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Soil Calcimetry Dynamics to Resolve Weathering Flux in Wollastonite-Amended Croplands

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Abstract

Enhanced Rock Weathering (ERW) is a promising carbon dioxide removal (CDR) strategy that accelerates mineral dissolution, sequestering atmospheric CO₂ while improving soil health. This study builds on prior applications of soil calcimetry by investigating its ability to resolve short-term carbonate fluxes and rainfall-modulated weathering dynamics in wollastonite-amended croplands. Conducted over a single growing season (May–October 2024) in temperate row-crop fields near Port Colborne, Ontario—characterized by fibric mesisol soils (Histosols, FAO-WRB)—this study tests whether calcimetry can distinguish between dissolution and precipitation phases and serve as a proxy for weathering flux within the upper soil horizon, under the assumption that rapid pedogenic carbonate cycling dominates alkalinity retention in this soil–mineral system. Monthly measurements of soil pH (Milli-Q and CaCl₂) and calcium carbonate equivalent (CCE) were conducted across 10 plots, totaling 180 composite samples. Results show significant alkalinization ($p < 0.001$), with average pH increases of $\sim +1.0$ unit in both Milli-Q and CaCl₂ extracts over the timeline. In contrast, CCE values showed high spatiotemporal variability (-2.5 to $+6.4\%$) without consistent seasonal trends. The calcimetry-derived weathering proxy, $\log(\Sigma \Delta \text{CCE} / \Delta t)$, correlated positively with pH ($r = 0.652$), capturing net carbonate accumulation, while the kinetic dissolution rate model correlated strongly and negatively with pH ($r \approx -1$), reflecting acid-promoted dissolution. This divergence confirms that the two metrics capture complementary stages of the weathering–precipitation continuum. Rainfall strongly modulated short-term carbonate formation, with cumulative precipitation over the previous 7–10 days enhancing formation rates up to a saturation point (~ 30 mm), beyond which additional rainfall yielded diminishing returns. In contrast, dissolution fluxes remained largely independent of rainfall. These results highlight calcimetry as a direct, scalable, and dynamic tool not only for monitoring solid-phase carbonate formation, but also for inferring carbonate migration and dissolution dynamics. In systems dominated by rapid pedogenic carbonate cycling, this approach captures the majority of alkalinity fluxes, offering a conservative yet comprehensive proxy for CO₂ sequestration.

Keywords: soil inorganic carbon (SIC) dynamics; pedogenic carbonate formation; silicate mineral weathering; carbon sequestration; soil pH evolution; rainfall–soil carbon interactions; field-based soil monitoring; land-based climate regulation



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1. Introduction

The widespread implementation of atmospheric carbon dioxide removal (CDR) strategies, in conjunction with efforts to reduce emissions, will be crucial to mitigating future

climate change driven by human-caused CO₂ and other greenhouse gas emissions [1]. Enhanced Rock Weathering (ERW) is an emerging climate solution that provides the dual benefits of long-term atmospheric carbon dioxide (CO₂) removal and improved soil health [2–5]. This approach involves the application of finely ground silicate minerals, such as wollastonite, basalt or olivine, onto agricultural soils to accelerate natural weathering processes. Specifically, this strategy promotes the dissolution of silicate rocks, releasing base cations (e.g., Ca²⁺ and Mg²⁺) that react with CO₂ to form bicarbonate (HCO₃[−]) in soil solutions. These bicarbonate ions are eventually transported to groundwater and oceans, where the captured carbon can be stably stored over timescales exceeding 10,000 years. In parallel, this geochemical process enhances soil fertility and pH, offering co-benefits for crop production and ecosystem resilience [2,3,6].

Field trials play a pivotal role in advancing Enhanced Rock Weathering (ERW) from a promising theoretical approach to a scalable and credible carbon dioxide removal (CDR) strategy. While modeling studies have long highlighted ERW's potential for long-term CO₂ sequestration and agronomic benefits [6–9], empirical data from field experiments are essential to reduce uncertainties around mineral dissolution rates, bicarbonate formation, and carbon permanence under real-world conditions. Recent four-year field studies, such as those conducted in the U.S. Corn Belt, have demonstrated that ERW can sequester up to $10.5 \pm 3.8 \text{ t CO}_2 \text{ ha}^{-1}$ while simultaneously increasing crop yields by 12–16% [2]. In Brazil, a sugarcane field experiment conducted on acidic Oxisols in São Paulo State demonstrated measurable carbon dioxide removal alongside substantive improvements in soil parameters, including increased pH, enhanced cation exchange capacity, and elevated nutrient availability, after basalt application rates ranging from 10 to 100 t/ha in a commercial-scale randomized block design [10]. Similarly, in western Germany, pilot field trials led by Project Carbdown and companies like InPlanet (with headquarters in Brazil and Germany) and ZeroEx (based in Munich, Germany) have applied basalt and olivine-rich rock dust to agricultural fields, reporting improvements in soil fertility, microbial activity, and nutrient cycling under temperate conditions (Remineralize.org overview; ZeroEx pilot project). Such tangible outcomes provide critical evidence for policy makers, farmers, and project developers, reinforcing the environmental and economic viability of ERW.

Moreover, field trials are central to building robust monitoring, reporting, and verification (MRV) frameworks that underpin the integrity of ERW-based carbon credits [11–14]. As observed in recent industry-standard protocols, such as the Puro.earth methodology and isometric methodology, carbon removal credits are issued only after field-data measurements validate model predictions, including soil chemistry changes and carbon fluxes [15,16].

These large-scale field trials are generating critical real-world insights that help refine MRV frameworks by grounding carbon removal estimates in actual soil and crop data. However, to translate these valuable field signals into robust and trustworthy MRV systems, there is a pressing need for the development of methodologies or technologies that can capture and process this information in a way that is simple, practical, and cost-effective. Although some MRV protocols have historically excluded pedogenic carbonates from formal CO₂ removal accounting due to concerns about reversibility, recent field studies and methodological advances increasingly recognize their value as indicators of silicate weathering and alkalinity migration. In field settings where direct bicarbonate tracking is impractical, calcimetry offers a scalable alternative for capturing the transformation of inorganic carbon pools. Ideally, these tools should minimize uncertainty and signal distortion, enabling the clear and consistent integration of field-based evidence into formal carbon accounting protocols.

Traditional laboratory-based models, such as those by Palandri and Kharaka [17] and White and Brantley [18], often overestimate mineral weathering rates because they do not

fully account for the complexities of field conditions, such as soil heterogeneity, limited mineral–soil contact, fluctuating moisture regimes, irregular dissolutions, and the formation of passivation layers that inhibit reactivity. To bridge this gap, researchers are increasingly relying on direct field measurements to calibrate and validate MRV approaches, ensuring that reported carbon removals more accurately reflect in situ weathering dynamics under real agricultural settings.

A variety of field-based tools are now being tested to turn silicate-weathering reactions into verifiable carbon-removal numbers. Cation-flux tracking follows the release of divalent base cations (Ca^{2+} , Mg^{2+}) and, with simple charge–balance models, infers the stoichiometric uptake of CO_2 as bicarbonate [19,20]. Lysimeter and soil-column systems extend this idea by capturing leachate so that dissolved inorganic carbon (DIC), bicarbonate and accompanying cations can be measured directly, enabling full mass-balance estimates of carbon export to deeper soil or groundwater [21]. Isotopic tracing with $\delta^{13}\text{C}$ or radiocarbon (^{14}C) adds still finer attribution, distinguishing newly formed pedogenic carbonates from geogenic sources and thus identifying the carbon truly sequestered by enhanced weathering [22,23]. Although these approaches deliver rich mechanistic insight, they depend on specialized equipment, continuous solution sampling, or high-cost isotope analyses—constraints that hinder their use at the scale of commercial croplands.

Soil calcimetry offers a pragmatic alternative. By simply reacting a small soil subsample with hydrochloric acid and measuring the CO_2 evolved, calcimetry yields the soil-inorganic-carbon (SIC) pool directly. Repeated sampling through time and depth converts this pool into a carbonate-formation flux ($\Delta\text{SIC}/\Delta t$), which can be integrated into MRV frameworks with minimal analytical overhead [9,24]. The method requires only inexpensive glassware or a portable volumetric calcimeter, tolerates field-moist samples, and is fast enough to process dozens of replicates per day, attributes that make it cost-competitive with standard agronomic soil tests. Crucially, the carbonate signal it records integrates all upstream processes (dissolution, transport, precipitation) without the need to monitor each step individually. These advantages, i.e., the low capital cost, high throughput and direct quantification, of the sequestration product explain why calcimetry is increasingly favored for large-area trials and why it forms the methodological core of the present study.

Rainfall plays a dual role in enhanced weathering systems, acting both as a solvent that promotes mineral dissolution and as a transport agent that mobilizes weathering products such as Ca^{2+} and HCO_3^- [3,25]. While this dual function is well acknowledged in modeling and soil column experiments [26–28] empirical validation under agronomic field conditions remains limited. One minor yet important objective of this work is to evaluate how variations in rainfall, both in volume and timing, affect the carbonation signal observed through soil calcimetry. Since rainwater influences the kinetics of mineral weathering and the leaching of carbonate and bicarbonate species, it may either enhance or dilute the apparent accumulation of soil inorganic carbon (SIC) over time. By tracking calcimetry responses alongside precipitation events, this study aims to better understand how rainfall modulates the detectability and interpretation of ERW-induced carbonate formation in the field. In this study, we assume that in the fibric mesisol soils amended with wollastonite, direct export of bicarbonate is minimal due to the rapid precipitation of pedogenic carbonates. Consequently, the dominant alkalinity flux is expressed through the formation and re-dissolution of these carbonates, which calcimetry can detect. This conceptual model implies that calcimetry may capture a substantial portion of the total weathering flux, provided that sampling frequency is sufficient to resolve transient dissolution–precipitation events. This understanding is essential for refining MRV approaches and improving the reliability of CO_2 removal estimates under real agronomic conditions.

Considering these gaps, the overall objective of this study is to evaluate the use of soil calcimetry as a field-based method to estimate the total weathering flux in wollastonite-amended agricultural soils. This general aim is addressed through the following specific objectives:

- To assess whether calcimetry can simultaneously reflect pedogenic carbonate formation and calcium loss via leaching.
- To evaluate the robustness of calcimetry as a dynamic indicator of weathering flux under varying precipitation regimes, under the assumption that carbonate cycling dominates alkalinity retention in the studied system.
- To compare field-derived measurements with carbon removal estimates predicted by kinetic mineral dissolution models.
- To investigate how precipitation dynamics influence the effectiveness of Enhanced Rock Weathering (ERW) in raising soil pH and promoting inorganic carbon accumulation.

Based on these objectives, the central research question guiding this study is as follows: Can soil calcimetry be used as a reliable and field-operational method to quantify mineral weathering and carbon sequestration resulting from silicate mineral application in agricultural soils, particularly under variable rainfall conditions?

The core hypothesis of this work is that calcimetry, when applied at appropriate temporal and spatial resolution, can capture both carbonate formation and base cation loss in deeper soil layers, serving as a practical indicator of weathering intensity in ERW systems. It is further hypothesized that rainfall acts as a key modulator of the carbonation signal's strength and detectability, potentially enhancing or attenuating the response observed through calcimetry measurements. To test this hypothesis and address the research objectives outlined above, the following sections describe the study site, experimental setup, sampling strategy, and analytical methods employed to quantify soil inorganic carbon and related weathering indicators under field conditions.

2. Materials and Methods

2.1. Study Area Description, Soil Characteristics, and Wollastonite Application

Wollastonite (CaSiO_3), a calcium silicate mineral, was selected due to its favorable properties for enhanced rock weathering [7,29]. Its performance remains effective in environmental conditions less favorable to silicate weathering such as alkaline soils or cooler temperate climates characteristic of Southern Ontario, where several field trials have already demonstrated significant accumulation of soil inorganic carbon (SIC) following wollastonite amendment [7,29,30]. Previous studies in Ontario reported SIC accumulation rates of up to $2 \text{ t CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ [29]. Wollastonite has also been shown to enhance plant growth, particularly in legumes like soybean and alfalfa, by supplying bioavailable silicon and calcium while buffering soil acidity [7,30]. These co-benefits position wollastonite as a promising alternative to conventional liming agents, with the added advantage of transforming agricultural soils into carbon sinks.

The study area is in Port Colborne, Ontario, Canada, with a significant land use (72% of farmland area), with field crops such as corn, wheat, oats, barley, soybeans, and hay [31]. The region's climate is classified as humid continental (Köppen Dfa), characterized by warm summers and cold, snowy winters. According to Environment and Climate Change Canada (1981–2010 climate normal), the region experiences an average annual temperature of $\approx 9.2^\circ\text{C}$ and total precipitation of $\approx 985 \text{ mm}$. Monthly averages range from -3.7°C in January to 21.9°C in July, with precipitation relatively evenly distributed throughout the year (e.g., 82.2 mm in July and 90.4 mm in October) [32]. Soils in the area are predominantly reddish-hued lacustrine heavy clays with poor or imperfect drainage, situated in smooth basins to very gently sloping terrains. The Ap horizon, which was sampled in studies, is characterized by a sandy texture, neutral pH (~ 6.5), negligible soil organic carbon

(<0.1 wt.%), and poor drainage [31]. This combination of soil characteristics and climate conditions influences the agricultural practices in Port Colborne, with a focus on field crops that are well-suited to the region's environmental conditions [31].

The Ap horizon was selected for sampling to provide a baseline soil condition with naturally low soil organic carbon (SOC) and moderately elevated soil inorganic carbon (SIC). Unlike deeper layers such as the Ck horizon, the Ap horizon remains more active in terms of soil formation processes and may participate more dynamically in carbonate precipitation due to occasional exposure to root activity, seasonal moisture fluctuations, and limited but relevant biological influence [33]. This makes it a suitable target for studying mid-term carbonate accumulation from enhanced rock weathering.

Soils at the study site were characterized by laboratory analyses conducted by the Agriculture and Food Laboratory at the University of Guelph. The results identified the soils as heavy clays, with clay contents exceeding 50% in both composite samples (52.1% and 54.1% for Composite A and B, respectively), and low sand fractions (~15%). The pH of the soils ranged from 6.26 to 6.72 (SMP buffer method), indicating a neutral to slightly acidic environment favorable for wollastonite dissolution. These soils are consistent with lacustrine clay landscapes typical of poorly drained, low-slope regions of southern Ontario. Based on their fine texture, low organic matter, and compaction potential, a bulk density of approximately 1500 kg/m³ was assumed for subsequent calculations of weathering rates and carbonate formation potential.

The site comprises two adjacent soyabean agricultural fields designated as Farm 1 (location 1) and Farm 1 (location 2), each hosting six and four experimental plots (1–6 and 7–10, respectively). The soil used for this study was collected from May to October 2024 at a depth of 20 cm. Prior to sampling, the entire area received an application of regular crushed wollastonite (30 µm) at a rate of 2.908 metric tons per acre (7.186 tonnes/ha) on 29 April 2024, as part of an enhanced weathering strategy aimed at increasing soil inorganic carbon through silicate mineral amendment. Following application, the wollastonite was incorporated into the topsoil to a depth of approximately 0–20 cm using a disk plow, consistent with common liming practices in Ontario, to ensure effective contact between the mineral particles and the soil matrix.

These plots were laid out in a grid format, with spatial reference coordinates recorded using GPS for precise geolocation and replication. As shown in the aerial imagery and map overlay, Farm 1 (location 1) is situated in the northern field, while Farm 1 (location 2) occupies a more forest-adjacent southern area, which reflect differences in microclimate and soil conditions. This geographic setup facilitates comparative analysis of treatments across similar but distinct field environments (Figure 1).

2.2. Soil Sampling and Analysis

Soil sampling was conducted at 0–20 cm depth, corresponding to the Ap (plow) horizon in conventionally managed cropland. This depth was selected because it represents the zone of mechanical incorporation of wollastonite (disk plow incorporation to ~0–20 cm), as well as the rooting and fertilization zone where pH and nutrient dynamics most directly influence crop performance. It also encompasses the layer where early inorganic carbonate formation and bicarbonate generation occur following silicate application and rainfall. The 0–20 cm composite is consistent with standard agronomic monitoring protocols (e.g., USDA, FAO, and previous ERW field studies).

Approximately 500 g of soil was collected per sample and stored in labeled zip-lock plastic bags. Upon arrival at the laboratory, each sample was weighed, air-dried for 24 h at room temperature, and weighed again to determine gravimetric moisture content. Initial measurements included soil pH and electrical conductivity (EC), both assessed

using handheld meters. A subset of the first batch of samples was further subsampled for commercial laboratory analysis, which included pH buffering capacity and particle size distribution from composited samples. Subsequently, all samples underwent additional testing for pH and inorganic carbon content via calcimetry.

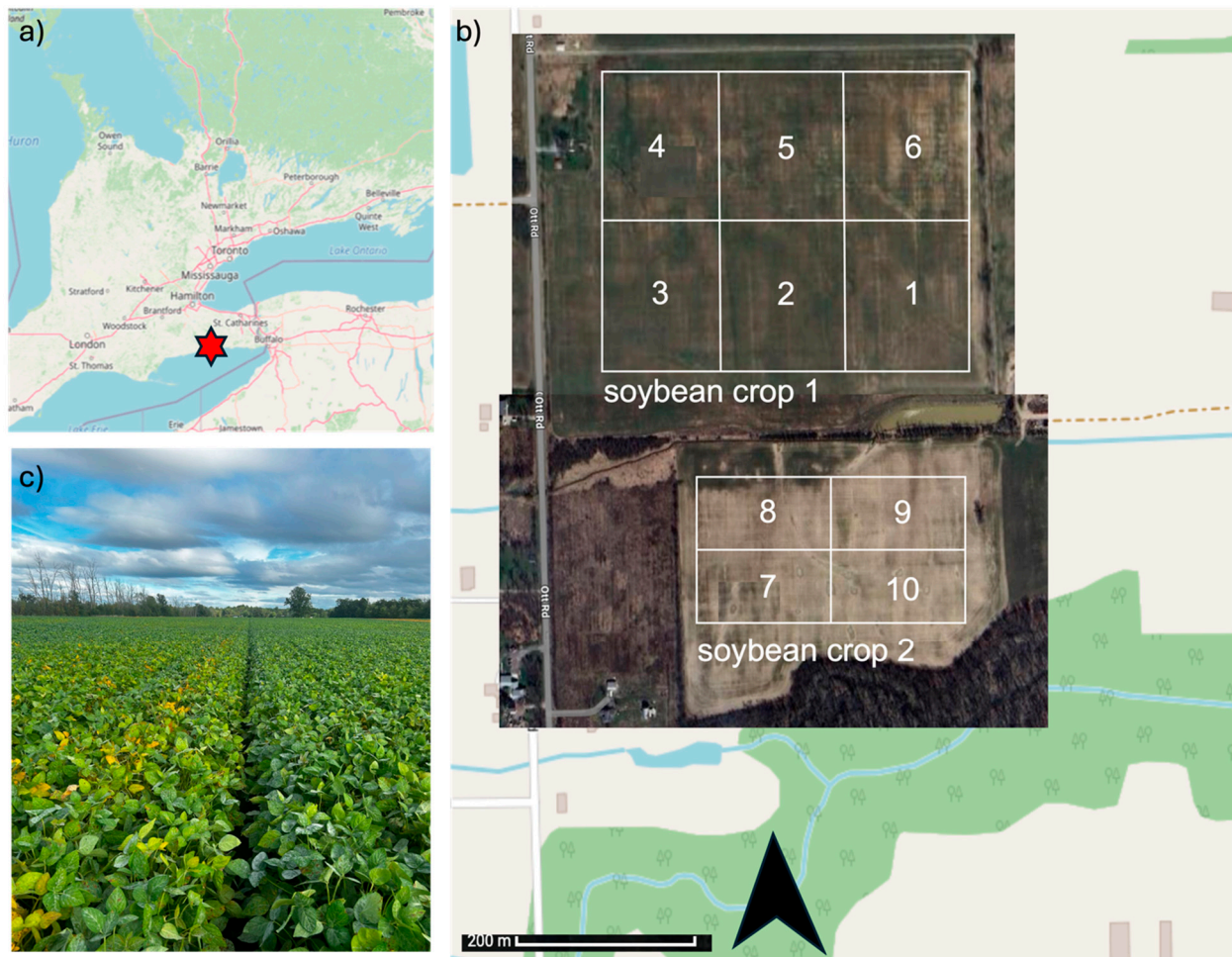


Figure 1. Location, layout, and field conditions of the Enhanced Rock Weathering (ERW) trial site in Port Colborne, Ontario. (a) Location of the field site (red star). (b) Aerial view, showing two soybean crops (crop 1: plots 1–6; crop 2: plots 7–10) with plot boundaries outlined. (c) Photograph of soybean growth during the trial period.

Soil pH was measured following the procedure outlined in ISO 10390:2005 [34]. Prior to measurement, air-dried soil samples were sieved to <2 mm. For each measurement, 10 g of sieved (mesh 10 or 2 mm) soil was weighed and placed into a 50 mL beaker. Two extraction methods were used: one with 25 mL of deionized Milli-Q water and another with 25 mL of 0.01 M CaCl_2 solution, both maintaining a 1:2.5 soil-to-solution ratio (mass: volume). The suspensions were stirred thoroughly and left to equilibrate for 30 min, with occasional agitation to ensure uniform mixing. After settling, pH was measured in the supernatant using a calibrated digital pH meter equipped with a glass electrode (Orion Star A329, Thermo-Fisher Scientific, Waltham, MA, USA). The meter was calibrated before each session using standard buffer solutions (pH 4.00, 7.00, and 10.00), and electrode performance was verified regularly. To minimize variability, all measurements were performed in triplicate, and the average value was reported for both water and CaCl_2 extractions.

For calcimetry, soil samples were prepared according to ISO 11465:1993 [35] (air-dried, sieved <2 mm). Triplicate subsamples (10 g) were suspended in 20 mL of deionized water

and reacted with 7 mL of 4 M HCl in a Royal Eijkelkamp carbonate content calcimeter for 5 min under constant agitation. The released CO₂ was quantified and expressed as calcium carbonate equivalent (CCE, %). Gravimetric water content was determined in accordance with ISO 11465:1993 [35]. Soil inorganic carbon (SIC) content, expressed as g CaCO₃ per kg of soil, was quantified using a volumetric calcimetry method with an Eijkelkamp calcimeter, based on ISO 10693:1995 [36]. In this procedure, 20 mL of Milli-Q water was first added to each soil sample in an Erlenmeyer flask. After sealing and agitation, 7 mL of 4 M HCl was introduced to initiate the reaction [37]. The CO₂ released was collected and its volume measured by observing the displacement of water in a connected graduated column, marked in 0.2 mL increments. The calculation of calcium carbonate equivalent $w(\text{CCE})$ of the sample followed the equation provided in the Eijkelkamp Calcimeter manual [17].

$$w(\text{CCE}) = 1000 \times \frac{m_2(v_1 - v_3)}{m_1(v_2 - v_3)} \times \frac{100 + w(\text{H}_2\text{O})}{100} \quad (1)$$

where $w(\text{CCE})$ = calcium carbonate equivalent content of the soil (g/kg); m_1 = the mass (g) of the test portion; m_2 = the mean mass (g) of the calcium carbonate standards; v_1 = the volume (mL) of carbon dioxide produced by the reaction of the test portion; v_2 = the mean volume (mL) of carbon dioxide produced by the calcium carbonate standards; v_3 = the volume changes (mL) in the blank determinations; $w(\text{H}_2\text{O})$ = the water content (wt. %) of the sample before drying.

All experimental analyses were performed in triplicate, and the results are reported as mean values with corresponding standard errors. To facilitate interpretation and comparison, the measured CCE values (expressed in g/kg) were also converted to total mass (CCE in grams) based on the actual soil mass used in each analysis. This adjustment helps account for potential dilution effects caused by the incorporation of mineral amendments. Additionally, a proportional average CCE (g/kg) was calculated for each amendment treatment by converting the total carbonate content back to a per-kilogram basis, considering only the soil fraction.

Then, weathering-fluxes are first derived from month-to-month changes in calcium-carbonate equivalent ($\Delta\text{CCE}/\Delta t$), expressed as g kg⁻¹ s⁻¹, and then normalized by soil bulk density and sampling depth to obtain a surface-area-based proxy (mol m⁻² s⁻¹) for silicate dissolution. These empirically measured fluxes are compared directly with theoretical dissolution rates predicted by the Palandri and Kharaka [38] kinetic model, revealing where laboratory rate laws tend to over- or underestimate in-field behavior. See Figure 2 for an overview of workflow. The outcomes are presented in Section 3 and further interpreted in Section 4.

2.3. Weathering Rate (Theoretical Approach)

To establish a baseline understanding of wollastonite weathering dynamics, we begin with estimating the weathering rates using a theoretical approach grounded in established geochemical kinetics developed by Palandri and Kharaka. This method provides an estimation of weathering rates based on mineral properties and reaction parameters. This theoretical framework provides a solid basis for interpreting empirical findings from calcimetry [17]. To begin, the logarithm of the Arrhenius pre-exponential factor at 25 °C (298.15 K) ($\log A$, in mol·m⁻²·s⁻¹) was obtained from Equation (2). Subsequently, the weathering rate was calculated using Equation (3), which incorporates both pH and temperature (fixed at 25 °C). For this calculation, we applied the coefficients K , E , and n , specific to the neutral pH range (~6–9), as provided by Palandri and Kharaka. We also followed the guidance of Haque et al. [7] for selecting an appropriate weathering mechanism applicable to mildly acidic conditions, situated between fully acidic and neutral regimes. In

this context, K represents the rate constant at 25 °C and $pH = 0$ ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), E is the Arrhenius activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), and n_{H^+} denotes the reaction order with respect to H^+ concentration.

$$\log A = \log K + \frac{E \times 1000}{2.3025 \times 8.314 \times 298.15} \quad (2)$$

$$\log W_r = \log A - \frac{E \times 1000}{2.3025 \times 8.314 \times T} - n_{H^+} \times pH \quad (3)$$

The equation for the theoretical model is given for (4):

$$\text{theoretical model l} = \log \left(\frac{SSA}{M \times \%purity} \times W_r \right) \quad (4)$$

To assess the applicability of this model under real field conditions, we developed an empirical proxy derived from calcimetry measurements, as detailed in Section 3.3. By comparing the model-derived W_r values with those calculated through changes in calcium carbonate content ($\Delta\text{CCE}/\Delta t$), we aim to evaluate the reliability of using calcimetry as a practical and field-accessible method to estimate silicate weathering rates in situ.

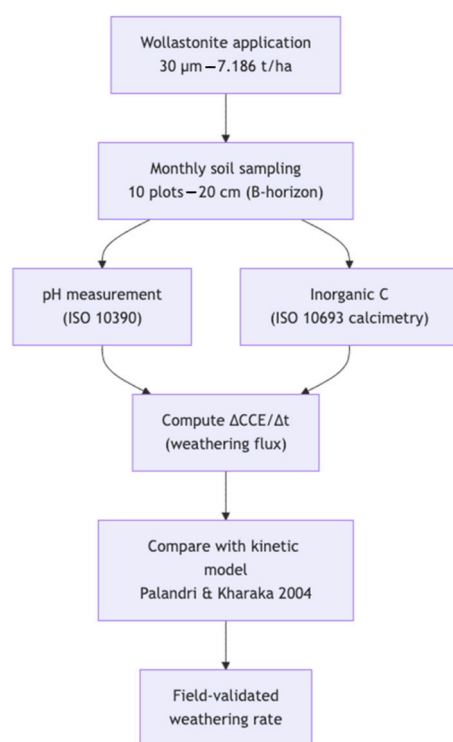


Figure 2. Workflow for field-scale validation of wollastonite-induced weathering rates [17]. ISO 10390:2005 [34]. ISO 10693:1995 [36].

2.4. Weathering Flux ($\Sigma\Delta\text{CCE}/\Delta t$)

The process for calculating $\Delta\text{CCE}/\Delta t$ involves determining the rate of accumulation in calcium carbonate content (g/kg) over time (flux) for each soil plot, serving as a proxy variable and the associated inorganic carbon sequestration. First, the differences in CCE between each pair of consecutive sampling dates (ΔCCE) were then calculated to capture the incremental change in carbon accumulation. Simultaneously, the time elapsed between sampling dates (Δt) was computed in seconds, allowing for high-resolution temporal comparisons. Finally, the rate of change in calcium carbonate accumulated was derived by dividing each ΔCCE by its corresponding Δt , yielding $\Delta\text{CCE}/\Delta t$ in units of $\text{g} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$. This approach quantifies the temporal dynamics of carbonate formation in the soil, enabling comparison of weathering activity across plots and over time. This flux ($\Delta\text{CCE}/\Delta t$) was

converted from $\text{g}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ to $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ using Equation (5), which accounts for soil bulk density (ρ_{soil}), sampling depth (d), wollastonite purity (m_{mineral}), molar mass (M_{mineral}) and specific surface area (SSA). This allows the proxy to reflect calcium release at the mineral–soil interface in standardized units for weathering rate comparisons.

$$\Sigma \frac{\Delta \text{CCE}}{\Delta t} (\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}) = \frac{\frac{\Delta [\text{CCE}]}{\Delta t} \left(\frac{\text{g}}{\text{kg}} \right) \times \rho_{\text{soil}} \times d}{M_{\text{mineral}} \times m_{\text{mineral}} \times \text{SSA}} \quad (5)$$

where $\Delta \text{CCE}/\Delta t$ is the temporal change accumulated in carbonate content ($\text{g CaCO}_3\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$), (ρ_{soil}), is the soil bulk density ($1500 \text{ kg}\cdot\text{m}^{-3}$), and d is the sampling depth (0.2 m). (M_{mineral}) refers to the applied wollastonite mass per surface area ($736.37 \text{ g}\cdot\text{m}^{-2}$), (m_{mineral}), refers to molar mass (g/mol), and SSA is the specific surface area considering cylinder format instead of sphere due his shaped form ($0.01146 \text{ m}^2\cdot\text{g}^{-1}$) [39].

For a complete description of the calculation steps, modeling parameters, and rainfall analysis procedures, see Supplementary Material Text S1. The resulting ($\Delta \text{CCE}/\Delta t$) values provide a normalized, surface-area-based estimate of silicate weathering dynamics under field conditions.

To capture short-term hydrological control on carbonate formation, we computed cumulative antecedent rainfall for the 7-, 10-, and 14-day windows preceding each sampling date. We initially explored 3–14-day accumulations, and the 7–14-day range consistently produced the strongest and most stable associations with the calcimetry-derived proxy flux ($\Sigma \Delta \text{CCE}/\Delta t$). This choice aligns with the well-established Antecedent Precipitation Index (API) framework used in hydrology and soil science, where cumulative rainfall over recent days is employed to represent antecedent soil moisture and infiltration dynamics when direct moisture data are unavailable.

Early work by Saxton and Lenz (1967) demonstrated that rainfall accumulated over previous days or weeks can effectively estimate soil wetness conditions [40]. Later, Xie et al. (2013) applied the API concept to assess soil water content in field conditions, confirming that short-term cumulative rainfall metrics capture antecedent soil moisture relevant to near-surface hydrological and biogeochemical responses [41]. Similarly, Li et al. (2021) showed that optimizing API window length enhances correlation with runoff and soil response variables, supporting the empirical range adopted here [42]. According to the American Meteorological Society (2024), API represents a weighted sum of rainfall over preceding days that characterizes soil wetness and its control on surface–subsurface processes [43].

Accordingly, the 7-, 10-, and 14-day windows were retained as parsimonious descriptors of recent hydrological forcing for use in correlation and stratification analyses with $\Delta \text{CCE}/\Delta t$. Cumulative rainfall (mm) was obtained from the nearest meteorological station [44].

2.5. The Role of the Rain

Rainfall plays a pivotal role in the enhanced rock weathering (ERW) process because it functions both as a catalyst for mineral dissolution and as a transport mechanism for dissolved products [45]. When rain infiltrates the soil, it facilitates the dissolution of silicate minerals by supplying water and protons (H^+), which are essential for the chemical breakdown of the mineral structure. This reaction releases base cations like Ca^{2+} and Mg^{2+} that subsequently bind with dissolved CO_2 to form bicarbonate ions (HCO_3^-), which can be leached into groundwater or eventually reach the oceans, where the carbon is stored for millennia [18]. The magnitude of this dissolution is influenced not just by total rainfall, but also by its timing and distribution, frequent light rains can sustain steady mineral–water contact, whereas prolonged dry spells followed by intense storms may lead to rapid but short-lived dissolution pulses [3,18,46].

Rainfall also drives the lateral and vertical movement of carbonate and bicarbonate species within the soil profile, affecting where and how carbonate precipitation occurs. Moderate, well-distributed rainfall can promote pedogenic carbonate formation in the rooting zone, enhancing in situ CO₂ sequestration. In contrast, heavy rainfall events may bypass this precipitation stage by flushing bicarbonate ions quickly through the profile before they can precipitate, effectively shifting the carbon storage pathway toward aquatic systems [3,29,33]. Studies such as Amann et al. [26] and Kelland et al. [27] have shown that cumulative rainfall in the preceding days or weeks can act as a strong predictor of bicarbonate flux in leachate, reinforcing the need to integrate precipitation patterns into ERW monitoring and verification protocols.

In carbonate weathering systems, cumulative precipitation over short preceding intervals (e.g., 7–10 days) can exert a saturating positive influence on mineral dissolution and carbonate formation. Deng et al. [3] observed diminishing marginal returns of weathering rates under high precipitation regimes, indicating that beyond a certain threshold, additional rainfall does not proportionally enhance dissolution. This saturation effect has been attributed to the finite availability of reactive mineral surfaces and to leaching losses that occur when infiltration exceeds the soil's water-holding capacity.

From an MRV perspective, understanding rainfall's dual role is essential for interpreting calcimetry data accurately. Without accounting for hydrological dynamics, weathering flux estimates could be misattributed to changes in mineral reactivity rather than to transient moisture conditions. Incorporating precipitation metrics into MRV models can improve the reliability of CO₂ removal estimates, especially in temperate agricultural systems where rainfall variability is high. This approach ensures that field-derived sequestration rates reflect both geochemical kinetics and the hydrological context that governs carbonate formation and transport.

3. Results and Discussions

3.1. pH and Calcimetry

The progressive increase in soil pH observed across both Milli-Q and CaCl₂ extracts during the soybean growing season indicates effective alkalization of the soil matrix following wollastonite application (see Figure 3 and Table 1). One-way ANOVA confirmed that these changes were statistically significant over time ($p < 0.001$), reinforcing the role of wollastonite in neutralizing soil acidity through silicate weathering reactions.

Table 1. Summary of average soil pH and calcium carbonate equivalent (CCE) over time and associated statistical tests.

Parameter	Mean $\pm$ SD	Min	Max	One-Way ANOVA (<i>p</i> -Value)	Pearson <i>r</i> (vs. CCE)	Pearson <i>p</i> -Value	Wilcoxon (May vs. Oct)
pH (Milli-Q)	6.169 $\pm$ 0.147	5.925	6.446	sig ($p < 0.001$)	0.420	sig ($p < 0.001$)	
pH (CaCl ₂)	5.726 $\pm$ 0.219	5.427	6.170	sig ($p < 0.001$)	0.470	sig ($p < 0.001$)	
CCE (g/kg)	1.321 $\pm$ 0.788	0.365	2.636	not sig ($p = 0.201$)			not sig ($p = 1$)

The pH increases coincided with the warmest months (Figure 4), when both temperature and biological activity reached their seasonal peaks [33,46]. In contrast, CCE values did not vary significantly over time (ANOVA $p = 0.201$; May vs. Oct Wilcoxon $p = 1.000$) and displayed high within-month dispersion, indicating heterogeneous carbonate distribution across plots. Overall, the data show that carbonate accumulation in the topsoil remained limited and spatially variable during the sampling period. Pearson correlation analysis between pH and CCE showed moderate but statistically significant relationships: for pH measured in CaCl₂, $r = 0.47$ ($p = 0.0001$), and for pH measured in Milli-Q, $r = 0.42$

($p = 0.0009$). These values indicate a consistent association between soil alkalization and inorganic carbon content, with variability attributable to plot-level differences.

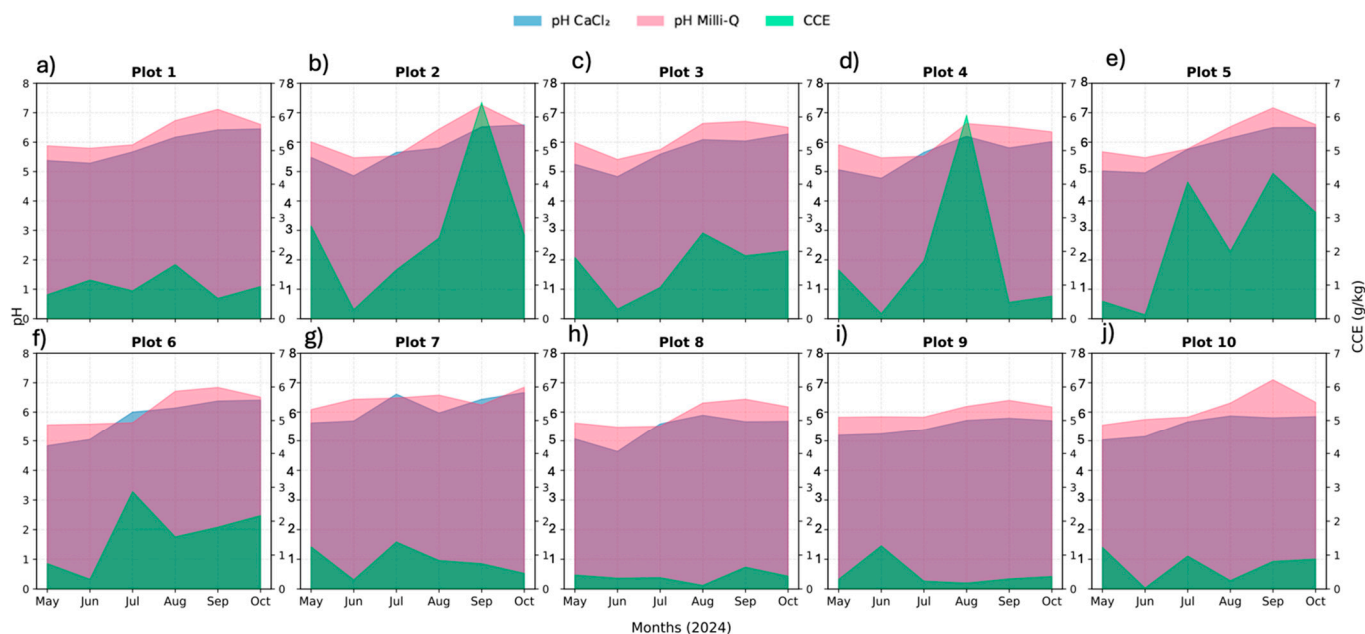


Figure 3. Seasonal pH and carbonate by plot (May–October 2024). The 10 panels show monthly data for each field plot (1–10), panels (a–j). Shaded pink areas are soil pH measured in Milli-Q water; shaded blue areas are pH in 0.01 M CaCl_2 (left y-axis, 0–8). Where they overlap, the hue appears purple. Shaded green areas show inorganic carbonate (CCE, g kg^{-1}) on the right y-axis (0–7). Months on the x-axis run from May to October.

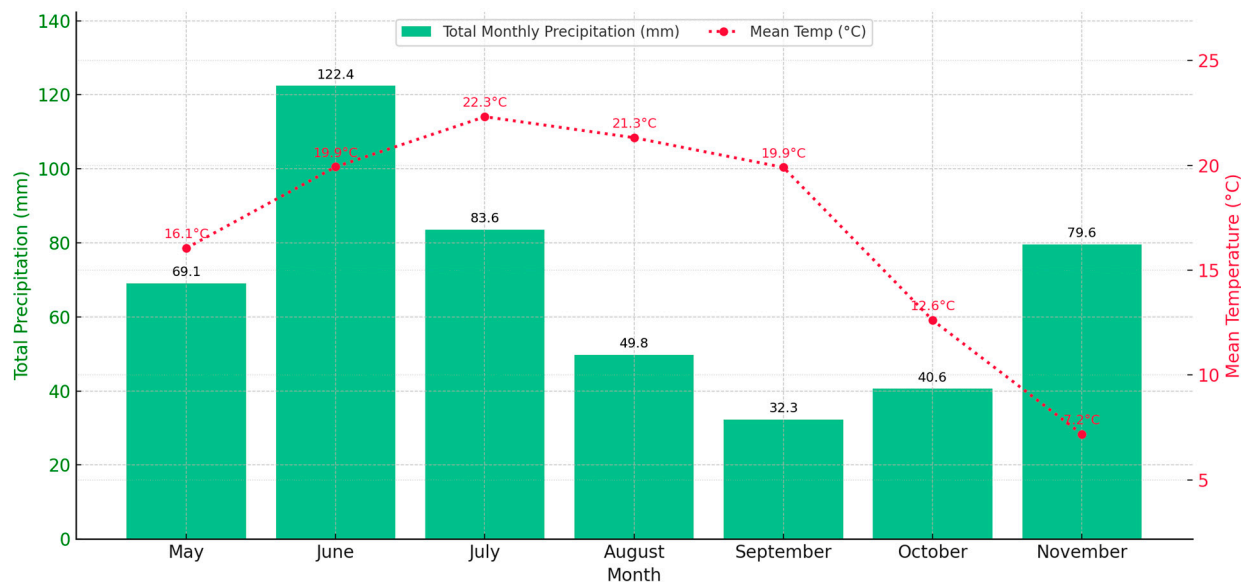


Figure 4. Monthly accumulated precipitation and mean air temperature in Port Colborne (Ontario, Canada) from May to November 2024. Total precipitation is represented by green bars (mm), and the red dotted line indicates monthly mean temperatures (°C). Data source: Environment and Climate Change Canada, Port Colborne (AUT) Station [11,12].

Collectively, the results confirm that wollastonite application increased soil pH and was associated with measurable but modest short-term carbonate accumulation. The spatial heterogeneity observed in CCE values aligns with field-scale variability commonly reported for agricultural soils, where differences in texture and moisture distribution influence carbonate occurrence.

Detailed plot-level data on soil pH (Milli-Q and CaCl_2) and calcium carbonate-equivalent (CCE) measurements from May to October 2024 are provided in the Supplementary Material (Tables S1–S3).

The two boxplots (Figure 5a,b) representing pH measured in MilliQ-water and in CaCl_2 from May to October together reveal a consistent trend of gradual alkalization across the monitored plots following wollastonite application. In both cases, the median pH values increase over time, indicating a cumulative response driven by progressive mineral weathering [7,29,33]. From May through July, both datasets show relatively stable behavior, with modest variability and fewer outliers. This early-phase uniformity reflects the initial buffering capacity of the soil or a lag in the weathering response. Several studies report a lag in alkalization after silicate amendment, due to soil buffering and delayed weathering responses. At Hubbard Brook, wollastonite-treated plots showed minimal pH or Ca change for years [47]. In rooftop and microplot trials, Haque et al. [7] found gradual pH increases despite initial buffering by organic matter and roots. Similar delays in pH rise have been observed in olivine- and basalt-amended mesocosms [26,27]. Silva et al. [24] observed that carbonate formation may remain below detection thresholds during the early stages of mineral. Additionally, Swoboda et al. [10] emphasized that weathering rates under field conditions are often initially limited by moisture availability and surface passivation, which can further contribute to slow early-phase geochemical responses.

However, From August onward, both CaCl_2 and Milli-Q datasets displayed greater dispersion, with the widest range in September [33]. We report this increase in variability without attributing a single mechanism; plot-level data are available in Tables S1–S3. Similar trends of early uniformity followed by increasing variance have been documented in field soils more broadly, where soil solution chemistry exhibits high spatial and temporal variability due to heterogeneous pore structure, moisture dynamics, and microbial community distribution [48,49]. Such heterogeneity means that even under the same treatment, different microsites within a field can respond differently over time.

The peak in September, especially prominent in the Milli-Q dataset, captures the highest pH values and the greatest variability, marking a dynamic phase in the system's evolution. By October, a slight decline or stabilization in pH points out the onset of a new equilibrium or a seasonal transition, as external drivers like temperature and biological activity begin to shift. Overall, the results reflect a soil system that evolves gradually under mineral amendment but becomes increasingly complex over time. This underscores the need for ongoing monitoring to better understand the temporal dynamics of alkalinity development and their potential agronomic or environmental implications.

The boxplot for inorganic carbonate content (CCE) from May to October (Figure 5c) displays a pattern marked by substantial variability across months, without a clear temporal trend. Such trends have been well documented in soil studies, where monthly sampling across field experiments showed significant temporal and spatial variability in inorganic carbon and soil solution chemistry [48,50]. Additionally, in ongoing ERW field trials in Malaysia, small plot-scale differences led to variable soil carbonate responses despite standardized treatments, highlighting how microsite conditions influence the consistency of weathering signals [51].

The monthly variation in CCE observed in this study, particularly the low and tightly clustered values in June contrasted with the higher median and broader spread in August, is consistent with findings in previous studies as reported by Cipolla et al. [18], who found that rainfall seasonality influenced carbonate fluxes, with wetter months yielding greater variability across sites. Field trials with kimberlite residues in Ontario also demonstrated significant microsite heterogeneity in dissolved inorganic carbon despite uniform application, attributed to localized differences in soil structure and moisture [52,53]. Furthermore,

broader studies on seasonal carbonate cycling, such as those by Kaufhold et al. [52] show substantial intra-seasonal variation in total alkalinity and dissolved carbon species linked to hydrologic pulses and microbial activity. Monthly CCE values lacked a consistent trend but showed broad dispersion, consistent with field observations of high spatial and temporal variance in inorganic carbon and soil solution chemistry.

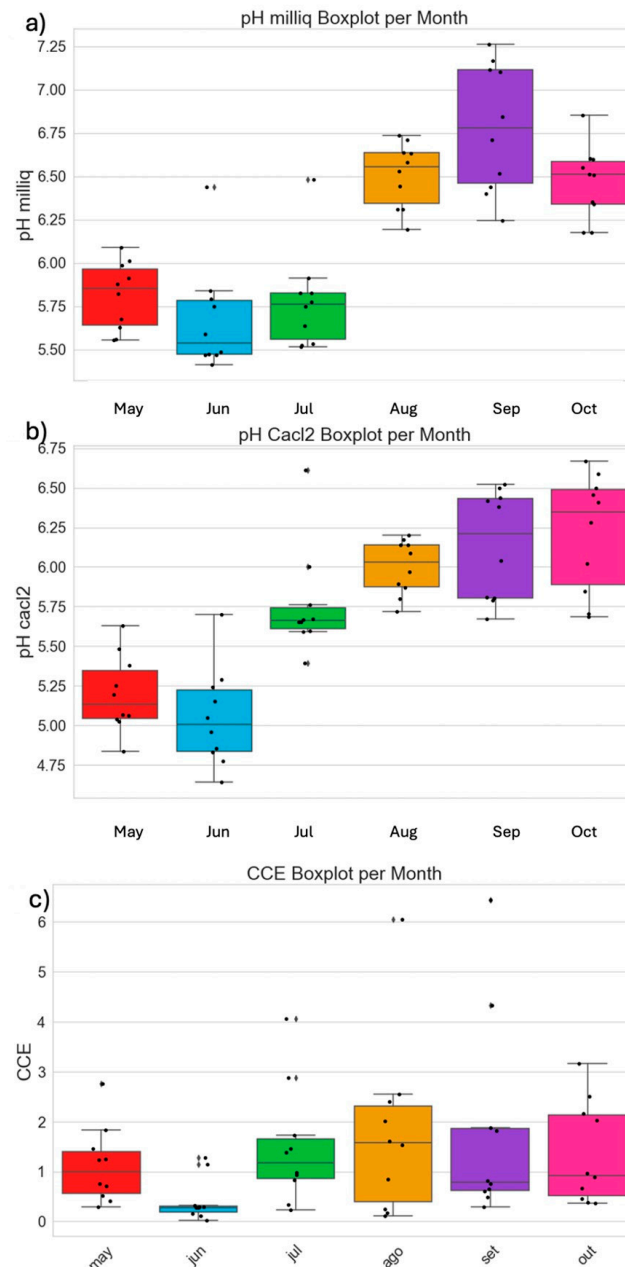


Figure 5. Monthly variation in soil pH (Milli-Q and CaCl_2 extractions) and inorganic carbonate content (CCE) across 10 field plots from May to October 2024. (a) Boxplot of soil pH measured in Milli-Q extracts; (b) Boxplot of soil pH measured in CaCl_2 extracts; (c) Boxplot of inorganic carbonate content (CCE, g kg^{-1}). Each color represents a different sampling month (May = red, June = blue, July = green, August = orange, September = purple, October = pink). Boxes show interquartile ranges (IQR), horizontal lines indicate medians, whiskers represent $1.5 \times \text{IQR}$, and dots represent outliers or individual observations.

Taken together, the three boxplots (pH in Milli-Q, pH in CaCl_2 , and CCE) reveal distinct yet interrelated trends that characterize the early-stage geochemical response to wollastonite amendment:

- pH in Milli-Q extracts showed a sharper and more variable increase over time, with a mid-season peak followed by stabilization. This dynamic pattern reflects evolving soil chemistry influenced by seasonal temperature changes, biological activity, and mineral dissolution.
- pH in CaCl_2 extracts exhibited a steady and more uniform rise throughout the season, indicating sustained alkalization of the soil matrix and a slower buffering effect in the exchangeable phase of the soil solution.
- CCE (inorganic carbonate content) displayed substantial spatial and temporal heterogeneity, without a clear seasonal trend. This highlights that carbonate accumulation is governed by microsite-specific factors such as moisture availability, root activity, and local soil structure, making it less predictable than pH response

3.2. Temporal Dynamics of Carbonate Accumulation and Weathering Fluxes

Table 2 shows the monthly variation in calcium carbonate equivalent (CCE), expressed as ΔCCE (change from the previous month), $|\Delta\text{CCE}|$ (absolute change), and $\Sigma |\Delta\text{CCE}|$ (absolute cumulative sum), for each of the 10 monitored plots. The columns labeled t_1 through t_5 correspond to five consecutive sampling intervals covering the 2024 growing season, from May to October. Each interval represents the time elapsed between two successive soil samplings (for example, t_1 refers to the change between May and June, t_2 between June and July, and so on). Positive ΔCCE values indicate a net increase in soil carbonate content during that interval, whereas negative values indicate a net decrease. Variability among plots represents the range of carbonate flux magnitudes observed under field conditions. The final column provides the duration of each interval (Δt) in seconds, used for flux calculations. In this scenario, we consider all monthly variations as positive by working with the absolute value of ΔCCE . This approach yielded the best regression performance and improved the correlation between measured carbonate accumulation and mineral weathering rates predicted by kinetic models (e.g., Palandri and Kharaka [39]). It is important to note that this use of absolute ΔCCE values reflects the intensity of carbonate transformation (both formation and loss) rather than net CO_2 sequestration. While carbonate dissolution may represent the remobilization of previously sequestered carbon, it does not imply a second sequestration event. Therefore, this approach does not double count CO_2 , but instead captures the dynamic turnover of inorganic carbon as a proxy for silicate weathering activity. The assumption underlying this approach is that in the studied soils, the majority of alkalinity generated by silicate dissolution is retained through rapid pedogenic carbonate formation, with negligible direct leaching of bicarbonate. Therefore, calcimetry captures the dominant flux pathway. If any bicarbonate is leached, it would represent additional CO_2 removal not accounted for in our measurements, implying that calcimetry provides a conservative estimate of total weathering flux rather than an overestimate. It is important to distinguish between carbonate transformation and carbon permanence. While calcimetry effectively captures the intensity and direction of inorganic carbon fluxes, it does not directly measure the long-term fate of sequestered CO_2 . Complementary methods such as isotopic tracing or leachate monitoring are needed to assess permanence.

We acknowledge that negative ΔCCE values may be interpreted as a loss of sequestered CO_2 . However, under field conditions, the dominant mechanism is not atmospheric degassing, but rather dissolution and downward migration of carbonate species. This interpretation is supported by column studies and reactive transport modeling, which show that carbonate phases can dissolve and migrate deeper into the soil profile, especially in clay-rich systems with imperfect drainage. Degassing would require a strong influx of acid or a significant drop in pH, which was not observed in our field data. Therefore,

while calcimetry cannot distinguish between dissolution and migration, the use of $|\Delta\text{CCE}|$ reflects the total transformation intensity of inorganic carbon, not net CO_2 re-release.

Table 2. Monthly changes in soil inorganic carbon (ΔCCE , g/kg) and cumulative sum over time across 10 field plots.

Plot	ΔCCE					$ \Delta\text{CCE} $					$\Sigma \Delta\text{CCE} $					Δt (s)
	t_1^*	t_2	t_3	t_4	t_5	t_1	t_2	t_3	t_4	t_5	t_1	t_2	t_3	t_4	t_5	
1	0.438	−0.321	0.782	−1.005	0.352	0.438	0.321	0.782	1.005	0.352	0.438	0.759	1.541	2.547	2.899	3,369,600
2	−2.491	1.184	0.949	4.030	−3.935	2.491	1.184	0.949	4.030	3.935	2.491	3.675	4.623	8.653	12.588	
3	−1.540	0.644	1.623	−0.677	0.144	1.540	0.644	1.623	0.677	0.144	1.540	2.184	3.807	4.484	4.628	2,505,600
4	−1.298	1.571	4.327	−5.564	0.185	1.298	1.571	4.327	5.564	0.185	1.298	2.869	7.196	12.760	12.945	
5	−0.403	3.950	−2.063	2.320	−1.161	0.403	3.950	2.063	2.320	1.161	0.403	4.353	6.415	8.735	9.896	2,937,600
6	−0.463	2.589	−1.338	0.287	0.342	0.463	2.589	1.338	0.287	0.342	0.463	3.052	4.389	4.676	5.018	
7	−0.974	1.118	−0.547	−0.093	−0.287	0.974	1.118	0.547	0.093	0.287	0.974	2.092	2.639	2.732	3.019	2,678,400
8	−0.093	0.016	−0.228	0.539	−0.267	0.093	0.016	0.228	0.539	0.267	0.093	0.109	0.338	0.876	1.143	
9	0.990	−1.042	−0.058	0.124	0.071	0.990	1.042	0.058	0.124	0.071	0.990	2.032	2.089	2.214	2.284	2,284
10	−1.202	0.946	−0.727	0.568	0.068	1.202	0.946	0.727	0.568	0.068	1.202	2.148	2.875	3.443	3.510	

* t_1 – t_5 denote consecutive sampling intervals across the 2024 growing season (e.g., May–June, June–July, etc.).

Table 3 presents the temporal flux of inorganic carbonate accumulation in soil, normalized by time (Δt) and surface area. The flux is expressed as $\Sigma\Delta\text{CCE}/\Delta t$ in both mass (g/kg/s) and molar ($\text{mol}/\text{m}^2/\text{s}$) units for each plot and time interval. These values serve as empirical proxies for carbonate formation in the field. Notably, higher fluxes indicate periods or locations with greater mineral reactivity, dissolution, or CO_2 sequestration rates, consistent with enhanced weathering activity. Data support subsequent modeling and comparison with kinetic rate laws.

Table 3. Surface-area-normalized weathering flux ($\Sigma\Delta\text{CCE}/\Delta t$).

Plot	$\Sigma \Delta\text{CCE}/\Delta t$ (g/kg/s)					$\Sigma \Delta\text{CCE}/\Delta t$ (mol/m ² /s)				
	t_1^*	t_2	t_3	t_4	t_5	t_1	t_2	t_3	t_4	t_5
1	1.30×10^{-7}	3.03×10^{-7}	4.96×10^{-7}	8.67×10^{-7}	1.08×10^{-6}	4.08×10^{-8}	9.51×10^{-8}	1.56×10^{-7}	2.72×10^{-7}	3.40×10^{-7}
2	7.39×10^{-7}	1.47×10^{-6}	1.49×10^{-6}	2.95×10^{-6}	4.70×10^{-6}	2.32×10^{-7}	4.60×10^{-7}	4.67×10^{-7}	9.25×10^{-7}	1.48×10^{-6}
3	4.57×10^{-7}	8.72×10^{-7}	1.22×10^{-6}	1.53×10^{-6}	1.73×10^{-6}	1.43×10^{-7}	2.74×10^{-7}	3.84×10^{-7}	4.79×10^{-7}	5.42×10^{-7}
4	3.85×10^{-7}	1.15×10^{-6}	2.31×10^{-6}	4.34×10^{-6}	4.83×10^{-6}	1.21×10^{-7}	3.59×10^{-7}	7.26×10^{-7}	1.36×10^{-6}	1.52×10^{-6}
5	1.19×10^{-7}	1.74×10^{-6}	2.06×10^{-6}	2.97×10^{-6}	3.69×10^{-6}	3.75×10^{-8}	5.45×10^{-7}	6.47×10^{-7}	9.33×10^{-7}	1.16×10^{-6}
6	1.37×10^{-7}	1.22×10^{-6}	1.41×10^{-6}	1.59×10^{-6}	1.87×10^{-6}	4.31×10^{-8}	3.82×10^{-7}	4.43×10^{-7}	5.00×10^{-7}	5.88×10^{-7}
7	2.89×10^{-7}	8.35×10^{-7}	8.48×10^{-7}	9.30×10^{-7}	1.13×10^{-6}	9.08×10^{-8}	2.62×10^{-7}	2.66×10^{-7}	2.92×10^{-7}	3.54×10^{-7}
8	2.77×10^{-8}	4.37×10^{-8}	1.09×10^{-7}	2.98×10^{-7}	4.27×10^{-7}	8.70×10^{-9}	1.37×10^{-8}	3.41×10^{-8}	9.37×10^{-8}	1.34×10^{-7}
9	2.94×10^{-7}	8.11×10^{-7}	6.72×10^{-7}	7.54×10^{-7}	8.53×10^{-7}	9.22×10^{-8}	2.55×10^{-7}	2.11×10^{-7}	2.37×10^{-7}	2.68×10^{-7}
10	3.57×10^{-7}	8.57×10^{-7}	9.24×10^{-7}	1.17×10^{-6}	1.31×10^{-6}	1.12×10^{-7}	2.69×10^{-7}	2.90×10^{-7}	3.68×10^{-7}	4.11×10^{-7}

* t_1 – t_5 denote consecutive sampling intervals across the 2024 growing season (e.g., May–June, June–July, etc.).

Note on weathering flux calculation: The empirical weathering rate in $\text{mol m}^{-2} \text{s}^{-1}$ was estimated using Equation (5), where SSA = specific surface area of wollastonite = $0.01146 \text{ m}^2/\text{g}$; $\text{Mass (wollastonite)}$ = applied mass per area = $718 \text{ g}/\text{m}^2$; $\rho(\text{soil})$ = soil bulk density = $1500 \text{ kg}/\text{m}^3$; Depth = soil sampling depth = 0.2 m , $M(\text{wollastonite})$ = molar mass of wollastonite = $116.15 \text{ g}/\text{mol}$; $\Delta[\text{CaCO}_3]/\Delta t$ = calcimetry-based carbonate accumulation rate in $\text{g}/\text{kg}/\text{s}$.

Table 4 shows the base-10 logarithm of empirical weathering flux values ($\Sigma\Delta\text{CCE}/\Delta t$), providing a normalized and scale-compressed view of temporal carbonate formation rates across plots. These values facilitate comparison with theoretical dissolution rate laws and enable improved statistical modeling of weathering kinetics under field conditions. Less negative values indicate higher weathering activity and potential CO_2 drawdown, while more negative values reflect lower carbonate accumulation or leaching-dominated phases.

Table 5 represents the dataset used to compare measured soil pH, the empirical weathering for the first three plots sampled in May; the full dataset for all plots is available in Table S4 (Supplementary Materials). Each row corresponds to an individual field sampling per plot and includes the following variables: the calculated weathering rate (WR) its logarithmic transformation ($\log\text{WR}$), the Arrhenius model parameters used (pre-exponential

factor A, activation energy E, and reaction order with respect to proton concentration nH), soil pH measured in 0.01 M CaCl₂, sampling date, and plot number. The final column contains $\log(\Sigma\Delta\text{CCE}/\Delta t)$, calculated from Table S4. This dataset forms the basis for the regressions and correlation analyses presented in the following tables, where we examine the relationship between soil pH and $\log(\Sigma\Delta\text{CCE}/\Delta t)$ and assess how well this proxy aligns with the theoretical logWR.

Table 4. Log-transformed surface-area-normalized weathering flux [$\log_{10}(\Sigma\Delta\text{CCE}/\Delta t)$] across five intervals.

Plot	$\log(\Sigma\Delta\text{CCE}/\Delta t)$				
	t_1^*	t_2	t_3	t_4	t_5
1	−7.390	−7.022	−6.808	−6.565	−6.469
2	−6.634	−6.337	−6.331	−6.034	−5.831
3	−6.843	−6.563	−6.415	−6.320	−6.266
4	−6.917	−6.444	−6.139	−5.865	−5.819
5	−7.426	−6.263	−6.189	−6.030	−5.936
6	−7.365	−6.418	−6.354	−6.301	−6.231
7	−7.042	−6.582	−6.575	−6.535	−6.451
8	−8.061	−7.863	−7.467	−7.028	−6.873
9	−7.035	−6.594	−6.676	−6.626	−6.572
10	−6.951	−6.570	−6.537	−6.434	−6.386

* t_1 – t_5 denote consecutive sampling intervals across the 2024 growing season (e.g., May–June, June–July, etc.).

Table 5. Dataset used to compare measured soil pH, the empirical weathering rate of wollastonite derived from Palandri and Kharaka’s kinetic model (log WR), and the proxy weathering rate measured via calcimetry ($\log(\Sigma\Delta\text{CCE}/\Delta t)$).

WR (mol/m ² /s)	Log WR	A (mol·m ^{−2} ·s ^{−1})	Log A	E kJ·mol ^{−1}	nH (Dimensionless)	pH	pH Date	Plot	Log K (mol·m ^{−2} ·s ^{−1})	T(K)	Log($\Sigma\Delta\text{CCE}/\Delta t$)
3.28×10^{-8}	−7.48	67.62	4.21	54.7	0.4	5.287	t_1	1	−5.37	298	−7.390
4.87×10^{-8}	−7.31	67.62	4.21	54.7	0.4	4.857	t_1	2	−5.37	298	−6.634
4.99×10^{-8}	−7.30	67.62	4.21	54.7	0.4	4.830	t_1	3	−5.37	298	−6.843

Table 6 summarizes the statistical relationships among modeled weathering rates (logWR), an empirical weathering proxy derived from soil calcimetry ($\log(\Sigma\Delta\text{CCE}/\Delta t)$), and measured soil pH. For each comparison, the table reports the Pearson’s r , Spearman’s ρ , and Kendall’s τ correlation coefficients, as well as the slope and R^2 of the linear regression.

Table 6. Statistical relationships among modeled weathering rates (log WR), an empirical weathering proxy derived from soil calcimetry ($\log(\Sigma\Delta\text{CCE}/\Delta t)$), and measured soil pH.

Comparison	Pearson’s r	Spearman ρ	Kendall’s τ (tau)	Regression Slope	R^2
$\log(\Sigma\Delta\text{CCE}/\Delta t)$ vs. pH	0.652	0.639	0.471	0.611	0.425
Log WR vs. pH	−0.9998	−1	−1	−0.4	0.9998
$\log(\Sigma\Delta\text{CCE}/\Delta t)$ vs. log WR	−0.651	−0.641	−0.473		

The results in Table 6 and Figure 6 show that the modeled weathering rate (log WR) has a strong negative correlation with pH ($r \approx -1$), consistent with the pH-dependent dissolution kinetics described by Palandri and Kharaka [17]. In comparison, the empirical weathering proxy obtained from soil calcimetry ($\log \Sigma\Delta\text{CCE}/\Delta t$) presents a moderate positive correlation with pH (Pearson’s $r = 0.652$), indicating that higher carbonate fluxes are measured under more alkaline conditions. These two indicators represent distinct yet complementary stages of the weathering–precipitation continuum: the kinetic model quantifies proton-driven dissolution of wollastonite, whereas the calcimetry-based proxy quantifies solid-phase carbonate accumulation resulting from Ca²⁺ release and subsequent carbonate precipitation. At higher pH, carbonate precipitation predominates, while at lower pH, dissolution dominates and carbonate retention decreases.

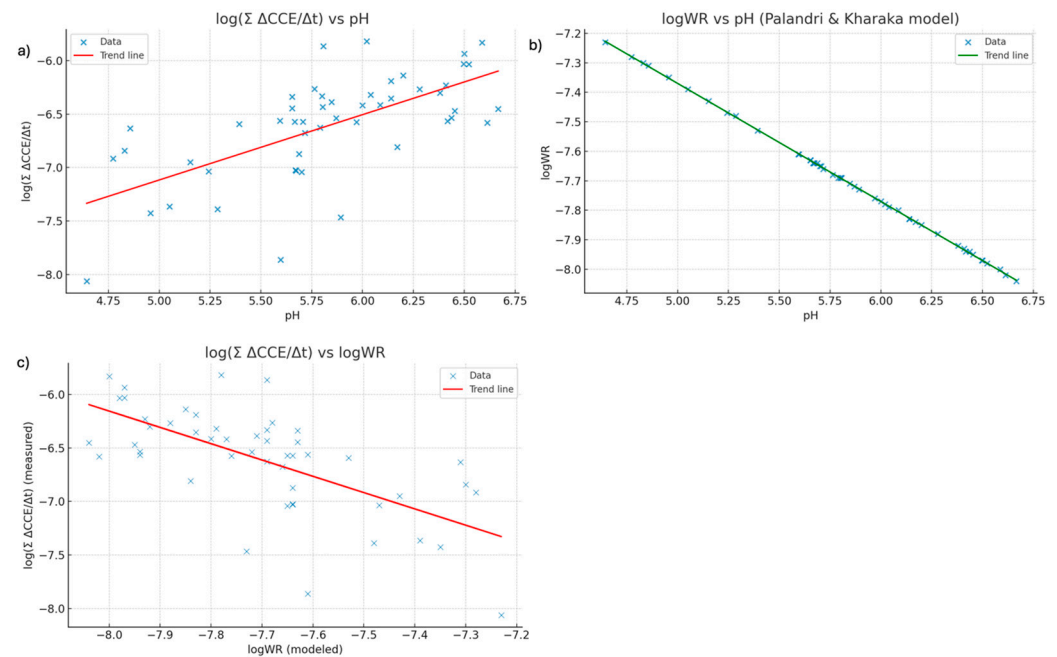


Figure 6. Relationships among modeled and measured weathering rates and soil pH. Panel (a) shows a linear regression between the empirical weathering proxy $\log(\Sigma \Delta CCE/\Delta t)$, derived from soil calcimetry, and measured pH. Panel (b) shows the modeled weathering rate ($\log WR$), based on Palandri and Kharaka [39], also regressed against pH. Panel (c) compares $\log(\Sigma \Delta CCE/\Delta t)$ with $\log WR$, revealing a moderate correlation between the two approaches, which reflects both their shared dependence on pH and methodological differences.

The application of absolute ΔCCE values emphasizes overall carbonate transformation intensity rather than net dissolution. In Figure 6c, the inverse relationship between $\log WR$ and $\log(\Sigma \Delta CCE/\Delta t)$ demonstrates that dissolution peaks and carbonate formation peaks do not occur simultaneously, reflecting differences in the controlling processes. Carbonate accumulation is influenced by saturation state, hydrological conditions, and pCO_2 , which together determine precipitation and re-dissolution dynamics. Sensitivity analyses performed with separated ΔCCE signs, standardized Δt intervals, and corrections for changes in reactive surface area confirmed the stability of these patterns. Both indicators should therefore be used jointly—rather than interchangeably—to represent dissolution and carbonate precipitation dynamics in MRV frameworks for Enhanced Rock Weathering.

Also, the distribution of points around the $x = y$ line in Figure 4 highlights that modeled dissolution rates ($\log WR$) and field-derived carbonate accumulation rates ($\log(\Sigma \Delta CCE/\Delta t)$) respond differently to environmental conditions. While the kinetic model is primarily driven by pH and temperature, the empirical proxy also integrates hydrological effects, carbonate saturation state, and potential losses through leaching or re-dissolution. This divergence means that neither metric can serve as a direct substitute for the other in MRV frameworks for Enhanced Rock Weathering. Instead, systematic offsets and deviations from the 1:1 line underscore the need to calibrate model predictions with field observations to capture the full range of processes influencing CO_2 drawdown.

The divergence between modeled and empirical rates reflects the contrasting processes they represent: $\log WR$ quantifies proton-driven dissolution, while $\log \Sigma \Delta CCE/\Delta t$ measures carbonate accumulation controlled by local saturation, pH, and hydrological conditions. Their moderate inverse correlation highlights that dissolution peaks and carbonate precipitation rarely coincide temporally in the field.

3.3. The Rain Effect

Table 7 presents log-transformed carbonate weathering fluxes, separated into dissolution ($(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$) and formation ($(\Delta\text{CCE}/\Delta t)_{\text{formation}}$) components, alongside cumulative precipitation in mm over the 7, 10, and 14 days prior to each sampling date for ten field plots monitored between June and October 2024. Fluxes were calculated by dividing the change in carbonate content (ΔCCE) between consecutive sampling dates by the number of days in the interval (Δt). Positive ΔCCE values were assigned to the formation column, while negative values were assigned to the dissolution column. This separation allows the dataset to distinguish between episodes of carbonate accumulation and carbonate loss. Zero values indicate no measurable flux in that direction for the given sampling interval. The data show that carbonate formation events are episodic and often coincide with periods of reduced dissolution, while dissolution peaks tend to occur independently of significant carbonate accumulation. Precipitation values vary considerably across sampling dates, with wetter periods (e.g., July) generally associated with higher carbonate flux magnitudes, indicating that short-term moisture availability may influence both dissolution and precipitation processes in the soil. The full dataset is available in Table S5 (Supplementary Materials).

Table 7. log-transformed carbonate weathering fluxes ($\log(\Delta\text{CCE}/\Delta t)$) for both dissolution and formation processes.

pH Date	plot	$\log(\Delta\text{CCE}/\Delta t)$ dissolution	$\log(\Delta\text{CCE}/\Delta t)$ formation	Precip_d7 (mm)	Precip_d10 (mm)	Precip_d14 (mm)
22 June 2024	9	0.000	−7.035	27.4	27.4	33
22 June 2024	10	−6.951	0	27.4	27.4	33
21 July 2024	1	−7.395	−6.829	36.6	36.6	80
21 July 2024	2	0.000	−7.093	36.6	36.6	80
21 July 2024	3	0.000	−6.706	36.6	36.6	80
30 October 2024	10	0.000	−8.100	0.9	3.9	3.9

The descriptive statistics for carbonate formation and dissolution fluxes (expressed as $\log(\Delta\text{CCE}/\Delta t)$) reveal a strongly skewed and truncated distribution (See Table 8). For both processes, the median is 0, indicating that in at least 50% of the observations, no detectable flux occurred in that direction. This signaling periods of carbon stability, where either no significant accumulation or loss of inorganic carbon was measured. The minimum values reach −8.235 for dissolution and −8.697 for formation, reflecting substantial fluxes when they do occur. However, the maximum value for both is 0, consistent with the mathematical transformation applied, where zero fluxes are retained and only positive $\Delta\text{CCE}/\Delta t$ values are log-transformed (resulting in negative log values). The means of −3.44 for dissolution and −3.74 for formation reflect the average magnitude of these processes, but the high standard deviations (both ~3.63–3.65) highlight significant variability across plots and sampling periods. This variability reflects micro-environmental differences (e.g., soil pH, moisture, mineral reactivity) and transient conditions such as rainfall. The absence of missing values (null = 0 for both variables) supports the reliability of subsequent correlation or regression analyses. Overall, these patterns suggest that carbonate dynamics in the field are intermittent, spatially variable, and possibly driven by short-term environmental fluctuations, particularly rainfall in the days preceding sampling.

The correlation analysis (Table 9) reveals a contrasting relationship between short-term rainfall and the direction of carbonate fluxes in soil. For carbonate formation ($\log(\Delta\text{CCE}/\Delta t)_{\text{formation}}$), results show a moderate to strong positive correlation with cumulative rainfall over the previous 7 and 10 days (Pearson's $r = 0.45$ – 0.46 ; Spearman's $\rho = 0.54$; Kendall's $\tau = 0.43$), indicating that increased precipitation promotes carbonate accumulation. This is attributed to enhanced mineral dissolution and ionic transport, which facilitate carbonate precipitation in wetter conditions. The correlation is slightly weaker for the 14-day window ($r = 0.34$), indicating that recent rainfall exerts a stronger influence on

carbonate formation than older precipitation events. In contrast, carbonate dissolution ($\log(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$) shows no meaningful correlation with rainfall at any time window, with Pearson's r values ranging from -0.11 to -0.05 and non-significant rank correlations. This is a signal of that dissolution may be governed by other localized factors, such as pH variability, microsite hydrology, or biological activity, rather than being directly driven by short-term moisture availability. Overall, these results highlight the asymmetry in weathering responses to rainfall: while formation of soil carbonates is sensitive to precipitation patterns, dissolution appears decoupled from them.

Table 8. Descriptive statistics show distinct patterns between carbonate dissolution and formation fluxes.

Statistic	$\log(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$	$\log(\Delta\text{CCE}/\Delta t)_{\text{formation}}$
Count	50	50
Mean	-3.437	-3.736
Std Dev	3.63	3.651
Min	-8.235	-8.697
25%	-7.024	-7.101
50%	0	-6.333
75%	0	0
Max	0	0
Nulls	0	0

Table 9. Pearson, Spearman, and Kendall correlation coefficients between cumulative rainfall (in the 7, 10, and 14 days prior to sampling) and log-transformed carbonate weathering fluxes.

Time Window (Days)	Variable	Pearson's r	Spearman's ρ	Kendall's τ
Precip_d7	$\log(\Delta\text{CCE}/\Delta t)_{\text{formation}}$	0.454	0.536	0.433
Precip_d7	$\log(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$	-0.108	-0.008	-0.008
Precip_d10	$\log(\Delta\text{CCE}/\Delta t)_{\text{formation}}$	0.461	0.536	0.433
Precip_d10	$\log(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$	-0.099	-0.008	-0.008
Precip_d14	$\log(\Delta\text{CCE}/\Delta t)_{\text{formation}}$	0.343	0.536	0.433
Precip_d14	$\log(\Delta\text{CCE}/\Delta t)_{\text{dissolution}}$	-0.052	-0.008	-0.008

These rainfall–flux relationships are consistent with the hydrologic logic of Antecedent Precipitation Indices (API), which quantify the influence of cumulative rainfall over prior days on soil moisture and near-surface reactivity. In this study, the 7–14-day rainfall windows captured the most relevant antecedent moisture dynamics governing carbonate formation, in agreement with well-established hydrologic applications of API models [40–43]. This reinforces that short-term cumulative precipitation effectively represents transient hydrological forcing on soil–CO₂–mineral interactions and carbonate precipitation under field conditions.

Across panels in Figure 7a–c, the red-median trend line climbs steadily from the driest bin (0–5 mm) to intermediate rain classes (≈ 25 –30 mm), showing that carbonate-formation flux increases as short-term rainfall rises. The effect is clearest in the 7- and 10-day windows, where the median flux strengthens by ~ 0.6 log units between the lowest and mid-rain bins. Beyond ~ 30 mm the curve flattens, indicating that once a threshold of soil moisture is reached additional rainfall adds little further benefit, perhaps because pores become saturated and diffusion-limited, or because leaching starts to remove $\text{Ca}^{2+}/\text{HCO}_3^-$ as fast as they are produced. Box widths narrow in the mid-rain classes (15–30 mm), indicating lower plot-to-plot variability under moderate, “just-right” moisture. Variability broadens again in the driest and wettest bins, implying that both water stress and water excess generate heterogeneous micro-environments in which some plots weather efficiently while others do not. A handful of low-flux outliers (< -8 log units) occur only at the rainfall extremes, reinforcing this interpretation. Comparing windows, the 7- and 10-day plots are almost identical, whereas the 14-day window dampens the slope and raises the inter-quartile ranges. This points to recent (1–10 day) rainfall as the dominant driver of carbonate formation, with older precipitation events contributing progressively less to the short-term weathering signal. In sum, the figure supports a “Balanced threshold” view of soil moisture for enhanced weathering: too little rain, and mineral surfaces remain dry; too much, and

carbonate gains are diluted or flushed. A running 7- to 10-day rainfall integral best captures the positive, yet saturating, response of carbonate formation flux to precipitation.

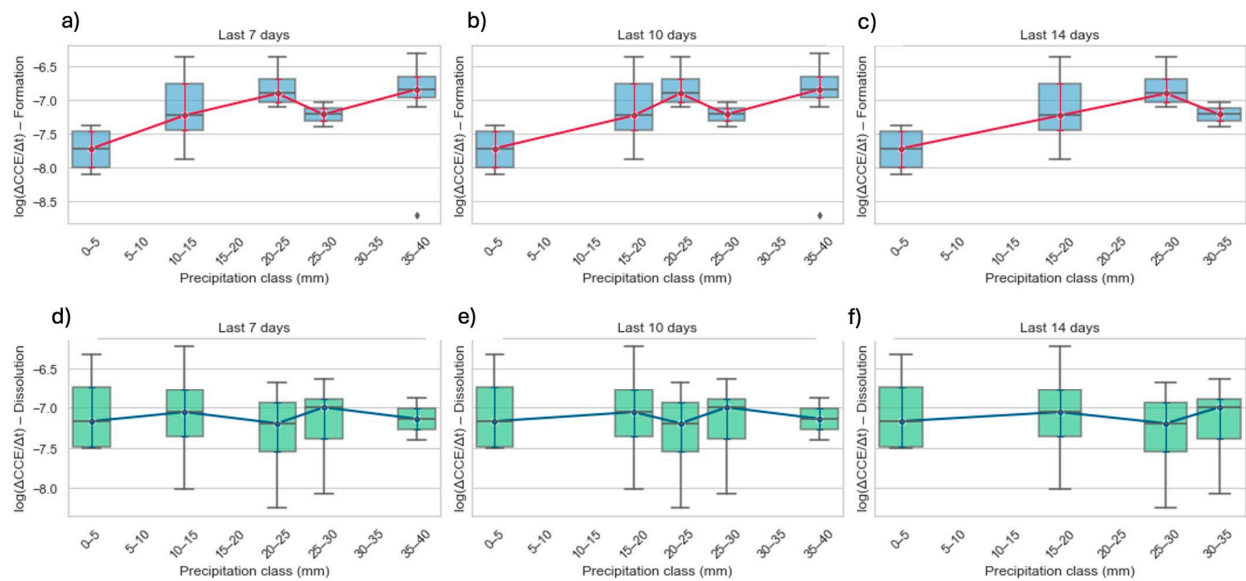


Figure 7. Effect of short-term rainfall on carbonate weathering fluxes. Boxplots (with median trend lines) show how carbonate formation (top row) and dissolution (bottom row) fluxes [$\log(\Delta\text{CCE}/\Delta t)$] vary across six precipitation classes (0–5, 5–10, 10–15, 15–20, 20–25, 25–30, and >30 mm) calculated for different antecedent rainfall windows. (a–c) Formation fluxes computed for the previous 7-, 10-, and 14-day periods, respectively (red median trend line); (d–f) Dissolution fluxes computed for the previous 7-, 10-, and 14-day periods, respectively (blue median trend line). Box colors indicate the analysis type: blue panels correspond to carbonate formation and green panels to carbonate dissolution. Boxes represent interquartile ranges (IQR), whiskers extend to $1.5 \times \text{IQR}$, central lines denote medians, and dots represent outliers.

In contrast, the accompanying boxplots for $\log(\Delta\text{CCE}/\Delta t)$ dissolution (Figure 7d–f) show a nearly flat median across all rain classes and time windows, with only a slight tendency toward less negative (i.e., weaker) dissolution at the highest rainfall bins. The wide, overlapping boxes and the rank-based correlations near zero confirm that short-term moisture is a poor predictor of carbonate loss. Instead, dissolution appears to be governed by plot-specific factors such as soil CO_2 build-up, redox pulses, or hydraulic flushing events that are not captured by simple rainfall totals. Although the net impact on weathering budgets is minor relative to formation, tracking this weak, decoupled signal is still useful for closing the mass balance and flagging occasional outliers where intense storms or waterlogged conditions may transiently remobilize previously sequestered carbonates.

While calcimetry does not directly measure leached bicarbonate, its ability to resolve solid-phase carbonate transformations provides a conservative proxy for alkalinity flux in systems where pedogenic carbonate cycling dominates. In such systems, the majority of alkalinity generated by silicate dissolution is retained through rapid precipitation of carbonates, which calcimetry captures. Therefore, leached bicarbonate would only represent a significant “missed” flux if precipitation of carbonates were suppressed. However, our data show that under higher rainfall, carbonate formation increases, suggesting that leaching losses are minimal during these periods. Conversely, negative ΔCCE values observed during drier intervals may reflect carbonate dissolution and potential leaching of bicarbonate, which calcimetry registers as a loss in solid-phase carbon. This pattern implies that dissolution and leaching may occur preferentially during low-rainfall periods, when silicate weathering is limited and soil solution alkalinity is insufficient to sustain carbonate precipitation. Thus, calcimetry may indirectly capture leaching-driven alkalinity export

through dissolution signals, even if it does not directly quantify dissolved bicarbonate. Compared to water sampling, which is logistically challenging in field soils due to spatial heterogeneity and transient hydrology, calcimetry offers a practical and scalable alternative for monitoring dominant weathering fluxes.

4. Conclusions

This study demonstrated that soil calcimetry can resolve short-term carbonate fluxes in wollastonite-amended croplands and capture rainfall-modulated weathering dynamics under real field conditions. Over a single growing season (May–October 2024), wollastonite application significantly increased soil pH by $\sim +1.0$ unit in both Milli-Q and CaCl_2 extracts ($p < 0.001$), confirming effective alkalization through silicate weathering. In contrast, calcium carbonate equivalent (CCE) values exhibited high spatial and temporal variability, reflecting heterogeneous carbonate formation and redistribution within the soil profile.

The calcimetry-derived proxy ($\log \Sigma \Delta \text{CCE} / \Delta t$) correlated positively with pH and therefore captured net carbonate accumulation, whereas the kinetic dissolution model ($\log \text{WR}$) correlated negatively with pH, consistent with acid-promoted dissolution kinetics. These contrasting relationships confirm that both metrics represent complementary phases of the weathering–precipitation continuum. Calcimetry does not directly quantify the total weathering flux—since it excludes leached bicarbonate—but in systems where rapid pedogenic carbonate formation dominates, it may approximate the total flux. In such cases, calcimetry captures the dynamic transformation of alkalinity through precipitation and re-dissolution, offering a conservative and field-accessible proxy for CO_2 removal. When combined, modeled and field-measured indicators provide a more comprehensive and realistic picture of silicate weathering intensity and carbonate storage under field conditions.

Rainfall acted as a short-term modulator of carbonate formation, with cumulative precipitation over the preceding 7–10 days exerting a positive but saturating influence, while dissolution remained largely decoupled. These dynamics indicate that soil moisture, rather than total rainfall, governs the transient balance between dissolution, transport, and carbonate precipitation.

The main limitations of this study include its single-season duration, shallow (0–20 cm) sampling depth, and the use of absolute ΔCCE values, which emphasize transformation intensity but not the net CO_2 balance. Moreover, while calcimetry captured short-term carbonate accumulation, it does not resolve the long-term stability of these phases. The durability of ERW-derived carbonates remains uncertain due to potential leaching, dissolution, or transformation processes, and future work should evaluate their persistence to assess the sustainability of ERW as a carbon sequestration pathway.

In addition, extending sampling beyond the 0–20 cm Ap horizon will be essential to determine whether part of the weathering signal is vertically redistributed, particularly in heavy clay soils with imperfect drainage. Deeper profiles and leachate monitoring will help quantify downward transport of Ca-HCO_3 and close the vertical carbon balance.

Future studies should also extend monitoring over multiple years and soil depths, incorporate hydrological and isotopic tracers, and quantify the leached bicarbonate fraction to close the carbon balance. While the single-season, monthly-resolution dataset captured meaningful short-term carbonate fluxes, future multi-year and high-frequency sampling—particularly following major rainfall events—will be essential to resolve transient dissolution–precipitation cycles and evaluate long-term carbonate stability under field conditions.

Overall, calcimetry represents a practical, low-cost, and field-deployable tool for quantifying solid-phase carbonate formation in Enhanced Rock Weathering (ERW) systems. When coupled with complementary hydrological and geochemical measurements, it can

serve as a robust component of MRV frameworks—linking kinetic predictions with real-world soil and climatic conditions in temperate agroecosystems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/land14102079/s1>, Table S1. Temporal evolution of pH (Milli-Q) across 10 field plots (May–October 2024). Table S2. Temporal evolution of pH (0.01 M CaCl₂) across 10 field plots (May–October 2024). Table S3. Inorganic carbonate content (CCE, g/kg) across 10 field plots (May–October 2024). Table S5. Log-transformed carbonate fluxes and recent rainfall (full dataset provided as CSV). Text S1. Procedure for calculation, modeling, and rainfall analysis. Table S1. Temporal evolution of pH (Milli-Q) across 10 field plots (May–October 2024). Table S2. Temporal evolution of pH (0.01 M CaCl₂) across 10 field plots (May–October 2024). Table S3. Inorganic carbonate content (CCE, g/kg) across 10 field plots (May–October 2024). Table S5. Log-transformed carbonate weathering fluxes (formation/dissolution) and short-term rainfall. Text S1. Procedure for Calculation, Modeling, and Rainfall Effect Analysis.

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References

1. Intergovernmental Panel on Climate Change (Ipcc). Climate Change 2021—The Physical Science Basis. In *Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, 1st ed.; Cambridge University Press: Cambridge, UK, 2023; ISBN 978-1-009-15789-6.
2. Beerling, D.J.; Epihov, D.Z.; Kantola, I.B.; Masters, M.D.; Reershemius, T.; Planavsky, N.J.; Reinhard, C.T.; Jordan, J.S.; Thorne, S.J.; Weber, J.; et al. Enhanced Weathering in the US Corn Belt Delivers Carbon Removal with Agronomic Benefits. *Proc. Natl. Acad. Sci. USA* **2024**, *121*, e2319436121. [[CrossRef](#)]
3. Deng, H.; Sonnenthal, E.; Arora, B.; Breunig, H.; Brodie, E.; Kleber, M.; Spycher, N.; Nico, P. The Environmental Controls on Efficiency of Enhanced Rock Weathering in Soils. *Sci. Rep.* **2023**, *13*, 9765. [[CrossRef](#)] [[PubMed](#)]
4. Ten Berge, H.F.M.; Van Der Meer, H.G.; Steenhuizen, J.W.; Goedhart, P.W.; Knops, P.; Verhagen, J. Olivine Weathering in Soil, and Its Effects on Growth and Nutrient Uptake in Ryegrass (*Lolium perenne* L.): A Pot Experiment. *PLoS ONE* **2012**, *7*, e42098. [[CrossRef](#)] [[PubMed](#)]
5. Hartmann, J.; West, A.J.; Renforth, P.; Köhler, P.; De La Rocha, C.L.; Wolf-Gladrow, D.A.; Dürr, H.H.; Scheffran, J. Enhanced Chemical Weathering as a Geoengineering Strategy to Reduce Atmospheric Carbon Dioxide, Supply Nutrients, and Mitigate Ocean Acidification. *Rev. Geophys.* **2013**, *51*, 113–149. [[CrossRef](#)]
6. Taylor, L.L.; Quirk, J.; Thorley, R.M.S.; Kharecha, P.A.; Hansen, J.; Ridgwell, A.; Lomas, M.R.; Banwart, S.A.; Beerling, D.J. Enhanced Weathering Strategies for Stabilizing Climate and Averting Ocean Acidification. *Nat. Clim. Change* **2016**, *6*, 402–406. [[CrossRef](#)]
7. Haque, F.; Santos, R.M.; Chiang, Y.W. Optimizing Inorganic Carbon Sequestration and Crop Yield with Wollastonite Soil Amendment in a Microplot Study. *Front. Plant Sci.* **2020**, *11*, 1012. [[CrossRef](#)]
8. Su, C.; Kang, R.; Huang, W.; Wang, A.; Li, X.; Huang, K.; Zhou, Q.; Fang, Y. CO₂ Removal with Enhanced Wollastonite Weathering in Acidic and Calcareous Soils. *Soil Ecol. Lett.* **2025**, *7*, 240273. [[CrossRef](#)]
9. Khalidy, R.; Haque, F.; Chiang, Y.W.; Santos, R.M. Monitoring Pedogenic Inorganic Carbon Accumulation Due to Weathering of Amended Silicate Minerals in Agricultural Soils. *J. Vis. Exp.* **2021**, *172*, 61996. [[CrossRef](#)]
10. Swoboda, P.; Larkin, C.S.; Rodrigues, M.M.; Kang, J.; Santoro, M.; Clarkson, M.O.; Chiapini, M. *Agronomic Co-Benefits of Enhanced Rock Weathering (ERW) with Basalt Applied to Sugarcane Grown on Acidic Soil in Brazil*; EGU General Assembly: Vienna, Austria, 2025.

11. Holzer, I.O.; Nocco, M.A.; Houlton, B.Z. Direct Evidence for Atmospheric Carbon Dioxide Removal via Enhanced Weathering in Cropland Soil. *Environ. Res. Commun.* **2023**, *5*, 101004. [CrossRef]
12. Call for Proposals: Join Milkywire's Climate Transformation Fund. 2025. Available online: <https://www.milkywire.com/impact-funds/climate-transformation-fund/call-for-proposals/open-call-2025> (accessed on 29 August 2025).
13. Measuring Carbon Removal: Inside UNDO's Sentinel Sites. UNDO Carbon. 2025. Available online: <https://un-do.com/resources/blog/measuring-carbon-removal-inside-undos-sentinel-sites/> (accessed on 29 August 2025).
14. Launching the Community Enhanced Rock Weathering Quantification Standard Process. Available online: <https://cascadecclimate.org/blog/introducing-the-cqs> (accessed on 30 August 2025).
15. Puro.Earth to Revise Enhanced Rock Weathering Methodology | Website (Puro.Earth). Available online: <https://puro.earth/our-blog/puroearth-to-revise-enhanced-rock-weathering-methodology> (accessed on 29 August 2025).
16. Enhanced Weathering in Agriculture—Isometric. Available online: <https://registry.isometric.com/protocol/enhanced-weathering-agriculture> (accessed on 30 August 2025).
17. A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling. Available online: <https://pubs.usgs.gov/of/2004/1068/> (accessed on 29 August 2025).
18. White, A.F.; Brantley, S.L. The Effect of Time on the Weathering of Silicate Minerals: Why Do Weathering Rates Differ in the Laboratory and Field? *Chem. Geol.* **2003**, *202*, 479–506. [CrossRef]
19. Hasemer, H.; Borevitz, J.; Buss, W. Measuring Enhanced Weathering: Inorganic Carbon-Based Approaches May Be Required to Complement Cation-Based Approaches. *Front. Clim.* **2024**, *6*, 1352825. [CrossRef]
20. Renforth, P.; Pogge Von Strandmann, P.A.E.; Henderson, G.M. The Dissolution of Olivine Added to Soil: Implications for Enhanced Weathering. *Appl. Geochem.* **2015**, *61*, 109–118. [CrossRef]
21. Reershemius, T.; Kelland, M.E.; Jordan, J.S.; Davis, I.R.; D'Ascanio, R.; Kalderon-Asael, B.; Asael, D.; Suhrhoff, T.J.; Epihov, D.Z.; Beerling, D.J.; et al. Initial Validation of a Soil-Based Mass-Balance Approach for Empirical Monitoring of Enhanced Rock Weathering Rates. *Environ. Sci. Technol.* **2023**, *57*, 19497–19507. [CrossRef]
22. Dietzen, C.; Harrison, R.; Michelsen-Correa, S. Effectiveness of Enhanced Mineral Weathering as a Carbon Sequestration Tool and Alternative to Agricultural Lime: An Incubation Experiment. *Int. J. Greenh. Gas Control* **2018**, *74*, 251–258. [CrossRef]
23. Andrews, M.G.; Taylor, L.L. Combating Climate Change Through Enhanced Weathering of Agricultural Soils. *Elements* **2019**, *15*, 253–258. [CrossRef]
24. Silva, J.M.P.; Bomio, M.R.D.; Motta, F.V.; Santos, R.M. Assessment of Calcimetry as a Reliable Method for Monitoring Soil Inorganic Carbon Stocks. *ACS Agric. Sci. Technol.* **2024**, *4*, 781–790. [CrossRef]
25. Beerling, D.J.; Kantzas, E.P.; Lomas, M.R.; Wade, P.; Eufrazio, R.M.; Renforth, P.; Sarkar, B.; Andrews, M.G.; James, R.H.; Pearce, C.R.; et al. Potential for Large-Scale CO₂ Removal via Enhanced Rock Weathering with Croplands. *Nature* **2020**, *583*, 242–248. [CrossRef]
26. Amann, T.; Hartmann, J.; Struyf, E.; De Oliveira Garcia, W.; Fischer, E.K.; Janssens, I.; Meire, P.; Schoelynck, J. Enhanced Weathering and Related Element Fluxes—A Cropland Mesocosm Approach. *Biogeosciences* **2020**, *17*, 103–119. [CrossRef]
27. 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.; et al. Increased Yield and CO₂ Sequestration Potential with the C₄ Cereal *Sorghum bicolor* Cultivated in Basaltic Rock Dust-amended Agricultural Soil. *Glob. Change Biol.* **2020**, *26*, 3658–3676. [CrossRef]
28. Iff, N.; Renforth, P.; Pogge Von Strandmann, P.A.E. 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.* **2024**, *6*, 1252210. [CrossRef]
29. Khalidy, R.; Haque, F.; Chiang, Y.W.; Santos, R.M. Tracking Pedogenic Carbonate Formation and Alkalinity Migration in Agricultural Soils Amended with Crushed Wollastonite Ore—Evidence from Field Trials in Southwestern Ontario. *Geoderma Reg.* **2025**, *40*, e00918. [CrossRef]
30. Haque, F.; Santos, R.M.; Dutta, A.; Thimmanagari, M.; Chiang, Y.W. Co-Benefits of Wollastonite Weathering in Agriculture: CO₂ Sequestration and Promoted Plant Growth. *ACS Omega* **2019**, *4*, 1425–1433. [CrossRef] [PubMed]
31. Government of Canada. The Soils of the Regional Municipality of Niagara (Volume 1 and 2). Available online: <https://sis.agr.gc.ca/cansis/publications/surveys/on/on60/index.html> (accessed on 29 August 2025).
32. Canadian Climate Normals 1981–2010 Station Data—Climate Environment and Climate Change Canada. Available online: https://climate.weather.gc.ca/climate_normals/results_1981_2010_e.html?dispBack=0&month1=0&month2=12&stnID=4671&utm_source=chatgpt.com (accessed on 3 October 2025).
33. Manning, D.A.C. Biological Enhancement of Soil Carbonate Precipitation: Passive Removal of Atmospheric CO₂. *Mineral. Mag.* **2008**, *72*, 639–649. [CrossRef]
34. ISO 10390:2005; Soil Quality—Determination of pH. ISO: Geneva, Switzerland, 2005. Available online: <https://www.iso.org/standard/40879.html> (accessed on 29 August 2025).
35. ISO 11465:1993; Soil quality—Determination of Dry Matter and Water Content on a Mass Basis—Gravimetric Method. ISO: Geneva, Switzerland, 1993. Available online: <https://www.iso.org/standard/20886.html> (accessed on 29 August 2025).

36. ISO 10693:1995; Soil quality—Determination of Carbonate Content—Volumetric Method. ISO: Geneva, Switzerland, 1995. Available online: <https://www.iso.org/standard/18781.html> (accessed on 29 August 2025).
37. Chen, A.; Chen, Z.; Qiu, Z.; Lin, B.-L. Experimentally-Calibrated Estimation of CO₂ Removal Potentials of Enhanced Weathering. *Sci. Total Environ.* **2023**, *900*, 165766. [CrossRef]
38. Royal Eijkelpamp | Products for Soil and Water Research. Available online: <https://www.royaleijkelpamp.com/> (accessed on 3 October 2025).
39. Huijgen, W.J.J.; Witkamp, G.-J.; Comans, R.N.J. Mechanisms of Aqueous Wollastonite Carbonation as a Possible CO₂ Sequestration Process. *Chem. Eng. Sci.* **2006**, *61*, 4242–4251. [CrossRef]
40. Saxton, K.E.; Lenz, A.T. Antecedent Retention Indexes Predict Soil Moisture. *J. Hydraul. Div.* **1967**, *93*, 223–244. [CrossRef]
41. Xie, W.; Yang, J. Assessment of Soil Water Content in Field with Antecedent Precipitation Index and Groundwater Depth in the Yangtze River Estuary. *J. Integr. Agric.* **2013**, *12*, 711–722. [CrossRef]
42. Li, X.; Wei, Y.; Li, F. Optimality of Antecedent Precipitation Index and Its Application. *J. Hydrol.* **2021**, *595*, 126027. [CrossRef]
43. Antecedent Precipitation Index—Glossary of Meteorology. Available online: https://glossary.ametsoc.org/wiki/Antecedent_precipitation_index (accessed on 7 October 2025).
44. Historical Climate Data—Climate Environment and Climate Change Canada. Available online: <https://climate.weather.gc.ca/> (accessed on 29 August 2025).
45. Cipolla, G.; Calabrese, S.; Noto, L.V.; Porporato, A. The Role of Hydrology on Enhanced Weathering for Carbon Sequestration II. From Hydroclimatic Scenarios to Carbon-Sequestration Efficiencies. *Adv. Water Resour.* **2021**, *154*, 103949. [CrossRef]
46. Schuiling, R.D.; Krijgsman, P. Enhanced Weathering: An Effective and Cheap Tool to Sequester CO₂. *Clim. Change* **2006**, *74*, 349–354. [CrossRef]
47. Cho, Y.; Driscoll, C.T.; Blum, J.D. The Effects of a Whole-Watershed Calcium Addition on the Chemistry of Stream Storm Events at the Hubbard Brook Experimental Forest in NH, USA. *Sci. Total Environ.* **2009**, *407*, 5392–5401. [CrossRef] [PubMed]
48. Stewart, A.J.; Halabisky, M.; Babcock, C.; Butman, D.E.; D’Amore, D.V.; Moskal, L.M. Revealing the Hidden Carbon in Forested Wetland Soils. *Nat. Commun.* **2024**, *15*, 726. [CrossRef] [PubMed]
49. Li, H.; Tang, B.; Lehmann, A.; Rongstock, R.; Zhu, Y.; Rillig, M.C. The Dissimilarity between Multiple Management Practices Drives the Impact on Soil Properties and Functions. *Soil Ecol. Lett.* **2025**, *7*, 240278. [CrossRef]
50. Schön, W.; Mittermayr, F.; Leis, A.; Mischak, I.; Dietzel, M. Temporal and Spatial Variability of Chemical and Isotopic Composition of Soil Solutions from Cambisols—Field Study and Experiments. *Sci. Total Environ.* **2016**, *572*, 1066–1079. [CrossRef]
51. 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.; et al. Quantification of CO₂ Removal in a Large-Scale Enhanced Weathering Field Trial on an Oil Palm Plantation in Sabah, Malaysia. *Front. Clim.* **2022**, *4*, 959229. [CrossRef]
52. Kaufhold, S.; Emmerich, K.; Dohrmann, R.; Steudel, A.; Ufer, K. Comparison of Methods for Distinguishing Sodium Carbonate Activated from Natural Sodium Bentonites. *Appl. Clay Sci.* **2013**, *86*, 23–37. [CrossRef]
53. Schaffer, Z.R.; Rausis, K.; Power, I.M.; Paulo, C. Enhanced Weathering of Kimberlite Residues in a Field Experiment: Implications for Carbon Removal Quantification and Mine Waste Valorization. *Front. Clim.* **2025**, *7*, 1592626. [CrossRef]

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