

Field Study of Ground Rock and Compost Amendments for Climate Change Mitigation at a Sonoma Dairy Farm

Caroline H. H. Combs

ABSTRACT

Climate change mitigation pathways include possible carbon dioxide removal strategies, one of which is enhanced weathering (EW). Theoretically, finely ground silicate rock applied to agricultural land can react with atmospheric carbon dioxide (CO₂) to produce inorganic carbon (IC) compounds that can result in long-term atmospheric CO₂ removal if the IC is transported to the ocean via leachate. However, field studies are needed to determine the efficacy of EW in the real world. We tested the effect of amending a field at a dairy farm in Sonoma County, CA with ground rock and compost amendments by measuring soil total carbon (TC) and IC content at the beginning and end of two growing seasons using elemental analyses of soil samples, and soil inorganic nitrogen concentrations weekly for one growing season. The first growing season was a drought year (273.1 mm precipitation) and the second growing season was non-drought (605.1 mm precipitation). This difference in precipitation played an important role in soil TC gains at the end of each growing season: TC and IC increased only over the course of the non-drought growing season under the ground rock treatment and the compost plus ground rock treatment respectively. However, there was no difference in TC and IC between the treatments and control for either growing season. This suggests that EW products may have leached out of the soil, that EW may occur at longer timescales than that of our experiment, or that EW is ineffective in this ecosystem. The nitrate concentrations measured during the non-drought growing season were lower under the ground rock treatment than under the control during the middle third of the growing season when nitrate concentrations were peaking for all treatments. Our results raise questions about the short-term efficacy of ground rock amendments and suggest that ground rock may inhibit the process of nitrification in soils or lead to high nitrate leaching.

KEYWORDS

Carbon dioxide removal, carbonate, basalt, agriculture, California

INTRODUCTION

The global average atmospheric CO₂ concentration has increased from the pre-industrial level of 280 ppm to the current level of 420 ppm (Tans and Keeling 2023, accessed 3/23/23) as a product of human activities, primarily fossil fuel combustion from the industrialized world (Ekwurzel et al. 2017). Most projected pathways to limit global warming require the use of some CO₂ removal (CDR) technology (IPCC 2018) in addition to reducing emissions. Although CDR is only part of the solution (Gasser et al. 2015), it may be useful as part of a portfolio of actions to lessen the severity of climate change (National Research Council 2015).

One CDR technology that shows promise is enhanced weathering (EW, IPCC 2022). Enhanced weathering as a climate change solution is based on the effects of natural chemical weathering of rocks. The reaction of silicate and carbonate minerals with aqueous CO₂ is a natural part of the carbon (C) cycle that has been removing CO₂ from the atmosphere at slow rates for eons (Hartmann et al. 2013) and is balanced over geologic timescales by the addition of CO₂ from volcanic eruptions (Renforth and Campbell 2021). Enhanced weathering increases the rate constant of this mechanism by crushing silicate minerals to small particle sizes to create a larger reactive surface area (Cipolla et al. 2021a). This material is then applied in a fine layer over the land surface where it can potentially enhance weathering rates.

Agricultural land has been proposed as an ideal surface for EW to occur for three main reasons. First, EW requires water because the minerals react with aqueous CO₂, and croplands are irrigated or located in places with sufficient rainfall (Strefler et al. 2018). Agricultural soils also have high concentrations of CO₂ from microbial and root respiration (Beerling et al. 2018) to react with the minerals. Second, application of ground silicate rock can improve the fertility of soils. These minerals contain nutrients that are depleted in intensively farmed lands, like silica (Beerling et al. 2020), phosphorous, and potassium (Lewis et al. 2021), and can act as fertilizer (Hartmann et al. 2013, Beerling et al. 2018). An additional benefit is that if the fertilization effect of the ground minerals increases crop production, they may sequester additional C because of the increased plant growth (Goll et al. 2021). Third, the necessary equipment and infrastructure to apply ground rock to agricultural land already exist, because farmers commonly add amendments like lime to their soils (Beerling et al. 2018). Enhanced weathering has been tested and modeled in lab studies and small-scale pilot trials but not in long-term field experiments at scale (Beerling et al. 2018, Cipolla

et al. 2021b). Many models of EW also do not include important agricultural processes and feedbacks that could impact the chemical reactions of EW (Taylor et al. 2017).

The presence of organic matter amendments such as compost could theoretically increase the climate change mitigation potential of EW because it enhances soil water-holding capacity and releases H^+ as it decomposes, thereby reducing soil pH. Low pH increases weathering rates (Cipolla et al. 2021b) and moisture is necessary for the EW reaction to occur.

In this study, we examined the effects of adding ground rock and compost to a silage field on soil C sequestration and nutrient cycling in the soil. We aimed to determine how total carbon (TC) and inorganic carbon (IC) changed in the soil under the different treatments from the beginning to the end of the growing season. We hypothesized that TC would be higher at the end of the growing season for the plots with ground rock and ground rock plus compost than for the control plots due to the effect of EW and soil organic C derived from the organic amendment. We hypothesized that the percent of IC in the soil that was treated with ground rock would be higher than the soils that have only been amended with manure due to formation of bicarbonate and carbonate from EW. We also examined concentrations of inorganic nitrogen (N) in the soil. We hypothesized that inorganic N will be higher in the compost plus ground rock plots throughout the growing season given compost's performance as a slow-release fertilizer. We hypothesized that ammonium (NH_4^+) and nitrate (NO_3^-) concentrations would be higher in all plots at the beginning of the growing season, but both would decrease with time due to microbial and plant uptake and leaching throughout the growing season.

METHODS

Study site

The scientists in the Silver Lab (University of California, Berkeley) conducted our study at an organic dairy farm in Sonoma County, California. The farm is located in a coastal grassland that experiences a Mediterranean climate, with clay loam and fine sandy loam soils. We used a field that was fertilized with liquid manure, disked, and planted with rye wheat annually after the first rains of the winter. The field was rain-fed and the crop was harvested in late spring or early

summer. During the first year of our data collection, the field received 273 mm of precipitation between 8/16/20 (the first rain of the growing season) and 3/19/21 (the last rain before our sample collection). In the second year of data collection, the field received 605 mm of precipitation between 9/19/21 (the first rain of the growing season) and 5/4/22 (the last rain before our sample collection) (NOAA station USCAMR0009, Petaluma 10.1 W, CA, US).

Soil amendments

In October 2019, nine 15 m x 100 m experimental plots were established. The nine plots extended radially outward from a central point (Figure 1), which was likely to capture patterns in soil spatial heterogeneity. At the dairy farm, soils were amended two to three times with liquid manure prior to seeding as a standard method of fertilization.

In October 2020, after manure fertilization, we amended three of the plots with ground silicate rock (GR), and three with both ground silicate rock and compost (CGR) (Table 1). The three control plots only had manure (M) applied to them. The ground rock consisted of meta-basalt that was high in potassium and silicon and low in toxic metals from Ione Mine (Specialty Granules, Inc, Amador County, California). We used compost from West Marin Compost (Marin County, California) that consisted of recycled yard trimmings, dairy manure, and horse manure. These amendments were only applied once.

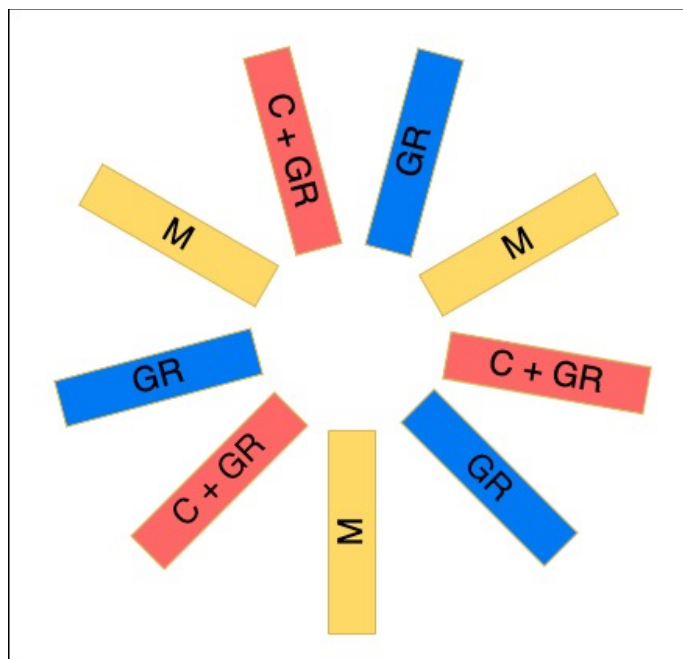


Figure 1. Treatment plot layout. C+GR is compost and ground rock, GR is ground rock, and M is manure (control). The plots are laid out in a radial distribution and the treatments alternate around the circle, to minimize the effect of hydrological or ecological difference between the sides of the field. The radial distribution allows us to capture more spatial variability.

Table 1. Concentrations of amendments.

Treatment	Number of plots	Application rate (US tons per acre)
Compost + Ground Rock	3	Compost: 4.08 Ground Rock: 22.42
Ground Rock	3	Ground Rock: 22.42
Control (Manure)	3	N/A

Soil collection

For soil C analyses we collected soil samples from the nine plots at the beginning (November or February) and end (March or May) of the growing seasons. Soils were collected with augers (AMS 417.04, American Falls, Idaho, USA) at 10 cm depth intervals from 0 to 30 cm of depth at the beginning and end of two growing seasons (see Table 2 for details). We placed each sample in a labelled Ziploc bag and transported them to the lab, where they were left open to dry.

Table 2. Soil collection for carbon analysis.

Growing season year	Collection date	Collection time	Sample collection depth	Number of samples per depth	Number of samples per treatment
2020 - 2021	November 23, 2020	t1	0-10, 10-20, 20-30 cm	3	9
	March 24, 2021	t2	0-10, 10-20, 20-30 cm	3	9
2021 - 2022	February 2, 2022	t3	0-10, 10-20, 20-30 cm	3	9
	May 9, 2022	t4	0-10, 10-20, 20-30 cm	15	45

At the beginning of each growing season, we also dug three pits (one per treatment) from whose walls we collected cored soils samples to determine soil bulk density and soil properties. For inorganic nitrogen analysis, we collected weekly 0-10 cm depth soil samples during the second growing season with an auger ($n = 3$ per treatment). These samples were placed into labelled Ziploc bags, which were kept closed until we processed them in the lab within 24 hours of collection.

Total and inorganic carbon analysis

After soils were air-dried, we sieved them (2 mm mesh) with a shaker (W.S. Tyler RX-812, Mentor, OH, USA). We used forceps to pick out all the visible organic matter and the rocks that did not pass through the sieve with tweezers. We weighed the sieved mineral soil, roots, and rocks to the nearest hundredth of a gram. We then ground a spoonful of each sample (SPEX Samples Prep Mixer Mill 8000D, Metuchen, New Jersey, USA). We weighed approximately 10 g of soil and dried it in a convection oven (Lindberg / Blue M GO1350A, Asheville, NC, USA) at approximately 105°C for five days. We determined the ground soil moisture content by the difference between the pre and post oven weight. We used the soil moisture ratio (g H₂O/g sieved soil) to correct the raw soil C content obtained by the elemental analyzer (see below) and express C content over dry-mass soil.

For soil TC analysis, we used elemental analysis (Carlo Erba Elentech, Lakewood, New Jersey, US) using atropine as our C standard. We created calibration curves with different masses of atropine and corroborated linearity by running the standard after every 10 samples. For soil IC analysis, we used controlled combustion under different temperatures (Elementar soliTOC cube,

Ronkonkoma, New York, USA) using a sandy soil standard (0.37% TOC, 0.09% TIC), a silty soil standard (1.5% TOC, 0.3% TIC), and a control standard (2.0% TOC, 2.0% TIC) (Elemental Microanalysis, Okehampton, Devon, UK).

Equivalent soil mass calculations

To determine C stocks in the soils under each amendment, we used the equivalent soil mass (ESM) method, which uses a consistent reference mass of mineral soil to compare changes in elemental stocks over time (Wendt and Hauser 2013). We chose to express our soil C in units of ESM rather than at fixed depths because the latter relies on soil bulk density, which can change over time (Haden et al. 2020). Using ESM requires determining the cumulative mineral soil mass per unit area at different depths in the soil profile and fitting that to a cubic spline model. We performed these calculations in an Excel spreadsheet provided by Wendt and Hauser (2013). We express TC content in units of Mg C ha^{-1} . We used the spreadsheet to convert TC in units of ESM. To calculate IC in units of ESM, we multiplied the TC in units of ESM by the ratio of the percent IC to percent TC.

Inorganic nitrogen analysis

We measured NH_4^+ and NO_3^- concentrations after extracting 15 g of fresh soil that were shaken with 75 mL of 2 M KCl for one hour. We filtered the contents through 2M KCl-pretreated filters. We stored the samples in sample cups in a freezer at -20°C , and then analyzed them on a colorimetric discrete analyzer (Seal Analytical Inc. AQ300, Mequon, WI, USA). This instrument determined NO_3^- concentration as the sum of NO_3^- and nitrite (NO_2^-) by cadmium reduction using the Griess-Ilosvay method and determined NH_4^+ concentration by the indophenol blue method (Mulvaney 1996). We expressed inorganic nitrogen concentrations as $\mu\text{g N per gram of dry soil}$ ($\mu\text{g N}\cdot\text{g}^{-1}$).

Statistical analysis

We used Student T-Tests to compare differences in the amount of total C at any two time points (t1 vs t2, t2 vs t3, t3 vs t4, and t1 vs t4) within each treatment (GR, CGR, and control) and depth (0-10 cm, 10-20 cm, 20-30 cm, and cumulatively from 0-30 cm). We used analysis of variance (ANOVA) to compare differences in the amount of TC between the three treatments at each time point (t1, t2, t3, and t4) and at each depth. We repeated these tests for IC. We used ANOVA to compare the concentrations of inorganic N species among the three treatments at each weekly sampling timepoint and used Tukey's Honestly Significant Difference (Tukey's HSD) as a means separation test when the ANOVA was significant. We performed our statistical analysis using R version 4.2.1.

RESULTS

Total carbon by depth, treatment, and time

Soil TC content decreased with soil depth under all treatments with mean values ranging from 45-65 Mg C ha⁻¹ (0-10 cm), 28-45 Mg C ha⁻¹ (10-20 cm) and 10-30 Mg C ha⁻¹ (20-30 cm) (Figure 2). When comparing the mean TC content from the beginning and end of each growing season, we only observed significant temporal differences for the GR treatment during the second growing season at 10-20 cm, 20-30 cm, and cumulative 0-30 cm depths (Table 3, Figure 3). However, when comparing the TC content over the course of the two combined growing seasons (t1 to t4), the TC gain was statistically significant within each treatment (CGR, GR, and the control) at selected soil depths (Table 4). There were no statistically significant differences in the amount of TC over time between t1 and t2 or between t2 and t3 for any of the two treatments and control at any of the three measured depths or cumulatively for all depths.

Table 3. Mean TC values for t3 and t4. Mean TC \pm standard error for t3 and t4 with statistically significant differences (t-student) between the two time points.

Treatment	Depth	TC at t3 (Mg C/ha)	TC at t4 (Mg C/ha)	P-value
Ground rock	10-20 cm	35.6 \pm 1.6	45.2 \pm 1.64	0.005
Ground rock	20-30 cm	21.5 \pm 0.787	29.3 \pm 1.27	< 0.001
Ground rock	0-30 cm	109.6 \pm 5.20	135.1 \pm 4.63	0.011

Table 4. Mean TC values for t1 and t4. Mean TC \pm standard error for t1 and t4 with statistically significant differences (t-student) between the two time points.

Treatment	Depth	TC at t1 (Mg C/ha)	TC at t4 (Mg C/ha)	P-value
Control	0-10 cm	53.2 \pm 0.960	59.1 \pm 2.01	0.019
Compost + Ground rock	0-10 cm	48.8 \pm 1.21	61.3 \pm 2.51	< 0.001
Compost + Ground rock	10-20 cm	35.2 \pm 1.18	45.7 \pm 2.17	< 0.001
Compost + Ground rock	0-30 cm	105.9 \pm 3.13	137.4 \pm 6.03	< 0.001
Ground rock	10-20 cm	31.8 \pm 3.23	45.2 \pm 1.58	0.033

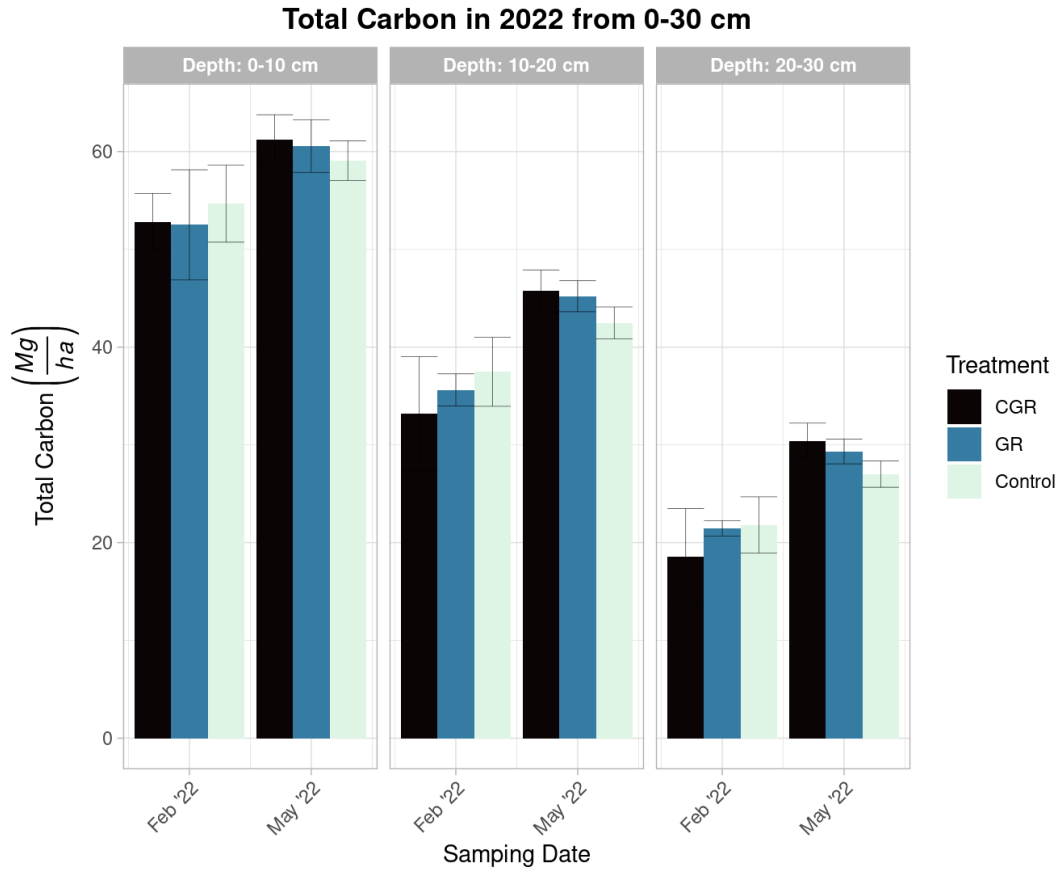


Figure 2. Total C in 2022 from 0-30 cm. Concentrations of TC in megagrams per hectare at the beginning and end of the growing season 2022. Error bars show the standard error of the measurements.

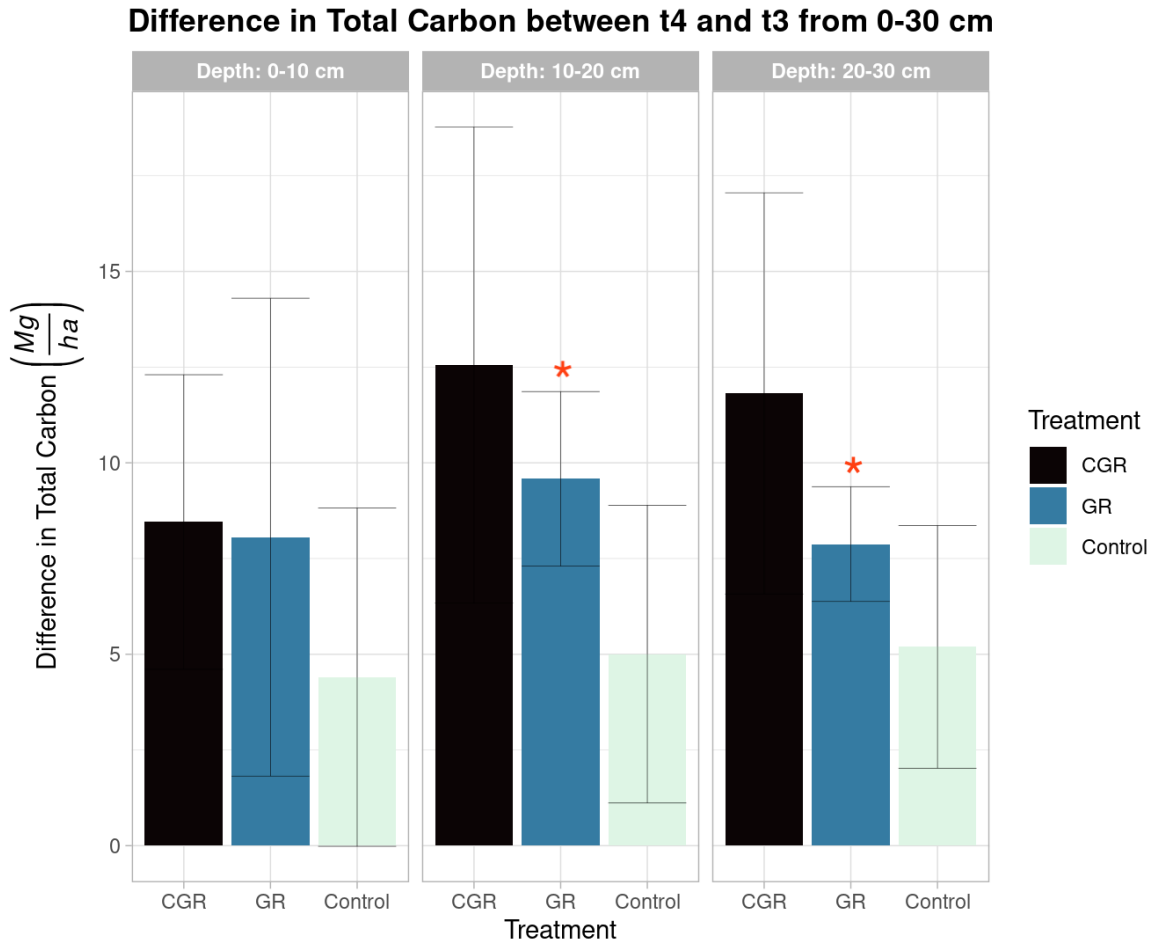


Figure 3. Differences in TC between the beginning and end of the growing season in year 2 (0-30 cm depth). Differences (t4 – t3) in total carbon in megagrams per hectare between the end (5/9/22) and the beginning (2/2/22) of the growing season 2022. Error bars show the propagation error of the calculation. Stars indicate a statistically significant difference (student-t) in the difference in mean TC between t4 and t3 at a particular depth for a particular treatment.

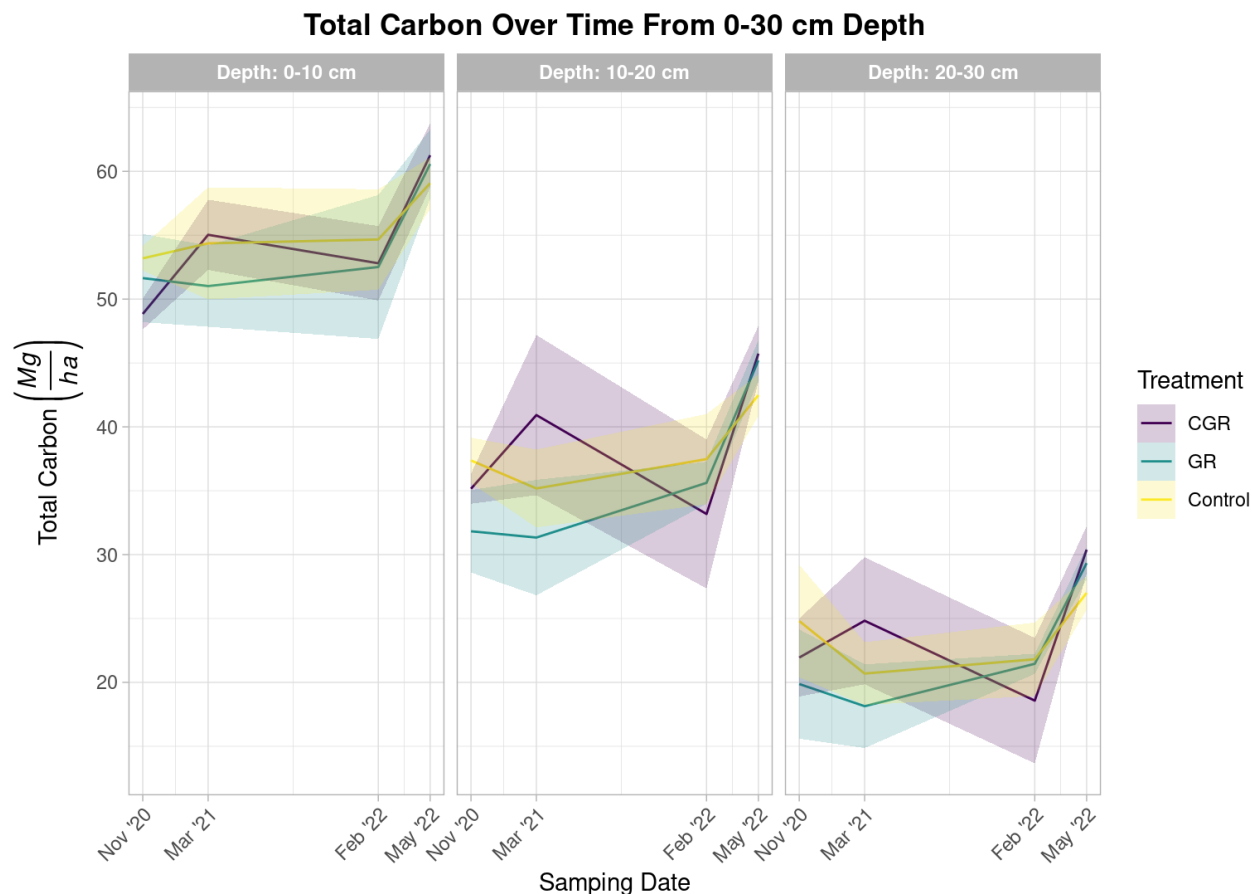


Figure 4. Total Carbon from 0-30 cm. Amount of total carbon in megagrams per hectare at the beginning and end of two consecutive growing seasons. The shaded regions represent the standard error of the measurements.

Inorganic carbon by depth, treatment, and time

As with TC, soil IC decreased with depth (Figure 5). Soil IC represented less than 1% of TC. When comparing the mean IC content from the beginning and end of each growing season within each treatment, in this case we only observed significant temporal differences for the CGR treatment during the second growing season at 10-20 cm and cumulative 0-30 cm depth (Figure 6, Table 5). We calculated the IC gained during the second growing season ($t_4 - t_3$) in the CGR treatment and found a mean total gain of $0.52 \pm 0.17 \text{ Mg IC ha}^{-1}$. Over the course of the two combined growing seasons (t_1 to t_4), mean soil IC increased significantly in at least one depth (Table 6) of the amended plots (CGR and GR) and did not change significantly at all under the control. A Student T-test did not find any statistically significant differences in the amount of IC over time between t_1 and t_2 or between t_2 and t_3 for any of the two treatments and the control at

any of the three measured depths. There were no statistically significant differences in IC between the two treatments and the control at any depth for each timepoint did not find any.

Table 5. Mean IC values for t3 and t4. Mean IC \pm standard error for t3 and t4 with statistically significant differences (t-student).

Treatment	Depth	IC at t3 (Mg IC/ha)	IC at t4 (Mg IC/ha)	P-value
Compost + Ground rock	10-20 cm	0.536 \pm 0.0289	0.738 \pm 0.0513	0.004
Compost + Ground rock	0-30 cm	1.68 \pm 0.0328	2.20 \pm 0.169	0.009

Table 6. Mean IC values for t1 and t4. Mean IC \pm standard error for t1 and t4 with statistically significant differences (t-student).

Treatment	Depth	IC at t1 (Mg IC/ha)	IC at t4 (Mg IC/ha)	P-value
Compost + Ground Rock	0-10 cm	0.628 \pm 0.0513	0.822 \pm 0.0706	0.047
Compost + Ground Rock	0-30 cm	1.73 \pm 0.0362	2.20 \pm 0.169	0.016
Ground Rock	20-30 cm	0.427 \pm 0.0403	0.602 \pm 0.0418	0.018

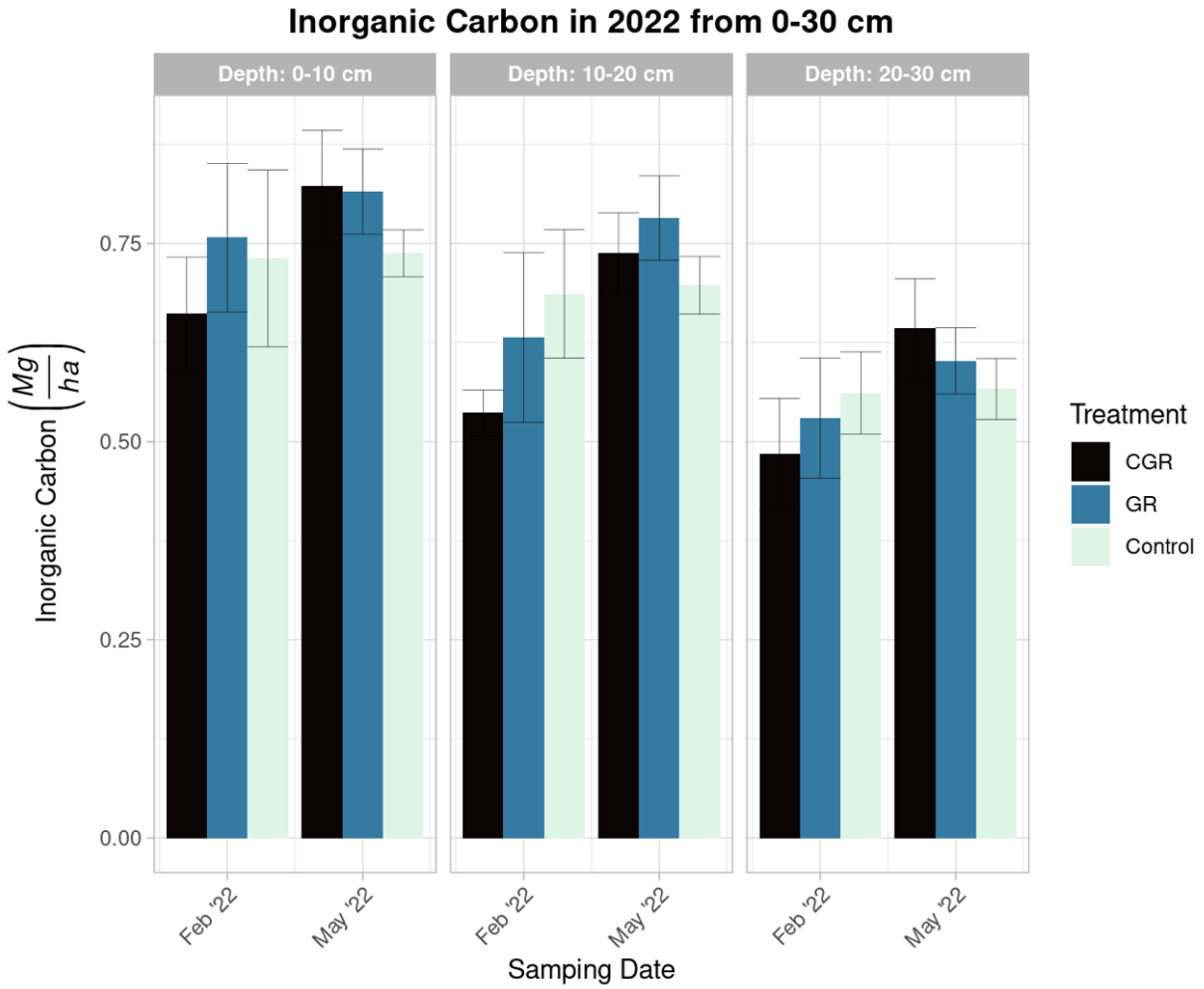


Figure 5. Inorganic Carbon in 2022 from 0-30 cm. Amount of inorganic carbon in megagrams per hectare at the beginning and end of the growing season 2022. Error bars show the standard error of the measurements.

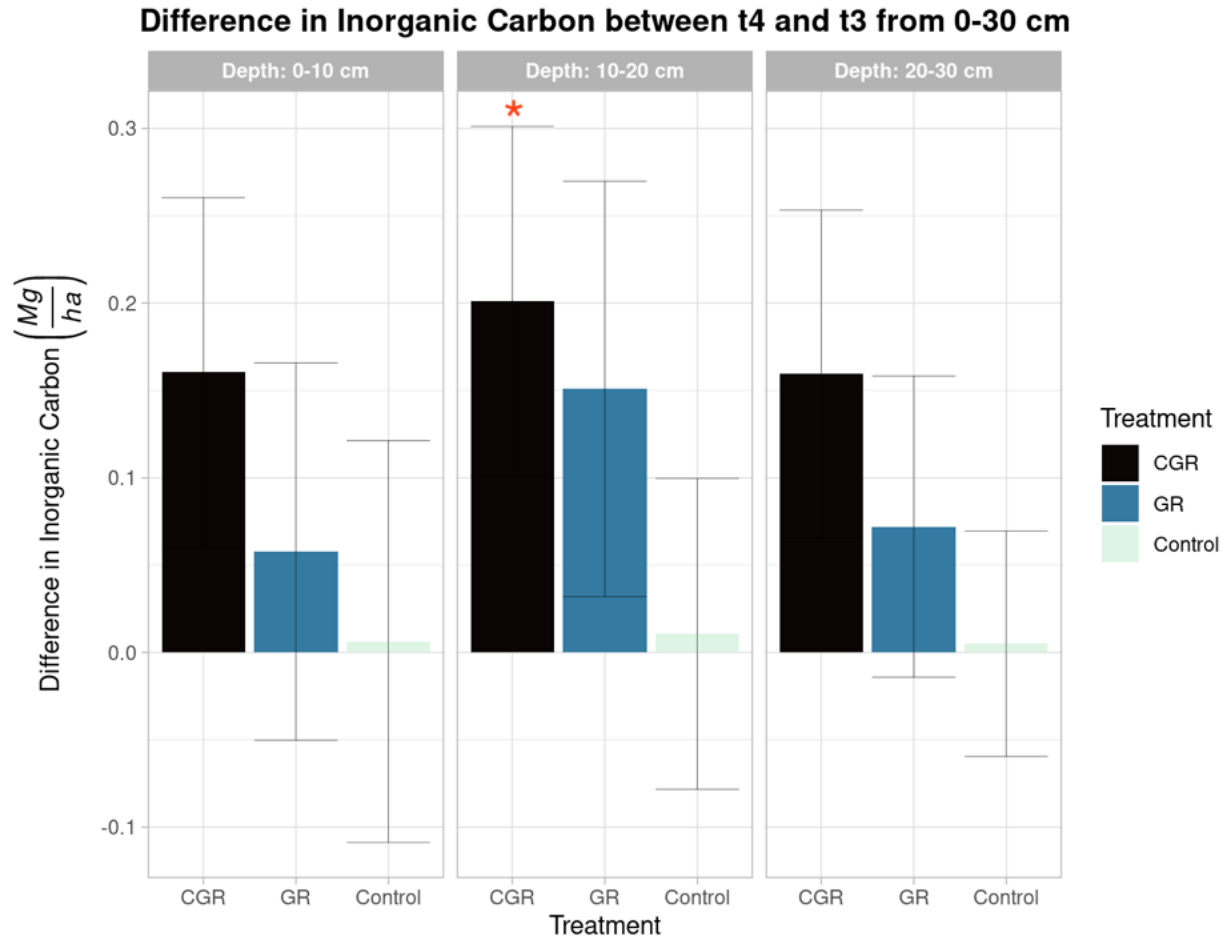


Figure 6. Differences in Inorganic Carbon between t4 and t3 from 0-30 cm. Differences (t4 – t3) in inorganic carbon in megagrams per hectare between the end (5/9/22) and the beginning (2/2/22) of the growing season 2022. Error bars show the propagation error of the calculation. Stars indicate a statistically significant difference (student-t) in the difference in mean IC between t4 and t3 at a particular depth for a particular treatment.

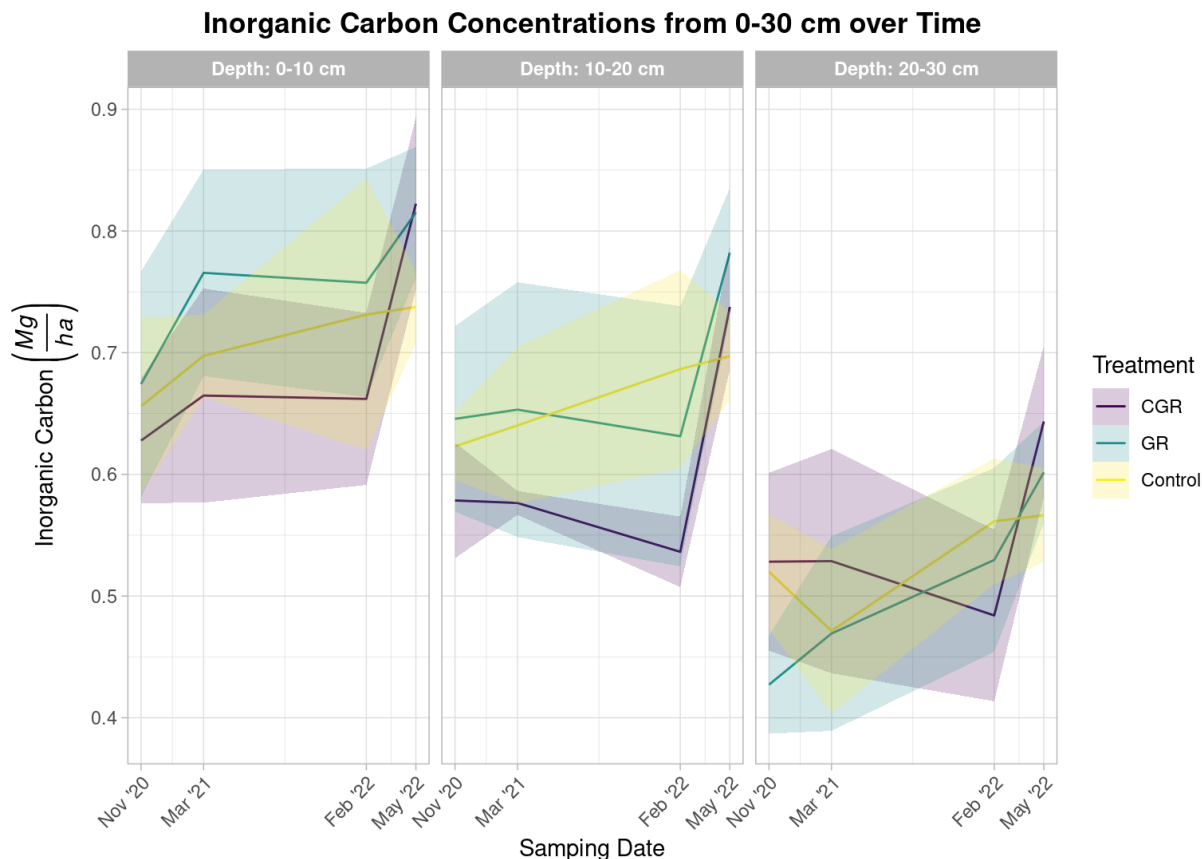


Figure 7. Inorganic Carbon from 0-30 cm. Amount of inorganic carbon in megagrams per hectare at the beginning and end of two consecutive growing seasons. The shaded regions are the standard error of the measurements.

Inorganic nitrogen

Inorganic N species showed temporal anti-correlation throughout the growing season, with a similar overall pattern under both treatments and the control during the measured timepoints of the second growing season. Ammonium concentrations rose and peaked during days 0-50 (with mean peak values ranging from 41 to 53 $\mu\text{g NH}_4^+\text{-N g}^{-1}$); then fell and remained low for the remainder of the growing season (with mean values $< 5 \mu\text{g NH}_4^+\text{-N g}^{-1}$, except for a few small peaks). Nitrate concentrations dropped during days 0-50 (from mean peak values ranging from 39 to 58 $\mu\text{g NO}_3^-\text{-N g}^{-1}$ to mean values below the detection limit of the analytical instrument, $< 0.1 \text{ ppm}$); peaked during days 51-100 (with mean peak values ranging from 25 to 38 $\mu\text{g NO}_3^-\text{-N g}^{-1}$); then dropped again and remained low for the remainder of the growing season (with mean values $< 7 \mu\text{g NO}_3^-\text{-N g}^{-1}$). During days 51-100 of the growing season, nitrate

concentrations peaked under all three treatments, but were significantly lower under the GR treatments than under the control (Table 7).

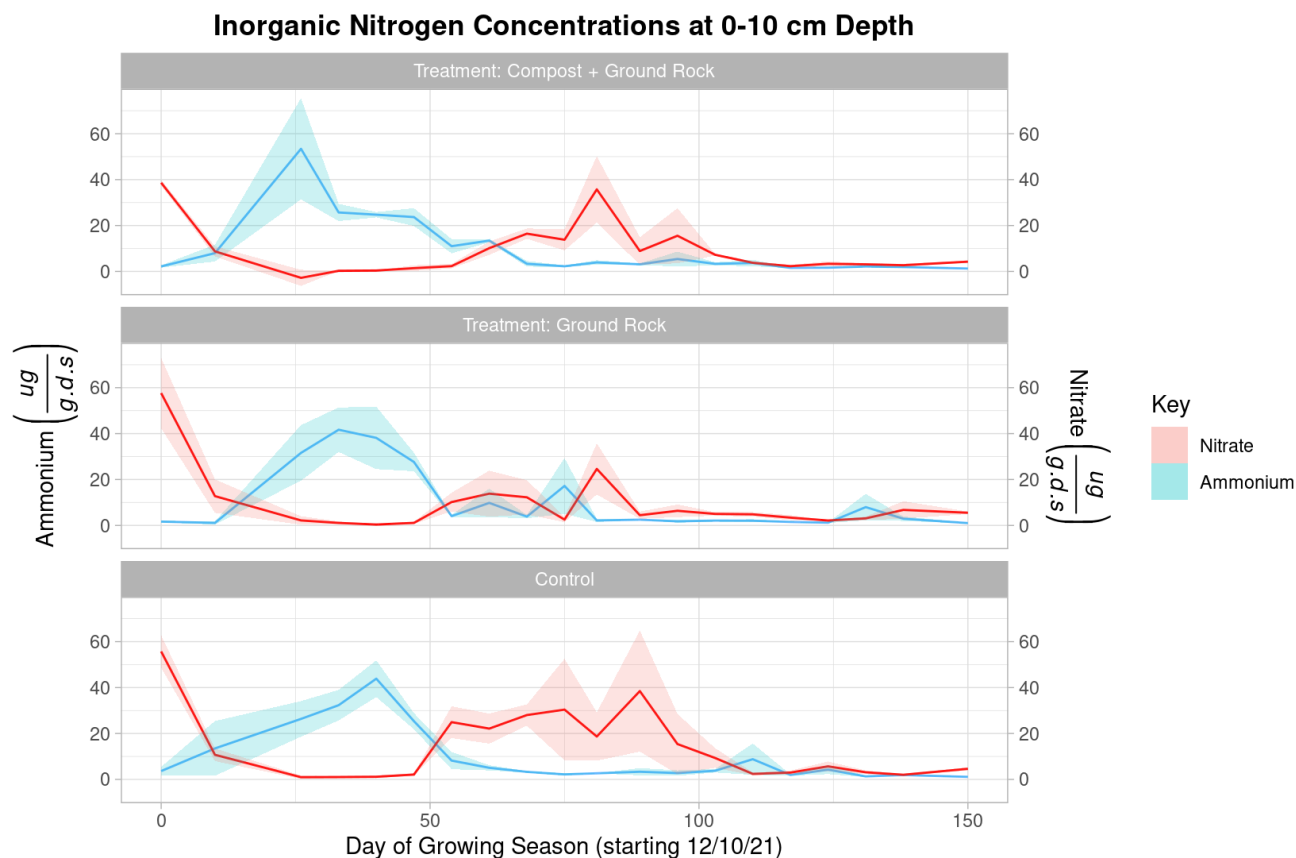


Figure 8. Inorganic Nitrogen concentrations. Concentrations of nitrate (NO_3^-) and ammonium (NH_4^+) in the top 10 cm of the soil from December 10, 2021 to May 9, 2022, measured in micrograms nitrogen per gram of dry soil. The shading shows the standard error of the measurements.

Table 7. Nitrate concentrations. Mean nitrate concentration \pm standard error with statistically significant differences between treatments over periods of days (ANOVA with Tukey’s HSD).

Treatment	Day(s)	Nitrate (ug g^{-1})	P-value
Compost + Ground rock	51-100	14.7 ± 3.28	0.117
Control	51-100	25.4 ± 5.01	
Ground rock	51-100	10.6 ± 2.60	0.019
Control	51-100	25.4 ± 5.01	

DISCUSSION

We found that TC increased significantly under the ground rock treatment over the course of the second growing season. Inorganic C increased significantly under the compost plus ground rock treatment over the course of the second growing season. Inorganic C also increased significantly under the ground rock and the ground rock plus compost treatments from the beginning of the first growing season to the end of the second growing season. The compost plus ground rock treatment and the ground rock treatment had significantly lower dissolved NO_3^- concentrations in the soil than the control in the middle third of the growing season, when NO_3^- was at a peak under all treatments.

Effect of precipitation on enhanced weathering

The fact that we did not find statistically significant differences in soil C (total and inorganic) between the beginning and end of the first growing season within treatments and between treatments relative to the control is attributable to the severe drought conditions experienced in the region during 2020-2021. During the 2020-2021 growing season, Sonoma County received only 273.1 mm total precipitation (NOAA station USCAMR0009, Petaluma 10.1 W, CA, US). We found significant changes in TC in the second growing season (between t3 and t4) only under GR (Table 2), when the farm received more than double the amount of rain as in the first year (605.1 mm). This result allowed us to identify under field conditions the importance of water availability to both enhanced soil organic carbon content and facilitate EW.

Significant increases in IC were found exclusively in the plots under the GR and CGR treatments (Table 3), and only after the second growing season. This result suggests that in the field, EW may only be detectable when water availability is able to facilitate it, as modeling efforts have predicted (Cipolla et al. 2022, Hartmann et al. 2013, Cipolla et al. 2021a). Other modeling and field studies have found that more precipitation leads to more C sequestration (Haque et al. 2020, Cipolla et al. 2022). The lack of significant increase in IC over the first growing season for any treatment is consistent with mesocosm and incubation studies of EW which have found lower C sequestration rates than the theoretical maximum (Buckingham et al. 2022, Amann et al. 2020, Dietzen et al. 2018) and with a field study in Malaysia which found CO_2 removal rates by EW that

were consistent with model predictions in only one out of three pairs of reference and control plots (Larkin et al. 2022). This lower rate could be partially due to suboptimal precipitation levels in the real world, but even after normalizing water flux results, one soil core study found that CO₂ uptake by EW was still 15 times lower than previous mesocosm studies (Buckingham et al. 2022). It is expected that soil, plant, animal, and hydrological interactions will complicate the weathering reaction in the field (Cipola et al. 2021b), but these dynamics are still not entirely understood.

Measurement of inorganic carbon formation

It is important to emphasize that IC at all time points was an order of magnitude lower than TC (Tables 5 and 6), but soluble IC may have leached down into groundwater such that we could not capture it in our measurements (Almaraz et al. 2022). The increase in IC under the CGR and GR treatments indicate that IC is being formed; we cannot say with certainty how much was leached, but at least we can identify changes in the IC soil pool. Methods for studying the effectiveness of the nascent practice of EW in the field have not yet been standardized but measuring dissolved IC (DIC) in soil pore water is likely important to fully understand the fluxes of C in the soil (Almaraz et al. 2022). We also observed more significant increases in IC at deeper soil layers or cumulatively at all soil layers rather than close to the surface (Tables 5 and 6), which could also be evidence that IC is leaching downwards through the soil after being formed at the surface.

Contribution of compost additions to enhanced weathering potential

Compost amendments have been shown to increase TC content in grasslands over timescales longer than one year (Ryals and Silver 2013, Ryals et al. 2015, Flint et al. 2018). Although TC appeared to increase more under CGR than GR between t3 and t4 (Figure 3), the differences were not statistically significant, possibly due to the shorter timescale which was not enough to capture the effect of compost on TC content as found in previous studies. However, IC content increased significantly between t3 and t4 under the CGR treatment from 10-20 cm and cumulatively from 0-30 cm (Table 3). Although IC content only represents a small fraction of TC this difference indicates that the compost amendment increased the potential for EW to occur. This

could be because heterotrophic respiration may be larger in soils with higher organic C content (e.g. soils amended with compost) which will enhance soil CO₂ concentrations which can then react with the ground rock to form IC compounds (Wood et al. 2023). Compost is also effective as a slow-release fertilizer because nutrients derived from organic C decomposition are available continuously throughout the growing season as opposed to mineral fertilizer. Thus, sustained nutrient release allows microbes, plants, and potentially ground rock to enhance soil C pools (Fischer and Glaser 2012, Ryals and Silver 2013). If the compost gives the ground rock a steady and continuous CO₂ source derived from decomposition of organic carbon and root and microbial respiration, the CGR treatment can sequester more carbon than the GR treatment. Although the significant differences were only found at some depths, IC did increase under both the GR and CGR treatments at all depths, while it barely changed under the control at any depth (Figure 6).

The increases in IC were small, and the much larger increases in TC that we observed came from *organic C*. Although the goal of EW is to increase soil IC, it has been speculated that ground rock amendments could also increase soil organic C. Silicate minerals that are added to soils for EW can increase the cation exchange capacity of soils and weather to form clay minerals that adsorb and protect organic matter (Beerling et al. 2018). Basalt minerals added to soils for EW also release nutrients, buffer soil pH, and retain soil water, which would increase plant growth and soil organic matter storage (Goll et al. 2021). Although the intention of EW is not to add organic C to soils, this biotic pathway is still a form of C sequestration that can be important. The results are not clear enough for any definitive conclusions to be drawn, but perhaps with sufficient rainfall and enough time, EW can help sequester C, especially if compost is added along with ground rock, though it may not be as effective as optimistic models have predicted.

Effects of amendments on inorganic nitrogen pools

Weekly sampling during the second growing season allowed us to see the dynamics of the inorganic N species in our agricultural system, which are explained by land management and the mechanisms of N transformation in soils: ammonification, nitrification, dissimilatory nitrate reduction to ammonium (DNRA), and denitrification. For example, the high NO₃⁻ concentrations found at the beginning of the growing season for all plots is related to land management. Over the summer this soil is fertilized with liquid manure, which is rich in reduced N. Once it is in contact

with the soil, nitrifying bacteria oxidize it to NO_3^- (Jamis et al. 1996). Because the soil eventually dries out after the liquid manure application, NO_3^- remains in the soil until the first rains start and it is reduced to nitrous oxide (N_2O) and dinitrogen (N_2) by denitrifying microorganisms under anaerobic conditions (Thomson et al. 2012), reduced to NH_4^+ by DNRA (Silver et al. 2001), or leached to deeper layers of the soils given its large mobility (Cameron et al. 2013). The field experienced heavy precipitation during the first part of the growing season, during which time NO_3^- concentrations decreased by a combination of the aforementioned processes and NH_4^+ concentrations increased correspondingly (Figure 8), likely because of the conversion of NO_3^- to NH_4^+ , proposed as a dominant N transformation pathway in saturated anaerobic soils (Choi and Ro 2003), and also by anaerobic organic matter decomposition (Myrold 2021). The rains abated between days 51-100 of our growing season, during which time NH_4^+ concentrations decreased and NO_3^- concentrations increased correspondingly (Figure 8), likely because nitrification is performed by aerobic chemoautotrophs and is thus a dominant N transformation pathway in dry aerobic soils (Choi and Ro 2003). During this period NO_3^- concentrations peaked several times under all treatments, but the peaks were highest under the control.

The mean concentration of NO_3^- in the middle third of the growing season was significantly lower under GR compared to the control (Table 7). This indicates that ground rock could potentially inhibit nitrification, enhance leaching losses, or lead to greater N-gas losses from soils. Nitrate is a more mobile form of N than NH_4^+ and is easily lost from soil through leaching (Cameron et al. 2013), which is problematic because it reduces productivity in N-limited systems and can lead to pollution of groundwater with NO_3^- (Bijay-Singh and Craswell 2021). However, there is currently no evidence that ground rock increases mobility of NO_3^- in soils. Although it is possible that the lower NO_3^- concentrations may be the result of N-gas losses, there is some evidence that GR can actually inhibit denitrification: a modeling study predicted a 9-16% reduction in fluxes of N_2O from croplands amended with basalt, probably due to increased soil pH, which reduces denitrification, or to immobilization of N by phosphorus (Blanc-Betes et al. 2021). Low NO_3^- concentrations could be caused by the inhibition of nitrification, but this also seems unlikely because ground rock can increase soil pH (Kantola et al. 2017) and nitrification rates are generally (though not always) higher at neutral or slightly alkaline soil pH than acidic (Li et al. 2018). A different explanation for the low NO_3^- in the GR treatment is that an increase in plant growth under

treated plots due to the fertilization effects of GR could have caused more NH_4^+ to be taken up by plants, which would have reduced the amount of available substrate for nitrification.

Unless the ground rock is in fact causing more denitrification, lower concentrations of NO_3^- in soils treated with GR could mean that EW is beneficial for climate change mitigation because of its effect on N_2O in addition to CO_2 weathering. Nitrous oxide is a potent GHG that is produced by the incomplete denitrification of NO_3^- (Thomson et al. 2012). Agriculture in California is a large source of N_2O emissions (California Air Resources Board 2021), so spreading ground rock on agricultural land and reducing NO_3^- concentrations could help to mitigate those emissions. Nitrate is also a more energy-intensive form of N for plants to uptake than NH_4^+ , especially when atmospheric CO_2 concentrations are elevated (Hachiya and Sakakibara 2016), so it is better for plant growth if more of the N in soils is in the form of NH_4^+ . Because no other field studies have examined the effect of ground rock on NO_3^- concentrations in soil, we do not know what the mechanism might be or even if our results are part of a consistent pattern, so future studies are needed to draw more concrete conclusions. Still, the possible reduction of N_2O emissions by ground rock is an exciting avenue for future study.

Limitations and future directions

We designed this study when no other field studies of EW had been published and there was no precedent to build on. Having now completed our study, it is apparent that future studies of EW in agroecosystems could benefit from gathering additional data, such as GHG emissions from the soil surface, which would allow researchers to present a full C balance for the agroecosystem (Almaraz et al. 2022). Measuring these fluxes will be important because the addition of ground rock to soils may increase respiration enough to counteract the effects of CO_2 sequestration (Dietzen et al. 2018). In addition, using lysimeters to measure DIC in the pore water will indicate whether IC products of weathering are successfully leaching into groundwater (Almaraz et al. 2022). Soil EW is also supposed to be a slow process, so long-term monitoring studies may have more opportunity to capture the full extent of carbon sequestration by EW than our two-year study. An unexpected result from this study is the possible effects of ground rock (with and without compost) on nitrification rates, and future studies specifically designed to

quantify nitrification rates in agroecosystems treated with ground rock could help to explore this discovery.

Conclusions

The results from this study indicate that precipitation is necessary for EW to have an effect on agricultural soils in Mediterranean climates, which aligns with model predictions. Soil-based EW may have more variable rates in regions that are subject to stochastic drought; farms that are irrigated may have more potential for C sequestration by EW than rain-fed ones. Ground rock appears to have a negative effect on soil NO_3^- concentrations, and EW should be explored for its potential to mitigate climate change by lowering emissions of N_2O . Future field studies of EW may benefit from measuring DIC in soil water and studying nitrification rates more closely.

ACKNOWLEDGEMENTS

I owe many thanks to the lovely members of the Silver Lab at UC Berkeley who mentored me, answered my questions, and kept up my morale with their encouragement, company, and excellent potluck contributions. In particular, I must thank Whendee Silver for accepting me to her lab and providing me with the opportunity to learn how to do research, and Tibusay Pérez for including me in her field study and spending countless hours guiding me in my research journey. In addition, Gisela Gonzalez Pagán, Zach Schwartz, Tyler Anthony, and Shane Russett taught me how to process samples on our lab instruments. Gisela Gonzalez Pagán, Tibusay Pérez, Charlotte Kwong, Adrienne Seiden, Zach Schwartz, Claire Beckstoffer, Shane Russett, and Jacqueline Gerson collected soil samples from our field site with me. Shane Russett collected and processed the carbon data from the first growing season that I used here in my Results. Kai Nittenberg, Amber Mars Viray, and Diana Lopez Allende helped me to sieve and grind samples during the summer of 2022. I must also thank Dr. Patina Mendez for giving me so much guidance and feedback on my drafts in ESPM 175 and for answering my late-night stressed-out emails. Thank you all so much for your help!

REFERENCES

- Almaraz, M., N. L. Bingham, I. O. Holzer, E. K. Geoghegan, H. Goertzen, J. Sohng, and B. Z. Houlton. 2022. Methods for determining the CO₂ removal capacity of enhanced weathering in agronomic settings. *Frontiers in Climate* 4:970429.
- Amann, T., J. Hartmann, E. Struyf, W. de Oliveira Garcia, E. K. Fischer, I. Janssens, P. Meire, and J. Schoelynck. 2020. Enhanced Weathering and related element fluxes – a cropland mesocosm approach. *Biogeosciences* 17:103–119.
- Beerling, D. J., E. P. Kantzas, M. R. Lomas, P. Wade, R. M. Eufrazio, P. Renforth, B. Sarkar, M. G. Andrews, R. H. James, C. R. Pearce, J.-F. Mercure, H. Pollitt, P. B. Holden, N. R. Edwards, M. Khanna, L. Koh, S. Quegan, N. F. Pidgeon, I. A. Janssens, J. Hansen, and S. A. Banwart. 2020. Potential for large-scale CO₂ removal via enhanced rock weathering with croplands. *Nature* 583:242–248.
- Beerling, D. J., J. R. Leake, S. P. Long, J. D. Scholes, J. Ton, P. N. Nelson, M. Bird, E. Kantzas, L. L. Taylor, B. Sarkar, M. Kelland, E. DeLucia, I. Kantola, C. Müller, G. Rau, and J. Hansen. 2018. Farming with crops and rocks to address global climate, food and soil security. *Nature Plants* 4:138–147.
- Bijay-Singh, and E. Craswell. 2021. Fertilizers and nitrate pollution of surface and ground water: an increasingly pervasive global problem. *SN Applied Sciences* 3:518.
- Blanc-Betes, E., I. B. Kantola, N. Gomez-Casanovas, M. D. Hartman, W. J. Parton, A. L. Lewis, D. J. Beerling, and E. H. DeLucia. 2021. In silico assessment of the potential of basalt amendments to reduce N₂O emissions from bioenergy crops. *GCB Bioenergy* 13:224–241.
- Buckingham, F. L., G. M. Henderson, P. Holdship, and P. Renforth. 2022. Soil core study indicates limited CO₂ removal by enhanced weathering in dry croplands in the UK. *Applied Geochemistry* 147:105482.
- California Air Resources Board. 2021. California Greenhouse Gas Emissions for 2000 to 2019: Trends of Emissions and Other Indicators. Sacramento, CA.
- Cameron, K. C., H. J. Di, and J. L. Moir. 2013. Nitrogen losses from the soil/plant system: a review: Nitrogen losses. *Annals of Applied Biology* 162:145–173.
- Choi, W.-J., and H.-M. Ro. 2003. Differences in isotopic fractionation of nitrogen in water-saturated and unsaturated soils. *Soil Biology and Biochemistry* 35:483–486.
- Cipolla, G., S. Calabrese, L. V. Noto, and A. Porporato. 2021a. The role of hydrology on

- enhanced weathering for carbon sequestration II. From hydroclimatic scenarios to carbon-sequestration efficiencies. *Advances in Water Resources* 154:103949.
- Cipolla, G., S. Calabrese, L. V. Noto, and A. Porporato. 2021b. The role of hydrology on enhanced weathering for carbon sequestration I. Modeling rock-dissolution reactions coupled to plant, soil moisture, and carbon dynamics. *Advances in Water Resources* 154:103934.
- Cipolla, G., S. Calabrese, A. Porporato, and L. V. Noto. 2022. Effects of precipitation seasonality, irrigation, vegetation cycle and soil type on enhanced weathering – modeling of cropland case studies across four sites. *Biogeosciences* 19:3877–3896.
- Dietzen, C., R. Harrison, and S. Michelsen-Correa. 2018. Effectiveness of enhanced mineral weathering as a carbon sequestration tool and alternative to agricultural lime: An incubation experiment. *International Journal of Greenhouse Gas Control* 74:251–258.
- Ekwuzel, B., J. Boneham, M. W. Dalton, R. Heede, R. J. Mera, M. R. Allen, and P. C. Frumhoff. 2017. The rise in global atmospheric CO₂, surface temperature, and sea level from emissions traced to major carbon producers. *Climatic Change* 144:579–590.
- Fischer, D., and B. Glaser. 2012. Synergisms between Compost and Biochar for Sustainable Soil Amelioration. Page in S. Kumar, editor. *Management of Organic Waste*. InTech.
- Flint, L. E., A. L. Flint, M. A. Stern, A. Myer, W. Silver, F. Franco, K. Byrd, B. Sleeter, P. Alvarez, T. Estrada, and D. Cameron. 2018. Increasing Soil Organic Carbon to Mitigate Greenhouse Gases and Increase Climate Resiliency for California.
- Gasser, T., C. Guivarch, K. Tachiiri, C. D. Jones, and P. Ciais. 2015. Negative emissions physically needed to keep global warming below 2 °C. *Nature Communications* 6:7958.
- Goll, D. S., P. Ciais, T. Amann, W. Buermann, J. Chang, S. Eker, J. Hartmann, I. Janssens, W. Li, M. Obersteiner, J. Penuelas, K. Tanaka, and S. Vicca. 2021. Potential CO₂ removal from enhanced weathering by ecosystem responses to powdered rock. *Nature Geoscience* 14:545–549.
- Hachiya, T., and H. Sakakibara. 2016. Interactions between nitrate and ammonium in their uptake, allocation, assimilation, and signaling in plants. *Journal of Experimental Botany*:erw449.
- Haden, A. C., W. H. Yang, and E. H. DeLucia. 2020. Soils' dirty little secret: Depth-based comparisons can be inadequate for quantifying changes in soil organic carbon and other mineral soil properties. *Global Change Biology* 26:3759–3770.
- Haque, F., R. M. Santos, and Y. W. Chiang. 2020. CO₂ sequestration by wollastonite-amended agricultural soils – An Ontario field study. *International Journal of Greenhouse Gas Control* 97:103017.

- Hartmann, J., A. J. West, P. Renforth, P. Köhler, C. L. De La Rocha, D. A. Wolf-Gladrow, H. H. Dürr, and J. Scheffran. 2013. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification: ENHANCED WEATHERING. *Reviews of Geophysics* 51:113–149.
- IPCC. 2018. Summary for Policymakers in Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty.
- IPCC. 2022. Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.
- Jamis, S. C., E. A. Stockdale, M. A. Shepherd, and D. S. Powlson. 1996. Nitrogen Mineralization in Temperate Agricultural Soils: Processes and Measurement. *Advances in Agronomy* 57.
- Kantola, I. B., M. D. Masters, D. J. Beerling, S. P. Long, and E. H. DeLucia. 2017. Potential of global croplands and bioenergy crops for climate change mitigation through deployment for enhanced weathering. *Biology Letters* 13:20160714.
- Larkin, C. S., M. G. Andrews, C. R. Pearce, K. L. Yeong, D. J. Beerling, J. Bellamy, S. Benedick, R. P. Freckleton, H. Goring-Harford, S. Sadekar, and R. H. James. 2022. Quantification of CO₂ removal in a large-scale enhanced weathering field trial on an oil palm plantation in Sabah, Malaysia. *Frontiers in Climate* 4:959229.
- Lewis, A. L., B. Sarkar, P. Wade, S. J. Kemp, M. E. Hodson, L. L. Taylor, K. L. Yeong, K. Davies, P. N. Nelson, M. I. Bird, I. B. Kantola, M. D. Masters, E. DeLucia, J. R. Leake, S. A. Banwart, and D. J. Beerling. 2021. Effects of mineralogy, chemistry and physical properties of basalts on carbon capture potential and plant-nutrient element release via enhanced weathering. *Applied Geochemistry* 132:105023.
- Li, Y., S. J. Chapman, G. W. Nicol, and H. Yao. 2018. Nitrification and nitrifiers in acidic soils. *Soil Biology and Biochemistry* 116:290–301.
- Mulvaney, R. 1996. Nitrogen – Inorganic forms: Chemical Methods. Page Methods of Soils Analysis. Soils Science Society of America, Madison, Wisconsin.
- Myrold, D. D. 2021. Transformations of nitrogen. Pages 385–421 *Principles and Applications of Soil Microbiology*. Elsevier.
- National Research Council. 2015. Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration. Page 18805. National Academies Press, Washington, D.C.

- Renforth, P., and J. S. Campbell. 2021. The role of soils in the regulation of ocean acidification. *Philosophical Transactions of the Royal Society B: Biological Sciences* 376:20200174.
- Ryals, R., M. D. Hartman, W. J. Parton, M. S. DeLonge, and W. L. Silver. 2015. Long-term climate change mitigation potential with organic matter management on grasslands. *Ecological Applications* 25:531–545.
- Ryals, R., and W. L. Silver. 2013. Effects of organic matter amendments on net primary productivity and greenhouse gas emissions in annual grasslands. *Ecological Applications* 23:46–59.
- Silver, W. L., D. J. Herman, and M. K. Firestone. 2001. Dissimilatory Nitrate Reduction to Ammonium in Upland Tropical Forest Soils. *Ecology* 82:2410–2416.
- Strefler, J., T. Amann, N. Bauer, E. Kriegler, and J. Hartmann. 2018. Potential and costs of carbon dioxide removal by enhanced weathering of rocks. *Environmental Research Letters* 13:034010.
- Tans, P., R. Keeling. 2023. Trends in Atmospheric Carbon Dioxide. NOAA. <https://gml.noaa.gov/ccgg/trends/data.html>
- Taylor, L. L., D. J. Beerling, S. Quegan, and S. A. Banwart. 2017. Simulating carbon capture by enhanced weathering with croplands: an overview of key processes highlighting areas of future model development. *Biology Letters* 13:20160868.
- Thomson, A. J., G. Giannopoulos, J. Pretty, E. M. Baggs, and D. J. Richardson. 2012. Biological sources and sinks of nitrous oxide and strategies to mitigate emissions. *Philosophical Transactions of the Royal Society B: Biological Sciences* 367:1157–1168.
- Wendt, J. W., and S. Hauser. 2013. An equivalent soil mass procedure for monitoring soil organic carbon in multiple soil layers. *European Journal of Soil Science* 64:58–65.
- Wood, C., A. L. Harrison, and I. M. Power. 2023. Impacts of dissolved phosphorus and soil-mineral-fluid interactions on CO₂ removal through enhanced weathering of wollastonite in soils. *Applied Geochemistry* 148:105511.