Raymond, P.A., Oh, N.-H., Turner, R.E., Broussard, W., 2008. Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. Nature 451, 449–452. https://doi.org/10.1038/nature06505

Reershemius, T., Kelland, M.E., Jordan, J.S., Davis, I.R., D'Ascanio, R., Kalderon-Asael, B., Asael, D., Epihov, D.Z., Beerling, D.J., Reinhard, C.T., Planavsky, N.J., 2023. A new soil-based approach for empirical monitoring of enhanced rock weathering rates. https://doi.org/10.48550/ARXIV.2302.05004

Renforth, P., 2019. The negative emission potential of alkaline materials. Nat. Commun. 10, 1401. https://doi.org/10.1038/s41467-019-09475-5

Renforth, P., Henderson, G., 2017. Assessing ocean alkalinity for carbon sequestration: Ocean Alkalinity for C Sequestration. Rev. Geophys. 55, 636–674. https://doi.org/10.1002/2016RG000533

Renforth, P., Pogge Von Strandmann, P.A.E., Henderson, G.M., 2015. The dissolution of olivine added to soil: Implications for enhanced weathering. Appl. Geochem. 61, 109–118. https://doi.org/10.1016/j.apgeochem.2015.05.016

Rennert, T., 2018. Wet-chemical extractions to characterise pedogenic Al and Fe species – a critical review. Soil Res. 57, 1–16. https://doi.org/10.1071/SR18299

Retallack, G.J., 2005. Pedogenic carbonate proxies for amount and seasonality of precipitation in paleosols. Geology 33, 333–336. https://doi.org/10.1130/G21263.1

Richards, P.L., Kump, L.R., 2003. Soil pore-water distributions and the temperature feedback of weathering in soils. Geochim. Cosmochim. Acta 67, 3803–3815. https://doi.org/10.1016/S0016-7037(03)00270-9

Ridgwell, A., Zeebe, R.E., 2005. The role of the global carbonate cycle in the regulation and evolution of the Earth system. Earth Planet. Sci. Lett. 234, 299–315. https://doi.org/10.1016/j.epsl.2005.03.006

Riebe, C.S., Hahm, W.J., Brantley, S.L., 2017. Controls on deep critical zone architecture: a historical review and four testable hypotheses. Earth Surf. Process. Landf. 42, 128–156. https://doi.org/10.1002/esp.4052

Riebe, C.S., Kirchner, J.W., Finkel, R.C., 2003. Long-term rates of chemical weathering and physical erosion from cosmogenic nuclides and geochemical mass balance. Geochim. Cosmochim. Acta 67, 4411–4427. https://doi.org/10.1016/S0016-7037(03)00382-X

Rieder, L., Amann, T., Hartmann, J., 2024. Soil electrical conductivity as a proxy for enhanced weathering in soils. Front. Clim. 5, 1283107. https://doi.org/10.3389/fclim.2023.1283107

Rigopoulos, I., Harrison, A.L., Delimitis, A., Ioannou, I., Efstathiou, A.M., Kyratsi, T., Oelkers, E.H., 2018. Carbon sequestration via enhanced weathering of peridotites and basalts in seawater. Appl. Geochem. 91, 197–207. https://doi.org/10.1016/j.apgeochem.2017.11.001

Rimon, Y., Nativ, R., Dahan, O., 2011. Physical and Chemical Evidence for Pore-Scale Dual-Domain Flow in the Vadose Zone. Vadose Zone J. 10, 322–331. https://doi.org/10.2136/vzj2009.0113

Rodriguez-Navarro, C., Ruiz-Agudo, E., Luque, A., Rodriguez-Navarro, A.B., Ortega-Huertas, M., 2009. Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals. Am. Mineral. 94, 578–593. https://doi.org/10.2138/am.2009.3021

Rosi-Marshall, E.J., Bernhardt, E.S., Buso, D.C., Driscoll, C.T., Likens, G.E., 2016. Acid rain mitigation experiment shifts a forested watershed from a net sink to a net source of nitrogen. Proc. Natl. Acad. Sci. 113, 7580–7583. https://doi.org/10.1073/pnas.1607287113

Rousk, J., Brookes, P.C., Bååth, E., 2009. Contrasting Soil pH Effects on Fungal and Bacterial Growth Suggest Functional Redundancy in Carbon Mineralization. Appl. Environ. Microbiol. 75, 1589–1596. https://doi.org/10.1128/AEM.02775-08

Rousseau, T.C.C., Roddaz, M., Moquet, J.-S., Handt Delgado, H., Calves, G., Bayon, G., 2019. Controls on the geochemistry of suspended sediments from large tropical South American rivers (Amazon, Orinoco and Maroni). Chem. Geol. 522, 38–54. https://doi.org/10.1016/j.chemgeo.2019.05.027

Rowley, M.C., Grand, S., Verrecchia, É.P., 2018. Calcium-mediated stabilisation of soil organic carbon. Biogeochemistry 137, 27–49. https://doi.org/10.1007/s10533-017-0410-1

Ryu, J.-S., Vigier, N., Decarreau, A., Lee, S.-W., Lee, K.-S., Song, H., Petit, S., 2016. Experimental investigation of Mg isotope fractionation during mineral dissolution and clay formation. Chem. Geol. 445, 135–145. https://doi.org/10.1016/j.chemgeo.2016.02.006

Ryu, J.-S., Vigier, N., Lee, S.-W., Lee, K.-S., Chadwick, O.A., 2014. Variation of lithium isotope geochemistry during basalt weathering and secondary mineral transformations in Hawaii. Geochim. Cosmochim. Acta 145, 103–115. https://doi.org/10.1016/j.gca.2014.08.030

Salinas-Garcia, J.R., Hons, F.M., Matocha, J.E., 1997. Long-Term Effects of Tillage and Fertilization on Soil Organic Matter Dynamics. Soil Sci. Soc. Am. J. 61, 152–159. https://doi.org/10.2136/sssaj1997.03615995006100010023x

Sánchez-Cañete, E.P., Scott, R.L., Van Haren, J., Barron-Gafford, G.A., 2017. Improving the accuracy of the gradient method for determining soil carbon dioxide efflux. J. Geophys. Res. Biogeosciences 122, 50–64. https://doi.org/10.1002/2016JG003530

Sanna, A., Uibu, M., Caramanna, G., Kuusik, R., M. Maroto-Valer, M., 2014. A review of mineral carbonation technologies to sequester CO 2. Chem. Soc. Rev. 43, 8049–8080. https://doi.org/10.1039/C4CS00035H

Santos, I.R., Maher, D.T., Larkin, R., Webb, J.R., Sanders, C.J., 2019. Carbon outwelling and outgassing vs. burial in an estuarine tidal creek surrounded by mangrove and saltmarsh wetlands. Limnol. Oceanogr. 64, 996–1013. https://doi.org/10.1002/lno.11090

Schuiling, R.D., Wilson, S., Power, Ian M., 2011. Enhanced silicate weathering is not limited by silicic acid saturation. Proc. Natl. Acad. Sci. 108, E41–E41. https://doi.org/10.1073/pnas.1019024108

See, C.R., Luke McCormack, M., Hobbie, S.E., Flores-Moreno, H., Silver, W.L., Kennedy, P.G., 2019. Global patterns in fine root decomposition: climate, chemistry, mycorrhizal association and woodiness. Ecol. Lett. 22, 946–953. https://doi.org/10.1111/ele.13248

Shen, C., Testa, J.M., Li, M., Cai, W.-J., Waldbusser, G.G., Ni, W., Kemp, W.M., Cornwell, J., Chen, B., Brodeur, J., Su, J., 2019. Controls on Carbonate System Dynamics in a Coastal Plain Estuary: A Modeling Study. J. Geophys. Res. Biogeosciences 124, 61–78. https://doi.org/10.1029/2018JG004802

Siebert, S., Burke, J., Faures, J.M., Frenken, K., Hoogeveen, J., Döll, P., Portmann, F.T., 2010. Groundwater use for irrigation – a global inventory. Hydrol. Earth Syst. Sci. 14, 1863–1880. https://doi.org/10.5194/hess-14-1863-2010

Singh, G., Kaur, G., Williard, K., Schoonover, J., Kang, J., 2018. Monitoring of Water and Solute Transport in the Vadose Zone: A Review. Vadose Zone J. 17, 1–23. https://doi.org/10.2136/vzj2016.07.0058

Skov, K., Wardman, J., Healey, M., McBride, A., Bierowiec, T., Cooper, J., Edeh, I., George, D., Kelland, M.E., Mann, J., Manning, D., Murphy, M.J., Pape, R., Teh, Y.A., Turner, W., Wade, P., Liu, X., 2024. Initial agronomic benefits of enhanced weathering using basalt: A study of spring oat in a temperate climate. PLOS ONE 19, e0295031. https://doi.org/10.1371/journal.pone.0295031

Slessarev, E.W., Chadwick, O.A., Sokol, N.W., Nuccio, E.E., Pett-Ridge, J., 2022. Rock weathering controls the potential for soil carbon storage at a continental scale. Biogeochemistry 157, 1–13. https://doi.org/10.1007/s10533-021-00859-8

Smith, D.M., Inman-Bamber, N.G., Thorburn, P.J., 2005. Growth and function of the sugarcane root system. Field Crops Res., Sugarcane physiology:Integrating from cell to crop to advance sugarcane production 92, 169–183. https://doi.org/10.1016/j.fcr.2005.01.017

Sokol, N.W., Sohng, J., Moreland, K., Slessarev, E., Goertzen, H., Schmidt, R., Samaddar, S., Holzer, I., Almaraz, M., Geoghegan, E., Houlton, B., Montañez, I., Pett-Ridge, J., Scow, K., 2024. Reduced accrual of mineral-associated organic matter after two years of enhanced rock weathering in cropland soils, though no net losses of soil organic carbon. Biogeochemistry 167, 989–1005. https://doi.org/10.1007/s10533-024-01160-0

Soulet, G., Hilton, R.G., Garnett, M.H., Roylands, T., Klotz, S., Croissant, T., Dellinger, M., Le Bouteiller, C., 2021. Temperature control on CO2 emissions from the weathering of sedimentary rocks. Nat. Geosci. 14, 665–671. https://doi.org/10.1038/s41561-021-00805-1

Spertus, J.V., 2021. Optimal Sampling and Assay for Estimating Soil Organic Carbon. Open J. Soil Sci. 11, 93–121. https://doi.org/10.4236/ojss.2021.112006

Sposito, G., 2016. The Chemistry of Soils, Third Edition, New to this Edition:, Third Edition, New to this Edition: ed. Oxford University Press, Oxford, New York.

Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S.T., Benettin, P., Dubbert, M., Hartmann, A., Hrachowitz, M., Kirchner, J.W., McDonnell, J.J., Orlowski, N., Penna, D., Pfahl, S., Rinderer, M., Rodriguez, N., Schmidt, M., Werner, C., 2019. The Demographics of Water: A Review of Water Ages in the Critical Zone. Rev. Geophys. 57, 800–834. https://doi.org/10.1029/2018RG000633

Stanley, P., Spertus, J., Chiartas, J., Stark, P.B., Bowles, T., 2023. Valid inferences about soil carbon in heterogeneous landscapes. Geoderma 430, 116323.

https://doi.org/10.1016/j.geoderma.2022.116323
Steefel, C.I., Yabusaki, S.B., Mayer, K.U., 2015. Reactive transport benchmarks for subsurface environmental simulation. Comput. Geosci. 19, 439–443. https://doi.org/10.1007/s10596-015-9499-2
Stets, E.G., Butman, D., McDonald, C.P., Stackpoole, S.M., DeGrandpre, M.D., Striegl, R.G., 2017. Carbonate buffering and metabolic controls on carbon dioxide in rivers. Glob. Biogeochem. Cycles 31, 663–677. https://doi.org/10.1002/2016GB005578
Stone, E.L., Kalisz, P.J., 1991. On the maximum extent of tree roots. For. Ecol. Manag. 46, 59–102. https://doi.org/10.1016/0378-1127(91)90245-Q
Striegl, R., Dornblaser, M., Aiken, G., Wickland, K., Raymond, P., 2007. Carbon export and cycling by the Yukon, Tanana, and Porcupine Rivers, Alaska, 2001–2005. Water Resour. Res. 43. https://doi.org/10.1029/2006WR005201
Stubbs, A.R., Paulo, C., Power, I.M., Wang, B., Zeyen, N., Wilson, S., 2022. Direct measurement of CO2 drawdown in mine wastes and rock powders: Implications for enhanced rock weathering. Int. J. Greenh. Gas Control 113, 103554. https://doi.org/10.1016/j.ijggc.2021.103554
Suarez, D.L., 1977. Ion Activity Products of Calcium Carbonate in Waters Below the Root Zone. Soil Sci. Soc. Am. J. 41, 310–315. https://doi.org/10.2136/sssaj1977.03615995004100020027x
Subhas, A.V., Dong, S., Naviaux, J.D., Rollins, N.E., Ziveri, P., Gray, W., Rae, J.W.B., Liu, X., Byrne, R.H., Chen, S., Moore, C., Martell-Bonet, L., Steiner, Z., Antler, G., Hu, H., Lunstrum, A., Hou, Y., Kemnitz, N., Stutsman, J., Pallacks, S., Dugenne, M., Quay, P.D., Berelson, W.M., Adkins, J.F., 2022. Shallow Calcium Carbonate Cycling in the North Pacific Ocean. Glob. Biogeochem. Cycles 36, e2022GB007388. https://doi.org/10.1029/2022GB007388
Suhrhoff, T.J., Reershemius, T., Wang, J., Jordan, J.S., Reinhard, C.T., Planavsky, N.J., 2024. A tool for assessing the sensitivity of soil-based approaches for quantifying enhanced weathering: a US case study. Front. Clim. 6, 1346117. https://doi.org/10.3389/fclim.2024.1346117
Sulman, B.N., Phillips, R.P., Oishi, A.C., Shevliakova, E., Pacala, S.W., 2014. Microbe-driven turnover offsets mineral-mediated storage of soil carbon under elevated CO2. Nat. Clim. Change 4, 1099–1102. https://doi.org/10.1038/nclimate2436
Swoboda, P., Döring, T.F., Hamer, M., 2022. Remineralizing soils? The agricultural usage of silicate rock powders: A review. Sci. Total Environ. 807, 150976. https://doi.org/10.1016/j.scitotenv.2021.150976
Takahashi, T., Ikeda, Y., Fujita, K., Nanzyo, M., 2006. Effect of liming on organically complexed aluminum of nonallophanic Andosols from northeastern Japan. Geoderma 130, 26–34. https://doi.org/10.1016/j.geoderma.2005.01.006
Taniguchi, M., Dulai, H., Burnett, K.M., Santos, I.R., Sugimoto, R., Stieglitz, T., Kim, G., Moosdorf, N., Burnett, W.C., 2019. Submarine Groundwater Discharge: Updates on Its Measurement Techniques, Geophysical Drivers, Magnitudes, and Effects. Front. Environ. Sci. 7. https://doi.org/10.3389/fenvs.2019.00141
Taylor, L.L., Driscoll, C.T., Groffman, P.M., Rau, G.H., Blum, J.D., Beerling, D.J., 2021. Increased carbon capture by a silicate-treated forested watershed affected by acid deposition. Biogeosciences 18, 169–188. https://doi.org/10.5194/bg-18-169-2021
Te Pas, E.E.E.M., Hagens, M., Comans, R.N.J., 2023. Assessment of the enhanced weathering potential of different silicate minerals to improve soil quality and sequester CO2. Front. Clim. 4, 954064. https://doi.org/10.3389/fclim.2022.954064
Ten Berge, H.F.M., Van Der Meer, H.G., Steenhuizen, J.W., Goedhart, P.W., Knops, P., Verhagen, J., 2012. Olivine Weathering in Soil, and Its Effects on Growth and Nutrient Uptake in Ryegrass (Lolium perenne L.): A Pot Experiment. PLoS ONE 7, e42098. https://doi.org/10.1371/journal.pone.0042098
Teng, F.-Z., Li, W.-Y., Rudnick, R.L., Gardner, L.R., 2010. Contrasting lithium and magnesium isotope fractionation during continental weathering. Earth Planet. Sci. Lett. 300, 63–71. https://doi.org/10.1016/j.epsl.2010.09.036
Tian, L., Tahmasebi, A., Yu, J., 2014. An experimental study on thermal decomposition behavior of magnesite. J. Therm. Anal. Calorim. 118, 1577–1584. https://doi.org/10.1007/s10973-014-4068-9
Tipper, E.T., Galy, A., Bickle, M.J., 2006. Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle. Earth Planet. Sci. Lett. 247, 267–279. https://doi.org/10.1016/j.epsl.2006.04.033
Tokunaga, T.K., Kim, Y., Conrad, M.E., Bill, M., Hobson, C., Williams, K.H., Dong, W., Wan, J., Robbins, M.J., Long, P.E., Faybishenko, B., Christensen, J.N., Hubbard, S.S., 2016. Deep Vadose Zone Respiration Contributions to Carbon Dioxide Fluxes from a Semiarid Floodplain. Vadose Zone J. 15, 1–14.

https://doi.org/10.2136/vzj2016.02.0014

Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., Hendricks, D.M., 1997. Mineral control of soil organic carbon storage and turnover. Nature 389, 170–173. https://doi.org/10.1038/38260

Turner, D.R., Whitfield, M., Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and sea water at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta 45, 855–881. https://doi.org/10.1016/0016-7037(81)90115-0

USDA, 2022. Sampling Soils For Nutrient Management.

Val Martin, M., Blanc-Betes, E., Fung, K.M., Kantzas, E.P., Kantola, I.B., Chiaravalloti, I., Taylor, L.T., Emmons, L.K., Wieder, W.R., Planavsky, N.J., Masters, M.D., DeLucia, E.H., Tai, A.P.K., Beerling, D.J., 2023. Improving nitrogen cycling in a land surface model (CLM5) to quantify soil N_2O, NO and NH_3 emissions from enhanced rock weathering with croplands (preprint). Biogeosciences. https://doi.org/10.5194/gmd-2023-47

Van der Kaars, S., Dam, R., 1997. Vegetation and climate change in West-Java, Indonesia during the last 135,000 years. Quat. Int. 37, 67–71. https://doi.org/10.1016/1040-6182(96)00002-X

Van Straaten, P., 2021. Nutrient Element Release from Volcanic Silicate Rocks: Examples from Quarternary Basalts of Queensland, Australia, in: IV Congresso Brasileiro de Rochagem.

Van Straaten, P., 2006. Farming with rocks and minerals: challenges and opportunities. An. Acad. Bras. Ciênc. 78, 731–747. https://doi.org/10.1590/S0001-37652006000400009

Van Straaten, P., 2002. Rocks for crops: agrominerals of sub-Saharan Africa. ICRAF ; University of Guelph, Nairobi, Kenya : Guelph, Canada.

Vargas, R., Detto, M., Baldocchi, D.D., Allen, M.F., 2010. Multiscale analysis of temporal variability of soil CO2 production as influenced by weather and vegetation. Glob. Change Biol. 16, 1589–1605. https://doi.org/10.1111/j.1365-2486.2009.02111.x

Verbruggen, E., Struyf, E., Vicca, S., 2021. Can arbuscular mycorrhizal fungi speed up carbon sequestration by enhanced weathering? PLANTS PEOPLE PLANET 3, 445–453. https://doi.org/10.1002/ppp3.10179

Vicca, S., Goll, D.S., Hagens, M., Hartmann, J., Janssens, I.A., Neubeck, A., Peñuelas, J., Poblador, S., Rijnders, J., Sardans, J., Struyf, E., Swoboda, P., Van Groenigen, J.W., Vienne, A., Verbruggen, E., 2022. Is the climate change mitigation effect of enhanced silicate weathering governed by biological processes? Glob. Change Biol. 28, 711–726. https://doi.org/10.1111/gcb.15993

Vienne, A., Frings, P., Poblador, S., Steinwidder, L., Rijnders, J., Schoelynck, J., Vindušková, O., Vicca, S., 2023. Soil Carbon Sequestration and the Role of Earthworms in an Enhanced Weathering Mesocosm Experiment. https://doi.org/10.2139/ssrn.4449286

Wang, Y., McDonald, E., Amundson, R., McFadden, L., Chadwick, O., 1996. An isotopic study of soils in chronological sequences of alluvial deposits, Providence Mountains, California. GSA Bull. 108, 379–391. https://doi.org/10.1130/0016-7606(1996)108<0379:AISOSI>2.3.CO;2

Watts, N.L., 1980. Quaternary pedogenic calcretes from the Kalahari (southern Africa): mineralogy, genesis and diagenesis. Sedimentology 27, 661–686. https://doi.org/10.1111/j.1365-3091.1980.tb01654.x

Weihermüller, L., Siemens, J., Deurer, M., Knoblauch, S., Rupp, H., Göttlein, A., Pütz, T., 2007. In Situ Soil Water Extraction: A Review. J. Environ. Qual. 36, 1735–1748. https://doi.org/10.2134/jeq2007.0218

Weil, R., Brady, N., 2016. The Nature and Properties of Soils, 15th ed. Pearson.

Wen, H., Sullivan, P.L., Billings, S.A., Ajami, H., Cueva, A., Flores, A., Hirmas, D.R., Koop, A.N., Murenbeeld, K., Zhang, X., Li, L., 2022. From Soils to Streams: Connecting Terrestrial Carbon Transformation, Chemical Weathering, and Solute Export Across Hydrological Regimes. Water Resour. Res. 58, e2022WR032314. https://doi.org/10.1029/2022WR032314

West, T.O., McBride, A.C., 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. Agric. Ecosyst. Environ. 108, 145–154. https://doi.org/10.1016/j.agee.2005.01.002

White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? Chem. Geol., Controls on Chemical Weathering 202, 479–506. https://doi.org/10.1016/j.chemgeo.2003.03.001

White, A.F., Brantley, S.L. (Eds.), 1995. Chemical Weathering Rates of Silicate Minerals, Reviews in Mineralogy & Geochemistry. De Gruyter. https://doi.org/10.1515/9781501509650

Wilson, C.G., Abban, B., Keefer, L.L., Wacha, K., Dermisis, D., Giannopoulos, C., Zhou, S., Goodwell, A.E., Woo, D.K., Yan, Q., Ghadiri, M., Stumpf, A., Pitcel, M., Lin, Y.-F., Marini, L., Storsved, B., Goff, K., Vogelgsang, J., Dere, A., Schilling, K.E., Muste, M., Blair, N.E., Rhoads, B., Bettis, A., Pai, H., Kratt, C., Sladek, C., Wing, M., Selker, J., Tyler, S., Lin, H., Kumar, P., Papanicolaou, A.N., 2018. The Intensively Managed Landscape Critical Zone Observatory: A Scientific Testbed for Understanding Critical Zone Processes in Agroecosystems. Vadose Zone J. 17, 1–21. https://doi.org/10.2136/vzj2018.04.0088

Wilson, M.J., 1999. The origin and formation of clay minerals in soils: past, present and future perspectives. Clay Miner. 34, 7–25. https://doi.org/10.1180/000985599545957

Wilson, S., Dipple, G.M., Power, I.M., Thom, J.M., Anderson, R.G., Raudsepp, M., Gabites, J.E., Southam, G., 2009. Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada. Econ. Geol. 104, 95–112. https://doi.org/10.2113/gsecongeo.104.1.95

Wilson, S., Harrison, A.L., Dipple, G.M., Power, I.M., Barker, S.L.L., Ulrich Mayer, K., Fallon, S.J., Raudsepp, M., Southam, G., 2014. Offsetting of CO2 emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining. Int. J. Greenh. Gas Control 25, 121–140. https://doi.org/10.1016/j.ijggc.2014.04.002

Wimpenny, J., Colla, C.A., Yin, Q.-Z., Rustad, J.R., Casey, W.H., 2014. Investigating the behaviour of Mg isotopes during the formation of clay minerals. Geochim. Cosmochim. Acta 128, 178–194. https://doi.org/10.1016/j.gca.2013.12.012

Winnick, M.J., Carroll, R.W.H., Williams, K.H., Maxwell, R.M., Dong, W., Maher, K., 2017. Snowmelt controls on concentration-discharge relationships and the balance of oxidative and acid-base weathering fluxes in an alpine catchment, East River, Colorado. Water Resour. Res. 53, 2507–2523. https://doi.org/10.1002/2016WR019724

Winter, T., Harvey, J., Franke, L., Alley, W., 1998. Ground Water and Surface Water: A Single Resource (No. USGS Circular 1139). US Geological Survey.

Wolf, A., Chang, E., Tank, A., 2022. Verification methods and agronomic enhancements for carbon removal based on enhanced weathering. US 11,644,454 B2.

Wolf-Gladrow, D.A., Zeebe, R.E., Klaas, C., Körtzinger, A., Dickson, A.G., 2007. Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Mar. Chem., Special issue: Dedicated to the memory of Professor Roland Wollast 106, 287–300. https://doi.org/10.1016/j.marchem.2007.01.006

Wood, C., Harrison, A.L., Power, I.M., 2023. Impacts of dissolved phosphorus and soil-mineral-fluid interactions on CO2 removal through enhanced weathering of wollastonite in soils. Appl. Geochem. 148, 105511. https://doi.org/10.1016/j.apgeochem.2022.105511

Wood, W.W., Hyndman, D.W., 2017. Groundwater Depletion: A Significant Unreported Source of Atmospheric Carbon Dioxide. Earths Future 5, 1133–1135. https://doi.org/10.1002/2017EF000586

Wu, L., Min, L., Liu, M., Zhang, Y., Pei, H., Li, H., Zhang, G., Wang, S., Shen, Y., 2023. Monitoring of Thick Vadose Zone Water Dynamics Under Irrigation Using a 48 m Deep Caisson at the Luancheng Critical Zone Observatory. Water Resour. Res. 59, e2022WR032965. https://doi.org/10.1029/2022WR032965

Wyatt, K., Stevenson, R., 2010. Effects of Acidification and Alkalinization on a Periphytic Algal Community in an Alaskan Wetland. Wetlands 30, 1193–1202. https://doi.org/10.1007/s13157-010-0101-3

Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth-Sci. Rev. 157, 1–17. https://doi.org/10.1016/j.earscirev.2016.03.003

Zavadlav, S., Rožič, B., Dolenec, M., Lojen, S., 2017. Stable isotopic and elemental characteristics of recent tufa from a karstic Krka River (south-east Slovenia): useful environmental proxies? Sedimentology 64, 808–831. https://doi.org/10.1111/sed.12328

Zeebe, R.E., Wolf-Gladrow, D.A., 2001. CO2 in seawater: Equilibrium, kinetics, isotopes. Elsevier.

Zhang, H.-M., Liang, Z., Li, Y., Chen, Z.-X., Zhang, J.-B., Cai, Z.-C., Elsgaard, L., Cheng, Y., Jan Van Groenigen, K., Abalos, D., 2022. Liming modifies greenhouse gas fluxes from soils: A meta-analysis of biological drivers. Agric. Ecosyst. Environ. 340, 108182. https://doi.org/10.1016/j.agee.2022.108182

Zhang, L., Xue, Z.G., 2022. A Numerical reassessment of the Gulf of Mexico carbon system in connection with the Mississippi River and global ocean. Biogeosciences 19, 4589–4618. https://doi.org/10.5194/bg-19-4589-2022

Zhang, S., Planavsky, N.J., Katchinoff, J., Raymond, P.A., Kanzaki, Y., Reershemius, T., Reinhard, C.T., 2022. River chemistry constraints on the carbon capture potential of surficial enhanced rock weathering. Limnol. Oceanogr. 67. https://doi.org/10.1002/lno.12244

Zhang, S., Reinhard, C.T., Liu, S., Kanzaki, Y., Planavsky, N.J., 2024. Constraining carbon loss from rivers following terrestrial enhanced rock weathering. https://doi.org/10.22541/essoar.171052489.97497425/v1

Zhang, X., Wang, W., 2015. The decomposition of fine and coarse roots: their global patterns and controlling factors. Sci. Rep. 5, 9940. https://doi.org/10.1038/srep09940

Zhou, X., Liu, D., Bu, H., Deng, L., Liu, H., Yuan, P., Du, P., Song, H., 2018. XRD-based quantitative analysis of clay minerals using reference intensity ratios, mineral intensity factors, Rietveld, and full pattern summation methods: A critical review. Solid Earth Sci. 3, 16–29. https://doi.org/10.1016/j.sesci.2017.12.002

Zhou, Y., Li, W., 2011. A review of regional groundwater flow modeling. Geosci. Front. 2. https://doi.org/10.1016/j.gsf.2011.03.003

Zhou, Y., Sawyer, A.H., David, C.H., Famiglietti, J.S., 2019. Fresh Submarine Groundwater Discharge to the Near-Global Coast. Geophys. Res. Lett. 46, 5855–5863. https://doi.org/10.1029/2019GL082749

Zhu, C., AE, B., Veblen, D., 2004. Feldspar dissolution rates and clay precipitation in the Navajo aquifer at Black Mesa, Arizona, USA.

Ziveri, P., Gray, W.R., Anglada-Ortiz, G., Manno, C., Grelaud, M., Incarbona, A., Rae, J.W.B., Subhas, A.V., Pallacks, S., White, A., Adkins, J.F., Berelson, W., 2023. Pelagic calcium carbonate production and shallow dissolution in the North Pacific Ocean. Nat. Commun. 14, 805. https://doi.org/10.1038/s41467-023-36177-w