A Novel Soil Porewater Extraction Technique for Enhanced Rock Weathering Products: SATuration - Centrifugation

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Abstract

Enhanced Rock Weathering (ERW) involves the application of crushed silicate-rich minerals to agricultural soils as a promising Carbon Dioxide Removal (CDR) strategy, with potential benefits for soil health and crop productivity. Effective Monitoring, Reporting, and Verification (MRV) techniques are essential for carbon credit validation and scalability of ERW. Current MRV methods, such as in-field soil porewater extraction, represent a potential barrier for scaling-up ERW because the accuracy, sensitivity, and consistency of this technique is limited by soil moisture availability. Here we test a new technique for quantifying ERW called the SATuration Centrifugation (SAT-C) technique, which could prove to be a more accurate, sensitive, and consistent means of quantifying ERW. This novel method combines soil core saturation using deionized water and centrifugation to extract porewater from a defined soil volume, independent of initial moisture conditions. Comparative analyses show strong concordance between SAT-C and conventional rhizon sampling for key elemental concentrations. Furthermore, bicarbonate concentrations inferred from charge balance correlate with measured alkalinity across distinct soil types from two grassland ERW trials. SAT-C provides a robust, consistent tool for soil porewater extraction in ERW MRV, improving sampling accuracy regardless of soil moisture and thereby supporting more reliable carbon accounting and verification frameworks.

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Keywords

Enhanced rock weathering, soil porewater extraction, CDR, crushed silicate rock, soil core centrifugation.

Synopsis
Traditional porewater extraction can fail under certain moisture conditions, causing incomplete time series that hinder Monitoring, Reporting, and Verification in Enhanced Rock Weathering. This study introduces a novel extraction method to overcome this issue.

1 Introduction

Enhanced Rock Weathering (ERW) is a proposed technique whereby crushed silicate rocks are spread in the open system, e.g. on agricultural fields, with the purpose of Carbon Dioxide Removal (CDR) and improved soil health (Levy et al., 2024, Beerling et al., 2020, Hartmann et al., 2013). At present, aqueous sampling is a requirement in monitoring, reporting and verification (MRV) methodologies (Puro.earth, 2025, Isometric, 2025). A common form of aqueous measurement is soil porewater, defined as the aqueous phase occupying the void spaces between soil particles (Di Bonito et al., 2008). Soil porewater is a critical component of subsurface geochemical systems, mediating the transport of nutrients, contaminants, and ions (Sposito, 2008). In the context of ERW, soil porewater acts both as a reagent, supplying carbonic and organic acids to mineral surfaces (Renforth and Campbell, 2021), and as a temporary reservoir of mineral hydrolysis reaction products (bicarbonate alkalinity and the cations that charge-balance it, typically Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) (McBride et al., 2025). The change in concentration of these components in soil porewaters may therefore indicate the extent to which weathering of an applied mineral feedstock has occurred (Clarkson et al., 2024). The presence of other anions can also be used to quantify the fraction of mineral weathering that was driven by strong acids, which must be deducted from CDR estimates (McDermott et al., 2024, Holden et al., 2024, Maxbauer et al., 2025). However, natural weathering of basalt in aquifers (Gastmans et al., 2016) or in natural catchments is dominated by carbonic acid (unless there are external inputs such as sea-derived chloride, Moulton et al., 2000).

Accurate extraction of soil porewater is essential for the understanding of soil processes, geochemical modelling and environmental monitoring (Di Bonito et al., 2008). Crucially, differences in the measured elemental composition of extracted soil porewater may depend on the choice of extraction method (Geibe et al., 2006). Challenges in using soil porewater measurements for the purpose of estimating elemental concentrations stem from its transient nature (Hirst et al., 2023, Milatz et al., 2018). The volume of pore water contained in topsoils changes as a function of precipitation and evapotranspiration, as well as porewater

leaching (Ehrhardt et al., 2025). Furthermore, dynamic processes result in elemental exchange between soil and porewater (Ben Moshe et al., 2021).

Traditional extraction methods, such as rhizon samplers and suction lysimeters, rely on porous membranes and vacuum or soil tension to draw porewater over time, and offer different operational characteristics (Di Bonito et al., 2008). Rhizon samplers are often smaller in size (e.g. 9 cm long and 0.5 cm in diameter) compared to suction lysimeters (e.g. 20 cm long, with the ceramic tip being ~5 cm long, and ~5 cm in diameter) and are more effective for obtaining porewater extracts from smaller soil volumes or depth increments in the root zone (Di Bonito et al., 2008). Rhizon samplers are also suitable for repeated measurements at the same location over time, but can cause disturbance to the soil system during and after installation (Di Bonito et al., 2008). However, due to sample volume limitations, rhizon samplers are not best suited for capturing the elemental flux to groundwater (Coutelot, et al., 2014). In contrast, suction lysimeters are larger devices, which sample from a larger volume of soil, typically having higher porewater yields than rhizon samplers, and are better-suited to capture bulk solute heterogeneity across a soil horizon (Geibe et al., 2006, Edaphic Sci., 2025). The trade-off is that lysimeters, due to their greater size, may result in greater alterations to soil structure and create preferential flow during installation (Geibe et al., 2006).

Traditional porewater extraction methods face a number of common challenges; for example, (1) vacuum may be lost during sample collection due to ingress of air (2) device effectiveness is often contingent upon soil moisture levels, with insufficient sample volumes obtained during dry periods for chemical analysis; and (3) device performance may differ substantially between different soil types (Orlowski et al., 2016). Moreover, (4) the volume of soil from which porewater is obtained for both rhizon samplers and suction lysimeters varies depending on soil moisture content and pore connectivity, making it difficult to determine the precise volume of soil sampled (Di Bonito et al., 2008), and consequently making it harder to estimate weathering rates in specific soil layers. This limits the granularity of mineral dissolution estimates in soils and adds further uncertainty to CDR estimates (Levy et al., 2024). Quantification of CDR requires year-round analysis of the products from enhanced weathering, regardless of soil moisture content or rainfall amount (te Pas et al., 2025). This means that data gaps from traditional extraction methods during dry periods, when rhizons or lysimeters are unable to obtain sufficiently large porewater samples, could lead to significant underestimates of ERW rates (Bertagni et al., 2025). Further, soil water-flow paths are three dimensional (Hu et al., 2013, Páez-Bimos et al., 2023), so there is a risk that the products from enhanced weathering may bypass traditional water extraction devices.

Centrifugation of soil cores, known as the drainage centrifuge method, is a well-established method that has been utilized to study soil properties, water

retention, solute concentrations, and structural changes (e.g. Fraters et al., 2017 and Di Bonito et al., 2008). The method is particularly useful for analyzing solute concentrations for highly mobile porewater constituents, such as dissolved nutrients or contaminants, e.g. nitrate (Fraters et al., 2017). In a recent ERW study, centrifugation was used to sample porewater composites of multiple aliquots of soil taken from a homogenized soil sample in order to yield sufficient sample for analysis (Jones et al., 2025). To the best of the authors' knowledge, the study carried out by Jones et al. (2025) is the first where soil porewater centrifugation has been presented in an ERW context. The study found elevated total alkalinity and calcium concentrations determined on samples obtained through centrifugation compared to samples from suction lysimeters (Jones et al., 2025). While the drainage centrifugation method is well-established, the availability of easily leachable porewater is still determined by the moisture content in the soil matrix at the time of sampling. Hence, higher centrifugation speeds may be needed to yield sufficient sample volumes during drier soil conditions, potentially leading to soil slumping and collapse of soil pore structures, as well as differences in pore sizes sampled over time.

To address the limitations of traditional porewater extraction techniques and established centrifugation methods, a SATuration Centrifugation technique (hereafter referred to as SAT-C) using complete soil cores is presented, designed to improve the accuracy and reliability of soil porewater sampling. In the SAT-C approach, a soil sample is saturated using de-ionized water and subsequently centrifuged. The saturation step is included as a novel addition to the drainage centrifuge method to counter challenges with low aqueous sample yield due to low soil moisture. The purpose of SAT-C is to alleviate some of the limitations of traditional soil porewater extraction methods by obtaining dissolved weathering products from a known soil volume, while enabling detection in specific soil layers. This study tested the SAT-C method against two traditional porewater extraction methods (rhizon samplers and suction lysimeters) and evaluated the impact of different extraction methods on estimated bicarbonate, derived through charge balance calculations of conservative cations and anions.

2 Methods

2.1 Site description

Porewater was extracted from two existing basalt ERW trials located in Scotland: Dumyat and Glensaugh. Dumyat is located on The Future Forest Company-managed Estate in central Scotland (56.14930789 N; -3.89292692). Glensaugh is located on land owned by the James Hutton Institute in Aberdeenshire, Scotland (56.89427868 N; -2.54168692). Both sites fall within the temperate oceanic climate zone, according to the Köppen-Geiger classification scheme (Beck et al., 2018), but with slight differences in the ten-year (2015-01-01 - 2025-01-01) mean annual temperature (9.1°C and 7.9°C for Dumyat and Glensaugh,

respectively) and the mean annual precipitation sum (1207.2mm and 1054.1mm) (Muñoz Sabater, 2019). According to the USDA soil taxonomy, the soils are classified as a silty clay loam (McBride et al., 2025) and sandy silt loam for Dumyat and Glensaugh, respectively. The soil organic carbon content is 3.55±0.37 wt.% (McBride et al., 2025) and 3.16±0.84 wt.%, respectively. Both trials are multiyear large plot trials on grassland that are periodically grazed by livestock. The Dumyat trial commenced in September 2022, with basalt applied between the 20th and 27th of September 2022 (McBride et al., 2025). At Glensaugh, basalt was applied on the 19th of May 2023. In both trials, the feedstocks were surface-applied to the grasslands.

2.2 Experimental layout

For the purpose of this study, porewater was extracted from one control and one high application plot in each trial. Within each plot, three sample arrays were installed with an approximate 5 m distance, thereby avoiding any edge effects. Within each array the three extraction methods were duplicated twice (see Figure 1), resulting in six duplicates for each extraction method in each plot, and a total number of 96 porewater samples across the two sites.

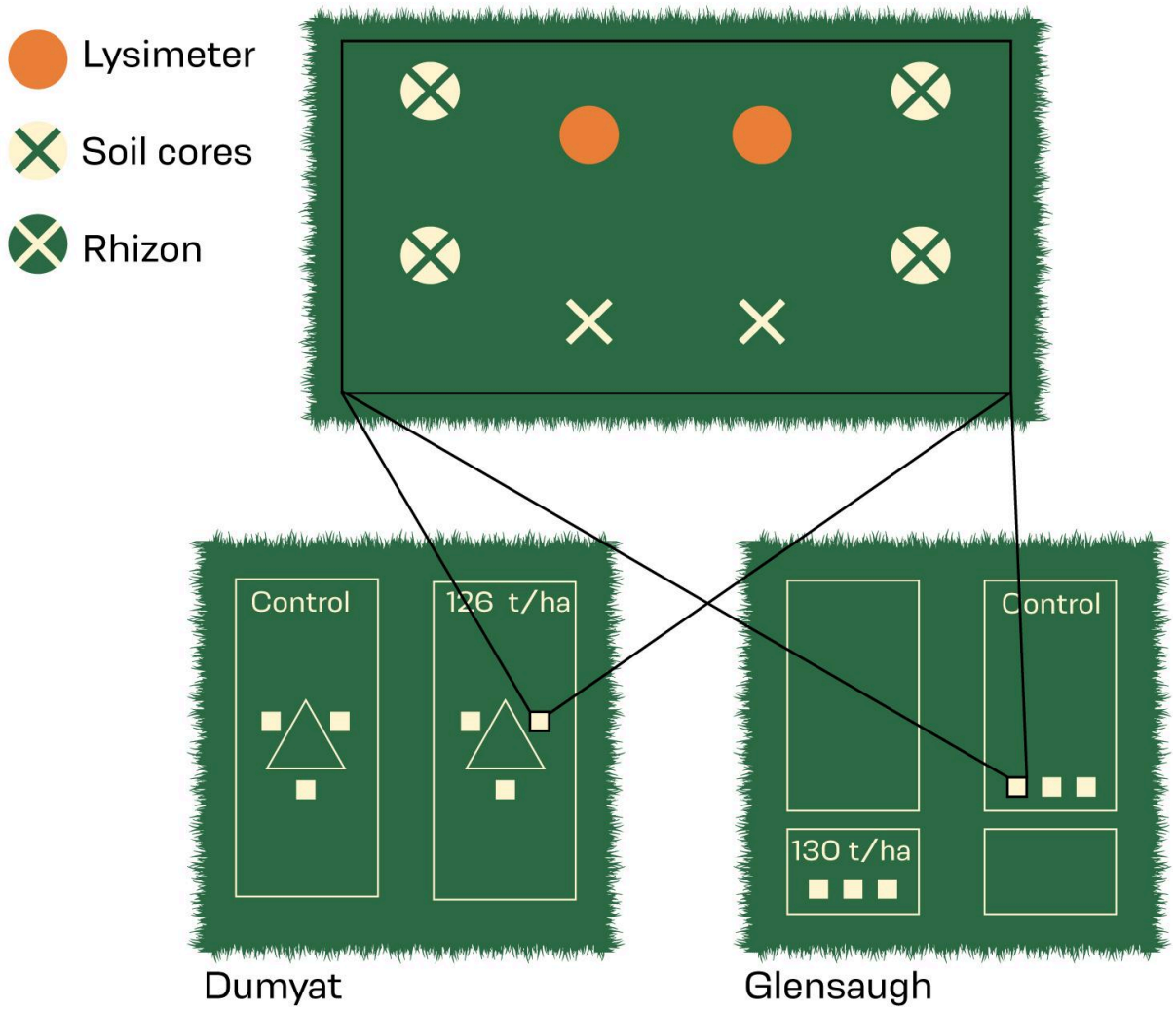

Figure 1: Overview of the relative location of the plots used in this study from Dumyat and Glensaugh, with a schematic representation of how different extraction methods (rhizon samplers, suction lysimeters and soil cores) were positioned relative to each other. The outer plot boundaries at Dumyat are 100 by 48 m and at Glensaugh the larger plots are 90 by 12 m and the smaller plots 12 by 12 m. Within each, three sample arrays were installed, each approximately 5 m apart. The horizontal distance between different extraction methods within each array is approximately 30 cm.

2.3 Feedstock description

The two trials were amended with feedstock sourced from local quarry by-products. For the Dumyat trial, basalt from the Hillend quarry was applied. The basalt is classified as a quartz microgabbro from the Carboniferous Midland Valley Sill Complex (Cameron et al., 1998). The quarry is situated near Airdrie, Ayrshire (55.88552, -3.88448) and is owned by Tillicoultry Quarries Ltd. For the Glensaugh trial, basalt from the Pitcaple quarry was applied. This basalt is classified as a norite and gabbronorite from the Ordovician Insch Pluton (Gould, 1997). The quarry is situated in Aberdeenshire (57.32786, -2.45161). Both of the samples contained 69.9% fast weathering minerals (plagioclase, pyroxene, ilmenite, amphibole and magnetite), when compared to mineral groupings from Lewis et al (2021), however, the Pitcaple material contained a lower proportion (*c.* 8.4 wt.% lower) of slow weathering minerals relative to that from Hillend (Table S1). The Pitcaple material also contained a higher proportion (*c.* 8.4 wt.% higher) of minerals with unknown dissolution rates, largely from uncharacterised amorphous phases.

The major element chemistry of the two samples is similar - with E_{pot} values of 0.28 tCO_2 $tRock^{-1}$ and 0.29 tCO_2 $tRock^{-1}$ for the Hillend and Pitcaple, respectively (S2). The mean particle size in the Pitcaple sample is considerably smaller (567 µm*)* than that of the Hillend sample (1279 µm). The Pitcaple sample also has a higher surface area (1.75 m^2 g^{-1}) relative to the Hillend (0.917 m^2 g^{-1}).

2.4 Extraction methods

The soil porewater extraction methods deployed are: (1) macro-rhizon samplers (Macro-rhizons, Rhizosphere, 2025), (2) ceramic lysimeters (1900 soil water sampler, Soilmoisture, 2025), and (3) soil cores extracted for saturation at two different intervals (24 and 72 hours).

Macro-rhizons were installed at 10 cm depth in mid-April at both Dumyat and Glensaugh, allowing more than a week for stabilization in the soil profiles. The two macro-rhizons in each sample array were installed 30 cm apart in the horizontal plane (Figure 1). Shallow soil pits were dug to allow for horizontal installation of the rhizon samplers. Prior to installation the porous polymer of the rhizon sampler was submerged into de-ionized water to ensure complete saturation of the sampler. An old macro-rhizon was used to ‘pre-drill’ the hole for the macro-rhizon, to ensure no obstacles in the soil which could have resulted in the rhizon sampler breaking during installation. Disposable 30 ml syringes were attached to the

rhizon tubing and vacuum was created 24 hours prior to collection by applying 10 cm wooden splints to extend the syringe plunger.

Lysimeters were likewise installed mid-April approximately 50 cm from the rhizon samplers, in the horizontal plane (Figure 1). The lysimeters were installed vertically to a depth of 20 cm, using an auger to remove soil down to the installation depth. The porous ceramic suction cup is 5 cm long, resulting in an effective sampling depth for the suction lysimeters of 15-20 cm. The excavated soil was sieved through a 9.5 mm sieve and mixed with de-ionized water to create a slurry, which was poured back into the auger hole before inserting the lysimeter suction probe. The last part of the mixture was poured around the samplers to ensure good connectivity with the soil and to secure the samplers in place. Similarly to the rhizons, the lysimeters were left in the field for a minimum of a week to achieve equilibrium with the surrounding soil. The lysimeters were pressurized to a target vacuum of 60 kPa using a hand pump attached to the exterior tubing of the lysimeter 24 hours prior to sample collection. Vacuum was applied and water samples collected concurrent with the rhizon samplers. In order to retrieve the water from the lysimeter samplers, these were removed from the ground and water was retrieved from the center of the lysimeters. For both the rhizon and lysimeter samplers the extracted water was poured into pre-labelled 50 mL centrifuge tubes.

Soil cores were taken with a spacing of approximately 30 cm outward from the lysimeter installation locations (Figure 1), to avoid any compaction of the soil caused by the installation of the lysimeters. Soil cores were extracted by inserting a metal collection ring (Ø = 5 cm, h = 5 cm, V = 95.03 cm^3) flush to the ground's surface using a wooden block and a hammer. The upper turf and root/litter zone was removed using a pallet knife before inserting the corer. A second metal ring of the same size was placed on top of the previous one and hit into the ground applying the same method. The two rings were then dug out using a trowel, carefully keeping the rings together until fully extracted. The rings were then separated using a pallet knife, and the lower core, 5-10 cm, was capped on both ends with matching core caps, to preserve the cores, prior to saturation and centrifugation.

Porewater samples and soil cores were collected from both sites in the morning of the 25th of April 2024, allowing for porewater collection from the rhizons and suction lysimeters for approximately 24 hours at both sites. The samples were stored in a sealed coolbox for immediate transport to James Hutton Institute (JHI) Invergowrie laboratory where they were stored in a refrigerator prior to analysis.

2.5 Soil core saturation and centrifugation

As soon as the soil cores arrived at the JHI lab, gauze was fitted around the bottom of the soil cores and secured with elastic bands to eliminate the risk of soil loss during the saturation and centrifugation process. The gauze and elastic

bands were weighed prior to use, followed by weighing of the soil cores (including gauze and elastic bands) prior to saturation. Following the saturation and centrifugation the cores were oven dried (at 105 ˚C for 24 hours) and the dry weight was recorded, to determine the initial soil moisture content and soil bulk density prior to saturation. For saturation, the prepared soil cores were placed in individual polythene bags and 60-100 mL of de-ionized water was added to the bags to ensure full saturation of the collected cores, reaching two-thirds of the core height, allowing air to leave the cores during the saturation process. Once water had been added to the bags, air was pushed out of the bags before they were sealed and stored in a cold room at 4°C, where they were left to saturate for either 24 or 72 hours to allow for sample equilibration. Following saturation, cores were transported in cool boxes from JHI Invergrowie to JHI Aberdeen (approximately 2 hour drive) where the centrifugation was conducted.

The cores were removed from the bags and transferred to a wire rack to allow any excess water to drip off, ensuring that any water extracted during the centrifugation process was contained within the soil pores. Porewater was extracted through the use of core holders which had two chambers: the upper chamber contained the core and was separated from the lower chamber by a perforated plastic disc with filter paper between the plastic disc and base of the soil core. The core, perforated disc, and filter paper were contained in the polythene bag to collect the extracted water and ensure no cross contamination between the cores. The cores were then placed in the core holders.

A pilot study, with a centrifuge spin speed of 1000 RPM for a duration of 30 minutes, was found to eliminate challenges with physical damage to core bags and deformation of the perforated plate. Hence, cores from this study were spun at a speed of 1000 RPM for 30 minutes using a Beckmann Coulter J6-MI temperature-controlled centrifuge and JS-4.2 swinging bucket rotor assembly to hold the core water extraction assembly. Following the centrifugation process, the soil core, perforated disc and filter paper were removed from the bag and the supernatant transferred, through filtration using a 0.22 µm filter, from the polythene bag into a 50 mL Falcon tube.

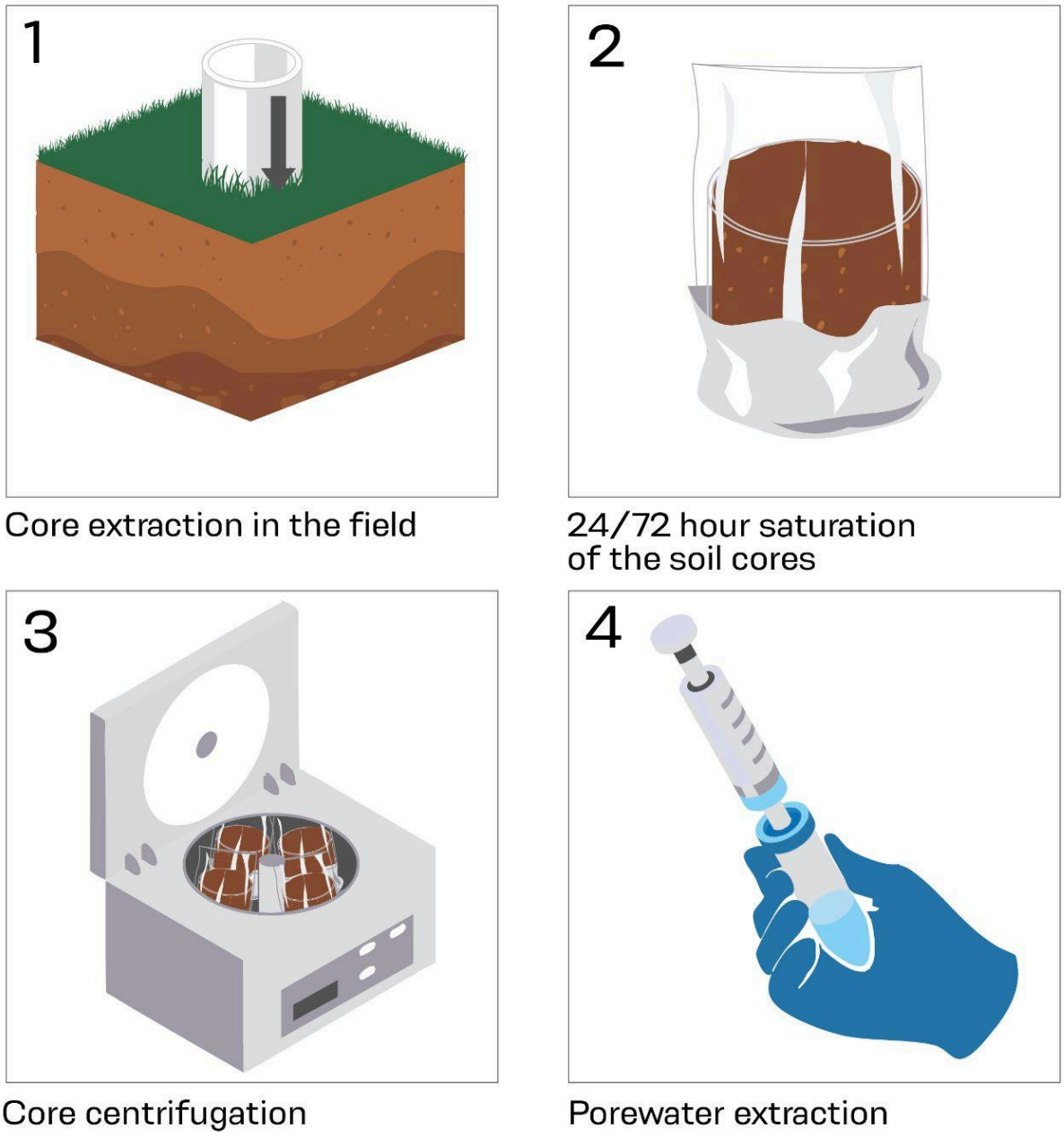

Figure 2: Schematic illustration of the SAT-C process from 1) soil core sampling in the field, 2) saturation in the lab, 3) centrifugation of saturated cores and 4) filtration of the supernatant extracted from the cores during centrifugation.

2.6 Chemical analysis

The soil porewater samples from all three extraction methods were analysed for cations (boron, calcium, magnesium, sodium, potassium, phosphorus, sulfur and silicon) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Aqueous samples were acidified using 2 M nitric acid and analysed using a Perkin Elmer AVIO 500 ICP-OES. The instrument was calibrated using multi-point calibration and standards were matrix matched to the samples as much as possible (see limits of detection in Table S3). Anions (fluoride, chloride, nitrate and sulfate) were analysed using a Thermo Aquion Ion Chromatography (IC) system. For low volume samples, dilutions were prepared manually with high

purity water using electronic dispensing pipettes. Phosphate and total alkalinity as calcium carbonate were analysed using a Seal AQ400 discrete colorimetric analyser. Alkalinity was determined following reaction with bromocresol blue solution. Phosphate was determined using a blue phosphomolybdic complex reaction.

2.7 SAT-C porewater concentrations

The cation and anion concentrations measured on the supernatant from SAT-C soil cores were diluted during the saturation process. In order to calculate the original concentrations, had the core not been saturated, the following mixing model was applied (Eq. 1):

$$C_1 V_1 = C_2 V_2$$

where, C_1 is the initial concentration of the solutions, V_1 is is the initial volume of the solution (found through fresh and dry weight of the cores), C_2 is the final concentration of the solution after dilution (the concentration of cations and anions in the supernatant) and V_1 is the final volume of the solution after dilution.

2.8 Bicarbonate estimation

The concentration of bicarbonate from each porewater sample was estimated by balancing the equivalents of the sum of major cations and anions with bicarbonate according to the following equation (Eq. 2, modified from McDermott et al., 2024):

$$[HCO_3^-] = (([Mg] + [Ca]) \cdot 2 + [K] + [Na]) - ([Cl] + [NO_3] + ([SO_4] \cdot 2) + ([PO_4] \cdot 3)$$

where the elements and compounds in the equation are expressed in mol L^{-1}.

2.9 Data analysis

The estimated bicarbonate from the different porewater extraction methods was evaluated using two linear mixed models, one for each of the study sites. The extraction method was included as a fixed categorical explanatory variable with the rhizon group as the reference level and application rate as a random effect, taking the clustering of samples within plots into account (West, Welch, and Galecki, 2022). Plots of model residuals were inspected to ensure that model assumptions of normality, homogeneity and independence of residuals were met. The normality and homoscedasticity was also evaluated using Shapiro-Wilk (Shapiro and Wilk, 1965) and White's Lagrange multiplier test (White, 1980), respectively. In order to evaluate extraction methods for each treatment, a pairwise comparison of each extraction method and treatment combination (a total of 12 comparisons) using Tukey's HSD post hoc test was performed (Tukey, 1953). Furthermore, the balance between the sum of conservative cation and anion equivalents, as measured on the diluted SAT-C porewater samples, was

compared using linear regression to the measured alkalinity converted to mol L^{-1}. For a further comparison of the relative proportions of major ions within and between the extraction methods, Piper diagrams for each site are presented. All statistical analyses were carried out using Python (version 3.9) and the package Statsmodels (version 0.14.4, Seabold and Perktold, 2010).

3 Results

The overall water yield from all four extraction methods was relatively good, with sufficient sample volume for analysis from 91 out of 96 samples (Table 1). However, at Glensaugh some of the rhizon samplers and lysimeters did not yield enough water for analysis of the chemical composition (3 mL). All SAT-C soil cores provided sufficient water for analysis from both Dumyat and Glensaugh.

Table 1: Table with number of samples from each group that yielded enough sample volume to determine the chemical composition of the soil porewater.

	Dumyat		**Glensaugh**	
	0	**130**	**0**	**130**
SAT-C 24	6	6	6	6
SAT-C 72	6	6	6	6
Rhizon	6	6	5	3
Lysimeter	6	6	5	6

The sum of major cation and anion equivalents is presented for the individual extraction methods, site and treatment in Figures 3 and 4. Concentrations from SAT-C samples have been corrected for the dilution of the saturation using the mixing model in Equation 1. Overall, the concentrations are of the same order of magnitude, with some variation within and between extraction methods observed for both major cations and anions. The largest variability between extraction methods is observed for the anions at Glensaugh (Figure 4), where concentrations are generally low for the rhizon samplers and high for the lysimeter samples from the control. The cation and anion concentrations from the soil cores that were exposed to different saturation intervals (24 and 72 hours) are very similar.

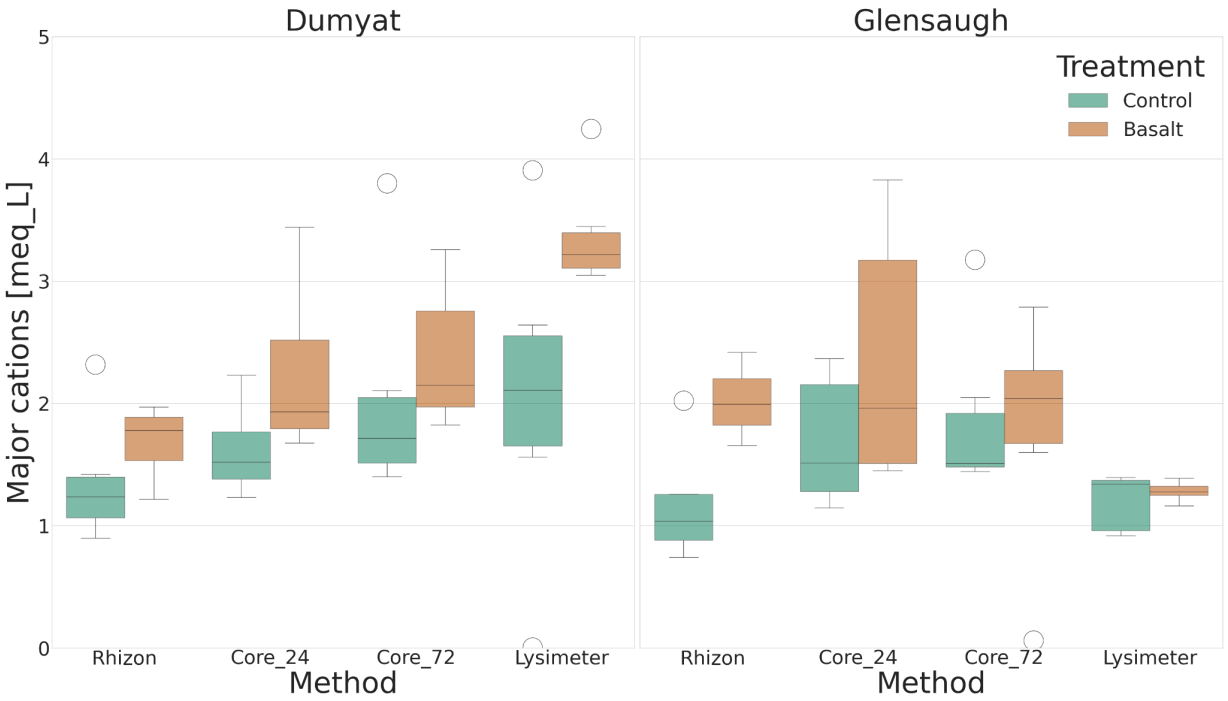

Figure 3: Sum of major cations (calcium, magnesium, sodium and potassium) in their equivalents, grouped by site (Dumyat, Glensaugh), extraction method (x-axis) and treatment (control vs. basalt application).

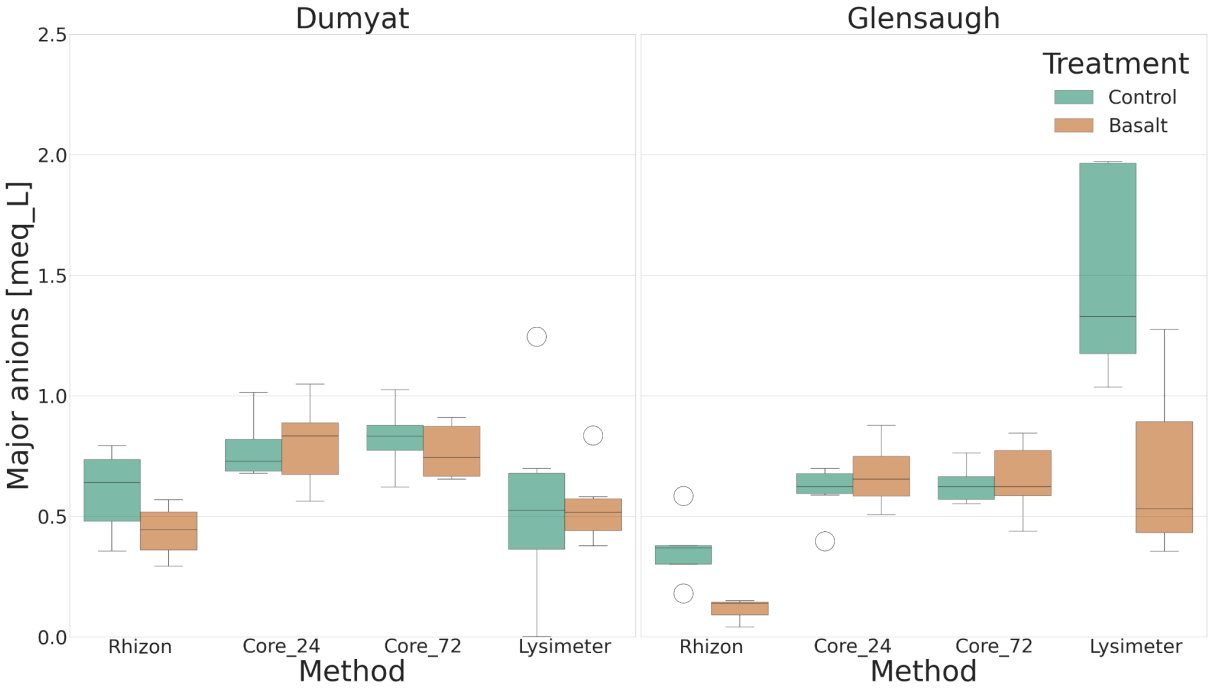

Figure 4: Sum of major anions (chloride, nitrate, sulfate and phosphate) in their equivalents, grouped by site (Dumyat, Glensaugh), extraction method (x-axis) and treatment (control vs. basalt application).

The estimated bicarbonate concentration from the different extraction methods is comparable, falling within the same order of magnitude across both sites and extraction methods. The linear mixed effect models showed that the only extraction method that was different from the rhizon was the lysimeters ($p < 0.001$

and p = 0.002 for Dumyat and Glensaugh, respectively). For both models the residuals met model assumptions of normality and homoscedasticity (Shapiro-Wilk and White Lagrange multiplier tests produced p > 0.05). Due to the high sum of anions in the lysimeter samples from the Glensaugh control plot, the resultant estimated bicarbonate is negative, which suggests an underlying issue with the analytical analysis of the samples. For that reason, the mixed linear model for Glensaugh was run with and without the lysimeter data. The models showed that the SAT-C groups were not significantly different from the rhizon group (p > 0.1). For Dumyat the Tukey's HSD post hoc test revealed that the basalt amended lysimeter concentrations were significantly higher than the rhizon and SAT-C cores that had been saturated for 24 hours (p < 0.05). For Glensaugh only the lysimeter concentrations from the control groups were significantly different from the control groups from the SAT-C cores (p < 0.05). None of the SAT-C groups were significantly different from the rhizon groups.

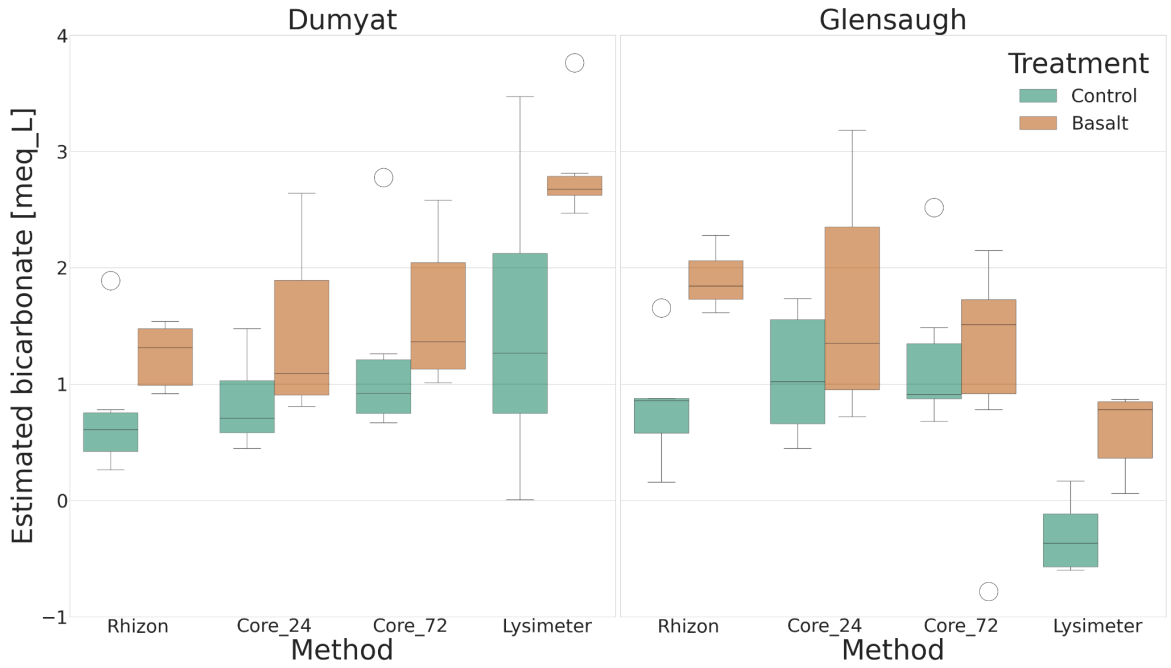

Figure 5: Estimated bicarbonate in equivalents found through charge balancing major cations and major anions, grouped by site (Dumyat, Glensaugh), extraction method (x-axis) and treatment (control vs. basalt application).

In order to check the validity of estimating bicarbonate from the conservative cations and anions, the balance between the two is compared to the measured alkalinity expressed in mmol L^{-1} (Figure 6). At Dumyat, the linear fit is good for each extraction method (R^2 ranging from 0.94 to 0.99, p < 0.005 for all extraction methods). At Glensaugh there is a strong linear relationship between alkalinity and the charge balance between major ions for the rhizon samples (R^2 = 0.97, p < 0.001) and SAT-C cores that were saturated for 24 hours (R^2 = 0.94, p < 0.001). Given the negative balance of cations and anions from the lysimeter samples at Glensaugh, the linear fit is predictably weaker (R^2 = 0.79, p < 0.001). However, the

lowest linear fit from Glensaugh is in the data from the SAT-C cores that were saturated for 72 hours (R^2 = -0.01, p = 0.7).

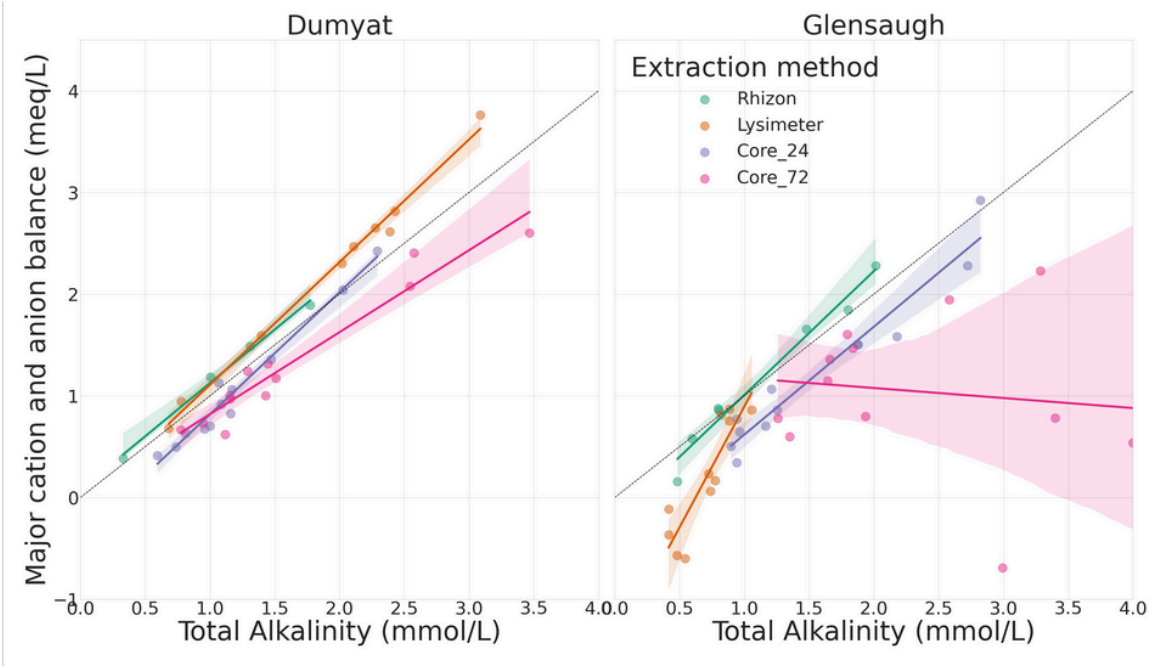

Figure 6: Scatter plots between total alkalinity and the balance between the conservative cations and anions. Note that for the SAT-C data the balance between major cations and anions plotted here is the actual measured concentrations on the diluted samples, not the corrected data.

Piper diagrams for both Dumyat and Glensaugh (Figure 7) express the relative proportions of major ions within the water samples from the different extraction methods, in their equivalents, and are not affected by dilution. They show consistent proportions of magnesium (around 20% of the cation charge), and differences in calcium, sodium and potassium for both Dumyat and Glensaugh. There is a tendency for centrifuged cores to have higher sodium and potassium relative to calcium than rhizon samples, most pronounced for Dumyat. The lysimeter samples (only shown for Dumyat, due to the negative charge balance at Glensaugh) show considerable variation. For anions, rhizon and core samples overlap, showing variation in chloride and bicarbonate with higher chloride contents for the centrifuged cores, especially at Glensaugh where the concentration of conservative anions was relatively low (see also Figure 4).

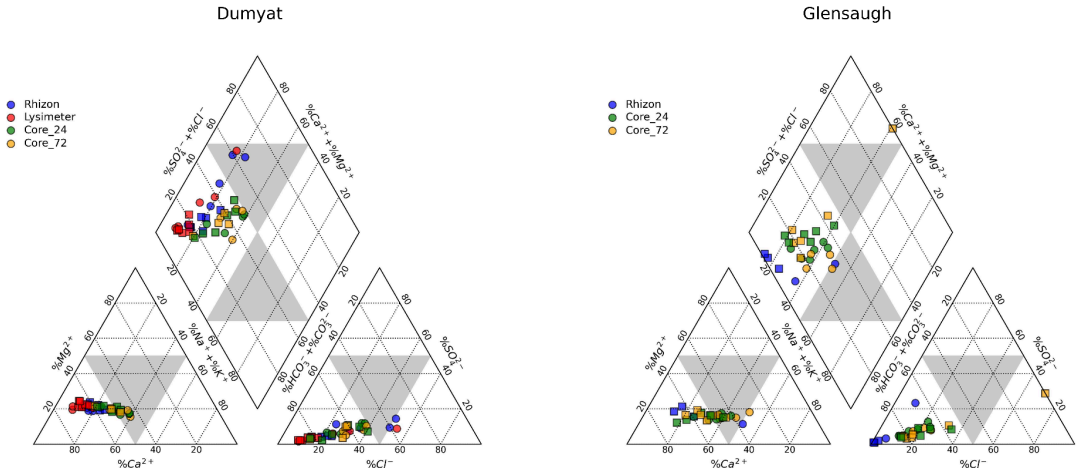

Figure 7: Piper diagrams showing the relative proportions of major cation and anions in the porewater samples taken using the four different extraction methods. Circles represent samples taken from the control plots, squares samples from the basalt amended plots. For Glensaugh the lysimeter data has not been plotted due to unrealistic estimated bicarbonate concentrations.

4 Discussion

4.1 Soil pore water yield

All SAT-C cores taken from both sites produced a sufficient volume of sample for chemical analysis. In contrast, one lysimeter and four rhizon samplers at the Glensaugh site failed to produce sufficient volume for analysis despite the experiment occurring at a time of year when soil water reservoirs are usually at their highest in Scotland (Table 1). This illustrates one of the main concerns of using traditional pore water extraction methods for quantifying ERW over time: low or no porewater recovery, whether due to low soil moisture or device failure, leading to low replication or uneven spatial and temporal coverage. The challenge of using traditional porewater extraction methods was also dealt with in Jones et al. (2025). In this study multiple aliquots of homogenized soil were centrifuged in order to yield sufficient porewater sample volumes for chemical analysis. Although smaller pore spaces can be sampled through this method compared to suction lysimeters, it may still be prone to low yields when natural soil moisture levels are low. The saturation step in the SAT-C method alleviates this issue, by ensuring that soil moisture is sufficient (e.g. at field capacity) to extract a porewater sample. Moreover, optimizing the temporal resolution of porewater sampling after ERW application is crucial for accurate estimations of in-field dissolution rates (Bertagni et al., 2025). Traditional sampling approaches are unable to guarantee a complete time series, because they are vulnerable to natural soil moisture fluctuations, leading to potentially large data gaps, further increasing uncertainty around ERW rates.

4.2 Major cations, major anions and estimated bicarbonate between extraction methods

The sums of major cations, major anions, and inferred bicarbonate concentrations show no significant differences between rhizon and SAT-C extraction methods. In Enhanced Rock Weathering (ERW), bicarbonate concentration in soil porewater is critical, representing the instantaneous carbon dioxide removal reservoir in the topsoil. The SAT-C method's ability to produce comparable concentrations to rhizon sampling, while yielding realistic levels of readily leachable mineral dissolution products, highlights its reliability for accurate porewater analysis in ERW studies.

In contrast, estimated bicarbonate determined from the lysimeter porewater were significantly different from the other sampling methods. Differences between the lysimeters and other methods varied depending on field site. At Dumyat, estimated bicarbonate was higher in the lysimeter measurements compared to rhizon or SAT-C measurements. whereas, at Glensaugh, lysimeters recorded significantly lower bicarbonate compared to the other methods (Figure 5). These discrepancies among sampling methods may be partially attributed to differences in the depth from which samples are collected - rhizons were installed to a depth of 10 cm, lysimeters to a depth of 15-20 cm, and SAT-C cores collected from the 5-10 cm depth. Other major sources of uncertainty are the volume of soil sampled and from which pore spaces water is sampled.

The three different extraction methods tested in this experiment differ from each other on two fundamental parameters that affect which pore spaces are sampled and for rhizons and lysimeters the volume of soil from which porewater is extracted, i.e. 1) the tension exerted on the soil and 2) the surface area of the sampler that is in touch with the soil itself, henceforth referred to as the soil interface.

The tension during the centrifugation was substantially lower than the target tension that was applied to the rhizon and suction lysimeters. The maximum tension that can be applied using the syringe connected to the rhizon sampler is 100 kPa. For the lysimeter the target tension was set at 60 kPa. A tension range of 60-80 kPa is generally considered the upper limit for soil pore water extraction (Carter and Gregorich, 2007). In contrast, the tension exerted during centrifugation is 22.25 kPa (with a rotor radius of 203 mm and 1000 rpm). This tension falls within the typical range of 10 - 30 kPa for the soil matrix potential at field capacity, depending on soil type (Datta et al., 2018). Notably, although the maximum tension of the rhizon samplers and the target tension of the lysimeters is known, it is impossible to record the actual tension exerted throughout the duration of the soil extraction (24 hours).

Despite the differences in tension exerted, the similar bicarbonate estimations may indicate that an equilibrium between the existing soil moisture content in

the soil cores and the de-ionized water was reached. As such, the chemical composition of the water extracted through SAT-C represents the 'water extractable ions' in the soil solution, i.e. the ions that are readily leachable during the next rain event, rather than a signature of the chemical composition in the smallest pore spaces of the soil matrix. This is contradictory to the centrifugation method proposed in Jones et al. (2025), in which aliquots of homogenized soil were centrifuged at a tension of 300 kPa, allowing for the extraction of porewater from small pores, resulting in alkalinity concentrations in the centrifuged soil samples to be significantly higher than that extracted using lysimeters.

The significant difference between lysimeter and rhizon groups is probably partially driven by the fact that the soil interface of the different samplers differs considerably. Due to differences in size of the rhizons (length of porous membrane: 9 cm, outer diameter: 4.5 mm) and the suction cup lysimeters (length of porous membrane: 5 cm, outer diameter: 4.8 cm) the soil interface differs from 12.7 cm^2 to 75.4 cm^2. While a theoretical surface area of the soil cores can be calculated, the direct comparison is arbitrary. Rather, the bicarbonate estimate suggests that the SAT-C groups are similar to the rhizon groups, regardless of the theoretical discrepancy in soil interface. The soil interface of traditional extraction methods reflect the maximum possible area, as this is influenced by soil moisture changes in time, hence introducing an uncertainty of the volume of soil sample. This uncertainty is alleviated through SAT-C. Hence, it is proposed that SAT-C porewater time series will be more comparable over time, compared to those from traditional soil porewater extraction methods.

4.3 Alkalinity

In natural, uncontaminated soils, bicarbonate is assumed to be the main contributor to alkalinity (Rounds and Wilde, 2012). In an ERW context, elevated levels of bicarbonate originate from silicate mineral dissolution, although hydroxide ions (in alkaline soils, pH > 7) and organic alkalinity (in organic matter-rich soils) may also contribute to alkalinity (Rounds and Wilde, 2012). Total alkalinity is often used as a measure of mineral dissolution in ERW studies (e.g. Amann and Hartman, 2022). However, total alkalinity for SAT-C samples cannot be determined by direct measurements of porewater alkalinity because of latent effects of de-ionized water on the carbonate system. This means that we are unable to compare direct measurements of total alkalinity for SAT-C samples against rhizon and lysimeter samples.

Instead, we used the measured alkalinity to compare to the charge balance of major conservative cations and anions (using the diluted/uncorrected concentrations from SAT-C), as a check of the validity of using conservative ions to estimate the bicarbonate concentration. In order to ensure that charge balance was a good proxy for alkalinity, we regressed direct measurements of alkalinity against charge balance for all extraction methods. We found that total alkalinity

was generally significantly correlated to the charge balance of conservative cations and anions, indicating that charge balance was an accurate proxy for alkalinity (Figure 6). However, at Glenasugh the SAT-C cores that were saturated for 72 hours showed a non-significant relationship (Figure 6, R^2 = -0.01, p = 0.7). SAT-C cores saturated for 24 hours showed a similar slope and curve shape to rhizon samples both from Dumyat and Glensaugh (Figure 6). For the lysimeter samples, there was good correspondence within SAT-C samples for Dumyat, but a poorer agreement for Glensaugh (Figure 6). This implies, overall, that charge balance for SAT-C samples incubated for 24 hours is a relatively good proxy for alkalinity and hence bicarbonate concentration.

4.4 Concentration of conservative cations and anions across extraction methods

The variability in the relative proportions of major ions between the different extraction methods is visually similar to the variability observed within each of the extraction methods (Figure 7). There is a tendency towards higher sodium and potassium concentrations relative to calcium in the SAT-C cores at both sites compared with the rhizon samples. This could be due to differences in the pore spaces contributing to the porewater extracts. The greater tension involved in extraction using the rhizon samplers may provide greater access to water located in the pore space of finer-grained (i.e. more clay rich) aggregates within the soil. Given the importance of clays as cation exchange sites for alkalis, it is possible that these contribute to proportionately greater sodium and potassium relative to calcium. However, the differences are small, and the populations overlap.

4.5 Saturation Period

The analysis of the estimated bicarbonate from the different extraction methods revealed no significant differences between the SAT-C cores that were saturated for 24 and 72 hours, indicating that no additional mineral dissolution occurred over this period. However, for SAT-C samples saturated over 72 hours, the relationship between direct measures of alkalinity and charge balance broke down for the Glensaugh site. This suggests that a 24-hour saturation period yields more reproducible results than longer saturation durations using the SAT-C method.

4.6 Prospects of the SAT-C method

While this paper has dealt with SAT-C as an alternative to traditional porewater extraction methods, the method can potentially provide additional insights into the physical and chemical properties of the soil important in relation to ERW. Considering that physical soil cores are taken to get the chemical composition of the porewater, the same soil core can be used to measure the ammonium-acetate extractable cations from the exchangeable surfaces of the soil colloids. This is of great importance in an ERW context, as it has been shown that the potential CDR stored on the soil cation exchange sites can be up to an order of magnitude higher than what can be estimated from the soil porewater

(McBride et al., 2025). Furthermore, the boundary conditions of taking a soil cores instead of extracting soil porewater or taking composite soil samples means that physical properties such as the water filled porosity and soil bulk density can be directly constrained from simple measurements done on the cores. Such physical properties are important in estimating the stocks of potential CDR, both in the aqueous and solid phase of the soil. Hence, the SAT-C method intrinsically offers parameters necessary for scaling the measurements of mineral dissolution products from the cores to the field scale.

5 Conclusion

Soil porewater extracted using the SAT-C method produced similar estimated bicarbonate concentrations as compared to rhizon samplers, across two different soil types. Porewater was extracted from two different ERW trials in Scotland (Dumyat and Glensaugh), using two traditional extraction methods: Rhizon samplers and suction lysimeters, as well as soil cores that were saturated for 24 and 72 hours, prior to centrifugation. Conservative cations and anions from all soil porewater samples were used to calculate an estimated bicarbonate concentration. The estimated bicarbonate concentrations from both SAT-C groups were not significantly different from each other or the rhizon groups, across both sites and treatments. The basalt-amended lysimeter group from Dumyat was significantly different from the amended rhizon group and SAT-C cores that were saturated for 24 hours. Regression analysis between total alkalinity and the charge balance between major conservative cations and anions revealed significant linear relationships for the rhizon groups and the SAT-C cores that were saturated for 24 hours, across both sites. Overall the SAT-C method alleviates some of the limitations during low soil moisture periods of traditional porewater extraction methods, while producing realistic concentrations of the readily leachable mineral dissolution products in soil porewater.

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Competing interests
The authors have the following competing interests: Kirstine Skov, Anežka Radková, Kitty Agace, Talal Albahri, Tzara Bierowiec, Giulia Cazzagon, Chieh-Jhen Chen, Declan DeJordy, Amy Frew, Sophie Harrity, Matthew Healey, Lucy Jones, Jim Mann, Callum Mitchell, Amanda Stubbs, Rosalie Tostevin, Will Turner, Peter Wade, Morven Wilkie and XinRan Liu all currently work or have recently worked (i.e. within the last 6 months) at UNDO Carbon Ltd.

Mike E Kelland and Amy L McBride are independent consultants for UNDO Carbon Ltd.

Jim Mann is the founder and CEO of UNDO Carbon Ltd.

David Manning is part of UNDO Carbon Ltd's scientific advisory board.

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Matt Aitkenhead, David Boldrin, Malcolm Coull, Kenneth Loades, Jason Owen declare no conflict of interest. This does not alter our adherence to policies on sharing data and materials within this study.

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Supplementary Information

Table S1 - Measured rock mineralogy, accompanied by log-dissolution rate constants for the acidic (H^+) and neutral (H_2O) dissolution rate mechanisms at 25˚C for the two feedstock materials used in this study: Hillend applied at Dumyat and Pitcaple applied at Glensaugh. Rate constants are according to general dissolution rate equations set out in Palandri and Kharaka (2004), with dissolution rate constants also taken from Palandri and Kharaka (2004). All data for the Hillend basalt can be found in McBride et al. (2025).

Mineral	Formula	Mineral, wt.%		Rate Constant, A (H^+)	Rate Constant, A (H_2O)
		Hillend	Pitcaple		
Fast weathering minerals					
Plagioclase Feldspar	$(Ca,Na)(Al,Si)_4O_8$*	43.8	48	-7.87	-10.91
Pyroxene	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$*	18.7	7.2	-6.82	-11.97
Ilmenite	$FeTiO_3$	3.8	2.6	-8.35	-11.16
Amphibole	$(Ca,Na)_2(Mg,Fe)_5(Al,Si)_8O_{22}(OH)_2$	0	12.1	-7.00	-10.30
Magnetite	Fe_3O_4	3.6	0	-8.59	-10.78
Total fast weathering		**69.9**	**69.9**		
Slow weathering minerals					
Chlorite	$(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	6.4	3.9	-12.71	-14.41
Smectite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	5.2	0.9	-12.71	-14.41
Quartz	SiO_2	7.5	5.9	-13.99	-16.29
Total slow weathering		**19.1**	**10.7**		
Unknown dissolution rate					
Amorphous	Variable	6.8	15		-
Illite+Mica	$K_{0.9}(Al,Fe,Mg)_2(Si_4O_{10})(OH)_2$	4.1	4.3		-
Total unknown		**10.9**	**19.3**		

[1]Plagioclase is identified as andesine in the Pitcaple ($Na_{0.7\text{-}0.5}Ca_{0.3\text{-}0.5}Al_{1.3\text{-}1.5}Si_{2.7\text{-}2.5}O_8$), and Labradorite ($Na_{0.5\text{-}0.3}Ca_{0.5\text{-}0.7}Al_{1.5\text{-}1.7}Si_{2.5\text{-}2.3}O_8$) in the Hillend basalt.

[2]Pyroxene identified as Augite through XRD in the Hillend sample, but a specific mineral was not distinguished in the Pitcaple.

Table S2 – A comparison of whole-rock elemental chemistry, as determined from x-ray fluorescence analysis, as well as surface area (obtained using 5-point Brunauer-Emmett-Teller (BET) methodology N_2-adsorption analysis) and mean particle size (from laser particle size analysis) for materials used in this study. All data, for the Hillend basalt, with the exception of the Mean particle size, can be found in McBride et al. (2025) (preprint). E_{pot} was calculated using the formula provided in Renfort, 2019.

Parameter		Unit	Hillend	Pitcaple
Oxide	Al_2O_3	Wt.%	13.53	18.96
	BaO		0.04	0.05
	CaO		8.62	10.1
	Cr_2O_3		0.01	0.01
	Fe_2O_3		13.73	9.99
	K_2O		1.11	0.86
	MgO		5.98	4.89
	MnO		0.18	0.15
	Na_2O		2.59	2.49
	P_2O_5		0.29	0.34
	SO_3		0.34	0.2
	SiO_2		50.41	49.44
	SrO		0.06	0.04
	TiO_2		2.32	1.66
	XRF total		100.75	100.55
E_{pot} (maximum theoretical CDR)		tCO_2 $tRock^{-1}$	0.28	0.29
BET surface area		$m^2 g^{-1}$	0.917	1.75
Mean particle size		µm	1279	567

Table S3 - Limits of detection of NIST certified standard and quality control solutions for calibrating Perkin Elmer AVIO 500 ICP-OES. Multi-point calibrations are plotted by diluting the top standard and two levels of quality control solution are run. QC solutions are run at the beginning and end of every run and every 20 samples in between. Standards are matrix matched to the samples as much as possible. LODs were previously calculated by using 3 * standard deviation of 10 blanks analyses. Calibrations are plotted by diluting the top standards to: 1/10th, 1/5th, 3/5th, 4/5th and top standard. The Top QC is run along with a 1/5th dilution QC solution.

Element	Instrument LOD mg/L	Top Standard Concentration mg/L	Top QC Concentration mg/L
Al	0.01	20	15
B	0.01	20	15
Ca	0.002	20	15
Cd	0.0008	3	2
Co	0.001	3	2
Cr	0.0005	3	2
Cu	0.001	3	2
Fe	0.0005	20	15
K	0.04	20	15
Mg	0.001	20	15
Mn	0.0003	20	15
Mo	0.0006	3	2
Na	0.02	20	15
Ni	0.001	3	2
P	0.02	20	15
Pb	0.008	3	2
S	0.02	20	15
Si	0.003	20	15
Zn	0.0004	3	2

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