

Enhanced Mineral Weathering

A study of the observed and potential effects on leachate pH and metal concentrations, soil microbial activity, and plant growth.

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Introduction

Weathering is the breakdown of rocks at the Earth's surface by physical, chemical, and biological processes. Rocks are aggregates of one or more minerals, which are naturally occurring inorganic solids. Mineral weathering is therefore a source of dissolved nutrients, such as Si, Al, Fe, Mn, Ca, Na, K, and Mg, and a source of alkalinity through hydrogen carbonate (HCO_3^-) production. As a result of this, mineral weathering is immensely important in offsetting cation losses from leaching and in restoring alkalinity consumed by soil acidification processes^{1,2}. Certain minerals, such as carbonates and silicates, consume carbon dioxide (CO_2) as they weather. Whilst carbonate weathering is a carbon neutral process, more CO_2 is consumed than released in silicate weathering^{3,4,5}.

It is a well-established fact that anthropogenic activity is causing a significant increase in the quantity of greenhouse gases (GHGs) released into the atmosphere, causing climate change. The Intergovernmental Panel on Climate Change has predicted that a global warming of more than 1.5°C by 2100 will cause catastrophic effects, therefore humankind must reduce the quantity of GHGs released and increase the quantity removed from the atmosphere⁶. One widely recognised method for sequestering atmospheric CO_2 is by enhanced mineral weathering (EMW) of silicate minerals.

The concept is to accelerate natural CO_2 -consuming weathering processes by pulverising rock, such as basalt, and distributing the powder across millions of hectares of land, thereby increasing the consumption of atmospheric CO_2 ^{7,8,9}. This enhanced weathering would produce an alkaline leachate which would be carried by rivers into oceans and mitigate ocean acidification^{10,11}. Alongside removing CO_2 from the atmosphere and mitigating ocean acidification, this strategy has the potential to rejuvenate soils, stabilise soil organic matter, conserve fertiliser resources, promote microbial activity, and improve crop yields through the release of mineral dissolution products (such as metal cations and HCO_3^-)^{12,13,14,15}. Therefore, EMW also has the potential to improve food security.

EMW has great potential as a low-cost carbon sequestration method to help mitigate ocean acidification and improve crop yields. It is a worthy area of research, that needs field-scale assessments with detailed environmental monitoring, which this study aims to contribute to. In theory, EMW releases metal cations and HCO_3^- into soil leachate, thus increasing the metal concentrations and pH, it also increases soil microbial activity and plant growth. An experiment was devised with Professor Mark Hodson, of the University of York, Environment and Geography Department, to study and quantify these effects.

Methodology

In theory, the pH of leachate from soil that has been treated with pulverised rock will be higher than the pH of leachate from soil that is untreated due to the release of HCO_3^- by weathering. Furthermore, as EMW is a source of dissolved nutrients, metal cation concentrations in the leachate of the soil treated with pulverised rock will be higher than in leachate from the untreated soil. In addition to this, greater microbial activity and plant growth should be observed in the soil samples treated with pulverised rock.

Pulverised basalt ($\text{CaMgO}_6\text{Si}_2$) was used as the source of mineral weathering because basalt is the most widely distributed basic extrusive rock, therefore it is readily available and relatively cheap¹⁶. For EMW to be a viable geoengineering method utilised to mitigate climate change, the rocks used must be easily accessible to limit the GHGs released during transportation. The rocks must be silicate bearing because the weathering of Ca and Mg-silicate minerals consumes more CO_2 than is released, therefore CO_2 is removed from the atmosphere^{3,4,5}. Basalt is ideal as it has a SiO_2 content ranging from 45% to 52%^{16,17,18}.

Most EMW studies are done in an agricultural setting monitoring crop growth^{12,13,19,20}. This study aims to observe the effects in a more natural habitat, therefore common beech saplings (*Fagus sylvatica*) were utilised to simulate a woodland habitat. To research the proposed effects of EMW four treatment groups were constructed: 1) Soil. 2) Soil with a sapling. 3) Soil with pulverised basalt. 4) Soil with pulverised basalt and a sapling. Each treatment group contains four samples giving an overall sample size of sixteen. To control the samples the same type of pots, commercial topsoil (a silty clay loam), and pulverised basalt was used. Each pot was filled with 4 kg of soil and pots in treatment groups 3 and 4 with an additional 0.3 kg of basalt; this value was based on a typical basalt application rate of 10 kg/m^2 with the surface area of each pot 0.0314 m^2 . Beech saplings of similar size were utilised in the experiment; saplings were measured at the start and the end of the research period to compare any differences in size between saplings grown in a treated vs untreated soil. A graphic depicting the four treatment groups is displayed in Figure 1.

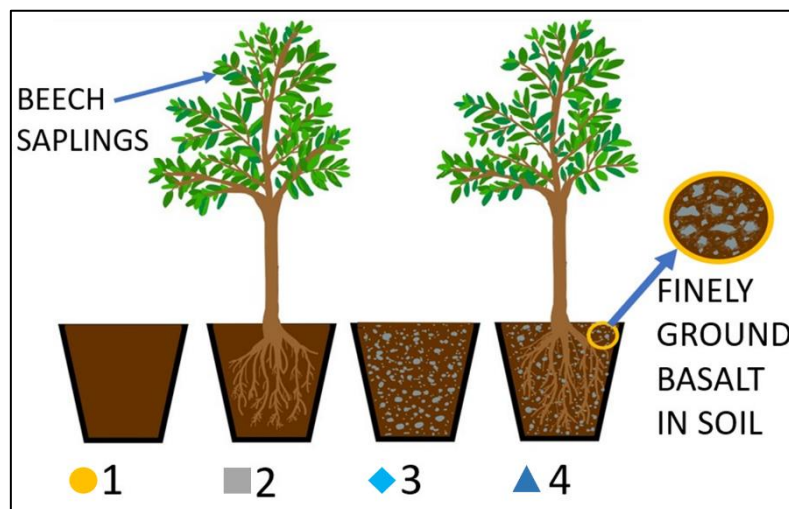
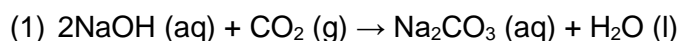


Figure 1: A graphic depicting the four different soil treatment groups. Group 1: soil without any treatment. Group 2: soil with a beech tree sapling planted. Group 3: soil treated with finely ground basalt. Group 4: soil treated with finely ground basalt and with a beech tree sapling planted. These groups allow the proposed effects of enhanced mineral weathering to be observed by comparisons. (The symbols representing each of the groups are repeated in the graphs within the results section for ease of viewing using a colour-blind friendly palette.)

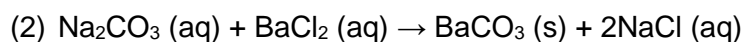
The sixteen samples were watered weekly with 545mL of deionised water and the leachate was collected over the span of four weeks, giving a final leachate sample size of sixty-four. Immediately after collecting the leachate samples a pH meter was used to measure the pH. Three replicates of the measurement were conducted for each sample then a mean calculated; after this the samples were immediately frozen to ensure the metal cation concentrations remained unaffected. At the end of the research period the sixty-four

leachate samples were defrosted and analysed on the ICP-OES at the appropriate dilutions to quantify the concentration of metals present in solution. The metals analysed were Si, Al, Fe, Mn, Ca, Na, K, and Mg. The metal concentrations were calibrated using a multi-element standard with concentrations of 0.25mg/L, 0.5mg/L, 1.0mg/L, 5.0mg/L, and 10.0mg/L; Si was calibrated with a separate set of Si standards at the same concentrations. The measured concentrations of Si, Al, Fe, and Mn fell within a range suitable based on the calibration curves. However, the concentrations of Ca, Na, K, and Mg were too high so after the first analysis the samples were diluted by x50 and run again.

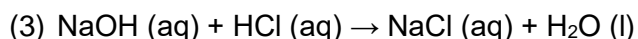
Soil microbial respiration rates were calculated by constructing five soil respirometer flasks: one flask containing a 50g sample of acid-washed sand, and four flasks each containing a 50g moist soil sample from a different treatment group. Soil was collected in the fourth week. Inside each respirometer flask included a 10mL vial of 0.3M NaOH(aq). The five airtight flasks were stored in the dark at room temperature for one week. In theory, the NaOH solution absorbs all the CO₂ released by microbial activity, this is shown in equation 1 below. The CO₂ already present in the airtight containers is accounted for by the sand control respirometer flask.



To quantify the mol of CO₂ reacted with the NaOH solution (released by microbial respiration) a titration with 0.1M HCl (aq) was conducted. In five separate 250mL conical flasks one 10mL NaOH solution sample was mixed with 6 drops of phenolphthalein indicator and 10mL of 1M BaCl₂ (aq). A titration with HCl would not distinguish between NaOH and Na₂CO₃ in solution so barium chloride (BaCl₂) is added to precipitate the carbonate, this is shown in equation 2.



After addition of BaCl₂, HCl is added to the conical flask. The HCl only reacts with the residual NaOH (aq), this is shown in equation 3.



In theory, due to EMW, smaller HCl titration volumes and greater microbial respiration rates should be expected from groups 3 and 4. This method is from Soil Science: Methods & Applications by D J Rowell²¹. The results are displayed in Table 2.

Results

1. Leachate pH

The mean pH values for each treatment group measured weekly are displayed in Figure 2. There is one pH value per group per week which is an average of the pH values of the four samples within each treatment group, and each of those individual sample pH values is an average of three replicates. The large sample size and use of replicates improves the accuracy of this data. Over the four-weeks the leachate pH increased for treatment groups 1 and 3, with a linear equation of $y = 0.083x + 7.09$ and $y = 0.11x + 7.3$ respectively. However, this is a weak trend as the R² value for group 1 is only 0.099; the R² value for group 3 is higher at 0.38. The leachate pH decreased for treatment groups 2 and 4, with a linear

equation of $y = -0.044x + 7.4$ and $y = -0.19x + 7.8$ respectively. The R^2 value for group 2 is 0.037 and for group 4 is 0.31.

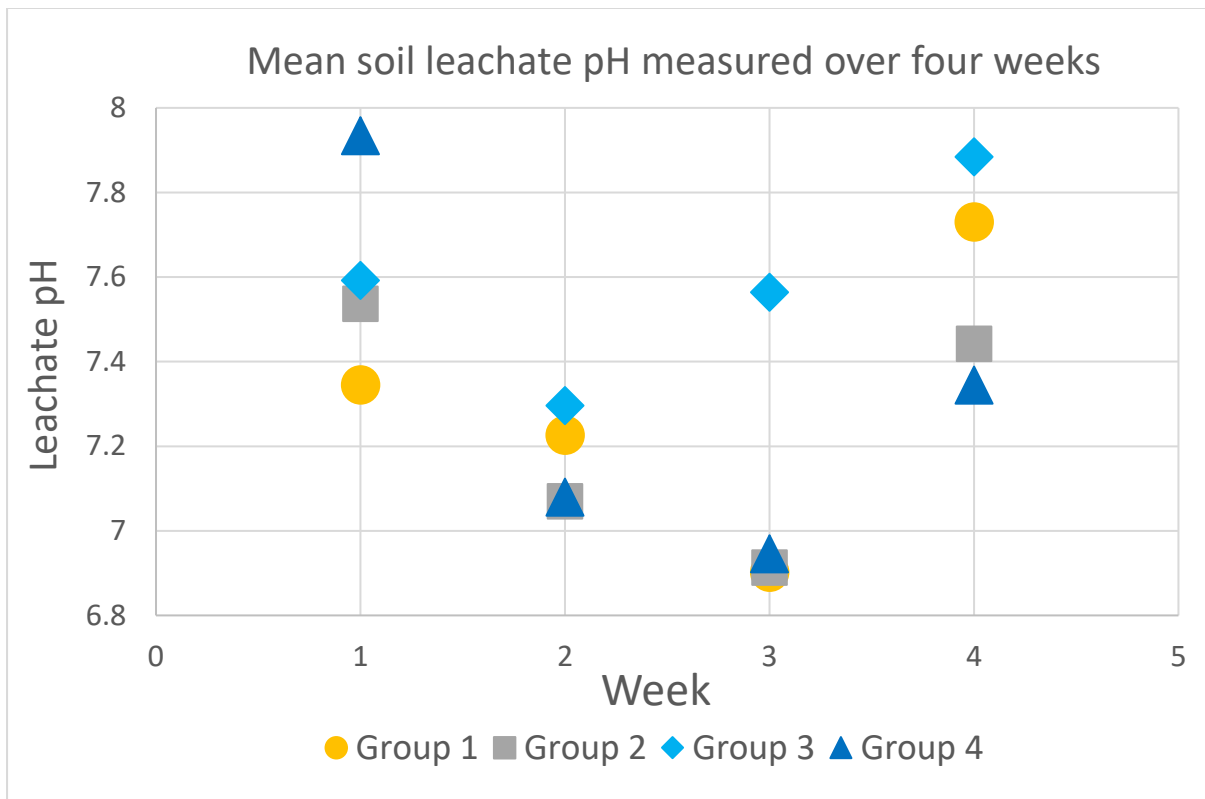


Figure 2: This graph shows the mean pH values for leachate from the different treatment groups measured weekly over the four-week research period. Each pH is an average of the pH values of the four samples within each treatment group; each of those individual sample pH values is an average of three replicates.

2. Leachate metal concentrations

The metals analysed on the ICP-OES were Si, Al, Fe, Mn, Ca, Na, K, and Mg. To consider the different dilution factors and different leachate concentrations the data was transformed into mmol/L to enable comparisons, this data is presented in Figures 3 to 10 below.

Quality control and analysis was conducted on the ICP-OES concentration data. All results determined were above the detection limits and method blanks returned concentrations below detection limits. For quality control a multi-element certified reference material was analysed, accuracies were 103.5% for Si, 110.8% for Al, 106.1% for Fe, 108.5% for Mn, 103.5% for Ca, 101.9% for Na, 113.4% for K, and 103.8% for Mg. The coefficient of variation determined from duplicate analysis of 10% of solutions was 3.40% for Si, 9.75% for Al, 10.8% for Fe, 9.82% for Mn, 0.48% for Ca, 1.06% for Na, 0.86% for K, and 0.45% for Mg. These analyses indicate that all the concentration data is accurate.

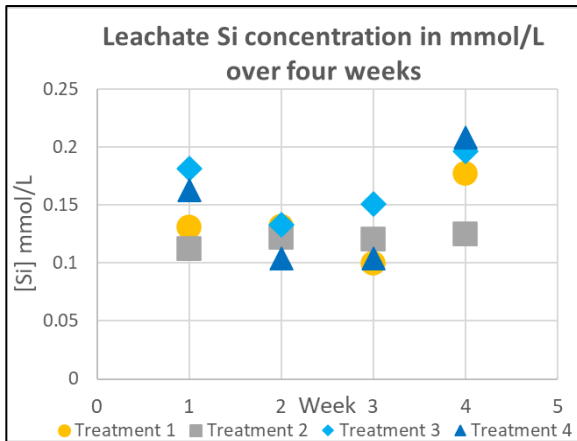


Figure 3: This graph shows the soil leachate Si concentration of the four different treatment groups across four-weeks, in mmol/L: radial analysis at 251.611 nm.

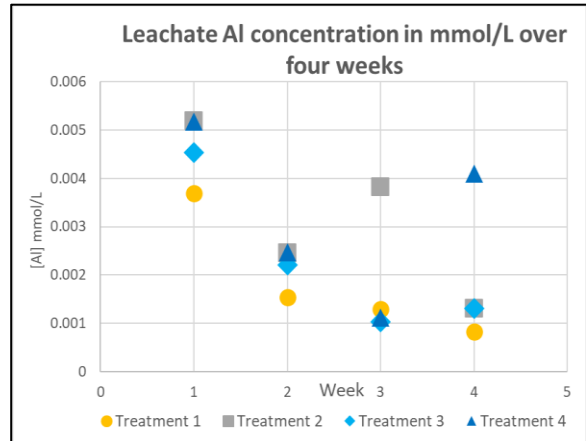


Figure 4: This graph shows the soil leachate Al concentration of the four different treatment groups across four-weeks, in mmol/L: axial analysis at 396.152 nm.

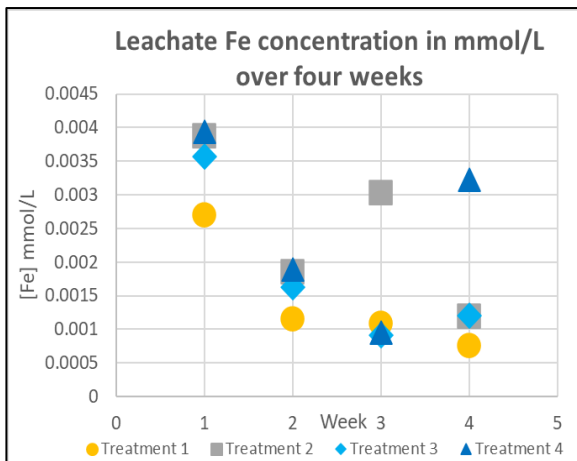


Figure 5: This graph shows the soil leachate Fe concentration of the four different treatment groups across four-weeks, in mmol/L: axial analysis at 259.940 nm.

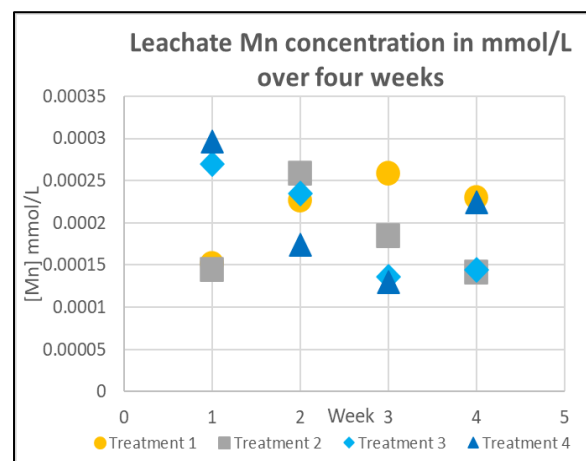


Figure 6: This graph shows the soil leachate Mn concentration of the four different treatment groups across four-weeks, in mmol/L: axial analysis at 257.610 nm.

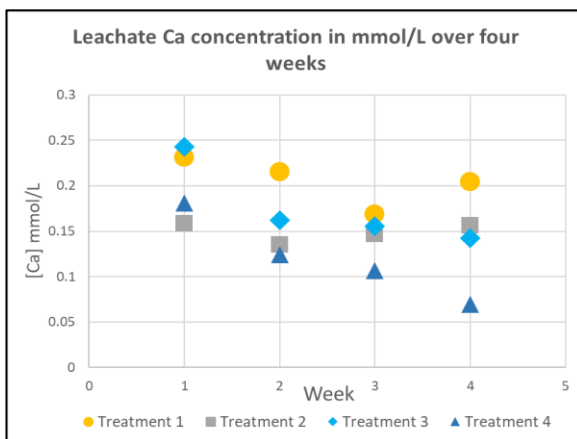


Figure 7: This graph shows the soil leachate Ca concentration of the four different treatment groups across four-weeks, in mmol/L: radial analysis at 317.933 nm.

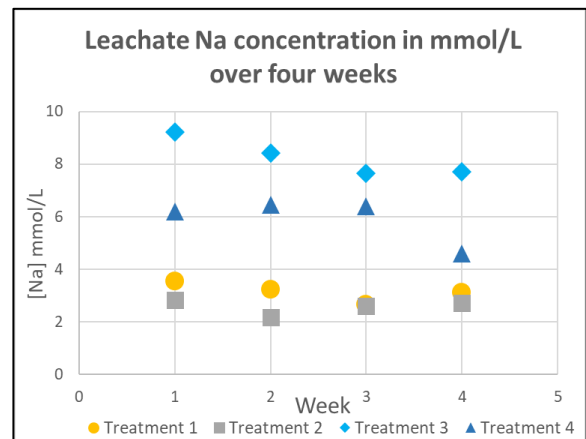


Figure 8: This graph shows the soil leachate Na concentration of the four different treatment groups across four-weeks, in mmol/L: axial analysis at 589.592 nm.

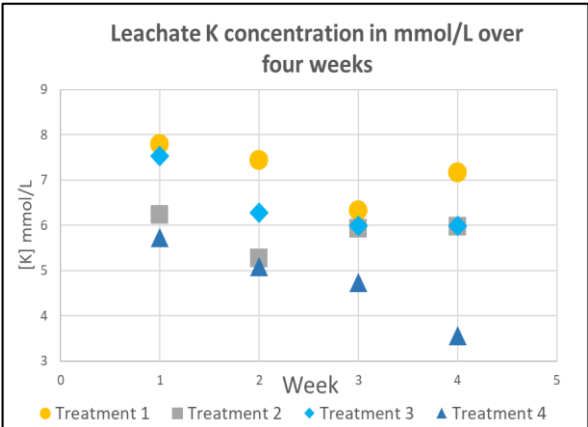


Figure 9: This graph shows the soil leachate K concentration of the four different treatment groups across four-weeks, in mmol/L: radial analysis at 279.553 nm.

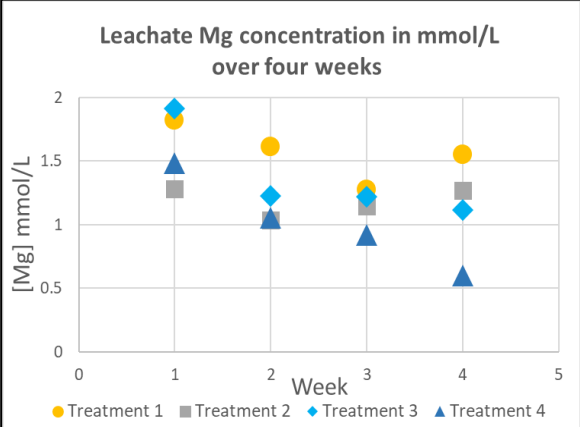


Figure 10: This graph shows the soil leachate Mg concentration of the four different treatment groups across four-weeks, in mmol/L: radial analysis at 766.490 nm.

The change in metal concentration is measured for each group over four-weeks. The linear equation for each group indicates whether the concentrations increased or decreased over time, and the R^2 value describes how close the data points lie to this trendline. For ease of comparison this information is not displayed on the figures above, it is displayed in Table 1.

Element for Analysis	Linear Equation			
	Treatment Group			
	1	2	3	4
Si	$y = 0.011x + 0.11$	$y = 0.0039x + 0.11$	$y = 0.0061x + 0.15$	$y = 0.014x + 0.11$
Al	$y = -0.0009x + 0.0041$	$y = -0.001x + 0.0058$	$y = -0.0011x + 0.005$	$y = -0.0005x + 0.0044$
Fe	$y = 0.0006x + 0.0029$	$y = 0.0007x + 0.0042$	$y = 0.008x + 0.0038$	$y = -0.0003x + 0.0033$
Mn	$y = (3 \times 10^{-5})x + 0.0002$	$y = -(8 \times 10^{-6})x + 0.0002$	$y = -(5 \times 10^{-5})x + 0.0003$	$y = -(3 \times 10^{-5})x + 0.0003$
Ca	$y = -0.013x + 0.24$	$y = 0.004x + 0.15$	$y = -0.031x + 0.25$	$y = -0.035x + 0.21$
Na	$y = -0.19x + 3.6$	$y = 0.0048x + 2.6$	$y = -0.53x + 9.6$	$y = -0.49x + 7.1$
K	$y = -0.30x + 7.9$	$y = -0.012x + 5.9$	$y = -0.50x + 7.7$	$y = -0.68x + 6.5$
Mg	$y = -0.11x + 1.9$	$y = 0.0079x + 1.2$	$y = -0.24x + 2.0$	$y = -0.28x + 1.7$
Element for Analysis	R ² -value			
	Treatment Group			
	1	2	3	4
Si	0.19	0.77	0.076	0.12
Al	0.81	0.62	0.77	0.11
Fe	0.77	0.55	0.71	0.088
Mn	0.57	0.039	0.86	0.22
Ca	0.39	0.0019	0.76	0.96
Na	0.46	0.0004	0.87	0.51
K	0.37	0.0015	0.75	0.94
Mg	0.43	0.0079	0.71	0.96

Table 1: This table displays the linear equation and R² values for the metal concentrations of each treatment group measured over the four weeks. The linear equation describes the upwards/downwards trend in concentration over time and the R² value describes how closely the concentration data points fall to the regression line. The metals analysed are Si, Al, Fe, Mn, Ca, Na, K, and Mg.

3. Soil microbial respiration rates and plant growth

The mean soil microbial respiration rate for the groups treated with basalt (3 and 4) and untreated groups (1 and 2) are displayed in Table 2, including the data used to calculate these values. The mean respiration rate for the treated groups is $8.615 \times 10^{-10} \text{ g CO}_2 \text{ g}^{-1} \text{ air-dry soil s}^{-1}$ and the mean for the untreated groups is $7.69 \times 10^{-10} \text{ g CO}_2 \text{ g}^{-1} \text{ air-dry soil s}^{-1}$. There is not a statistically significant difference in respiration rates between the treated and untreated groups. A one-tailed T-test gives a p value of 0.29, as $p > 0.05$, the hypothesis that treatment with basalt does not an effect on the soil microbial respiration rate is therefore accepted. Furthermore, no changes in plant growth were recorded.

Soil Treatment Groups	Titration Volume (cm ³)	NaOH reacted with CO ₂ (mol)	Mass of CO ₂ (g)	Mass of oven-dry soil (g)	Respiration rate (g CO ₂ g ⁻¹ air-dry soil s ⁻¹)	Mean respiration rate (g CO ₂ g ⁻¹ air-dry soil s ⁻¹)
1	12.5	0.51 x10 ⁻³	0.01122	28.6	6.99 x10 ⁻¹⁰	7.69 x10 ⁻¹⁰
2	11.2	0.64 x10 ⁻³	0.01408	29.6	8.39 x10 ⁻¹⁰	
3	9.8	0.78 x10 ⁻³	0.01716	31.3	9.76 x10 ⁻¹⁰	8.615 x10 ⁻¹⁰
4	11.8	0.58 x10 ⁻³	0.01276	30.4	7.47 x10 ⁻¹⁰	

Table 2: This table shows the soil microbial respiration rates for each of the four treatment groups in g CO₂ g⁻¹ air-dry soil s⁻¹. These values were calculated using the data shown in second, third, fourth, and fifth column of the table. Calculations based on the method from *Soil Science: Methods & Applications* by D J Rowell.

Discussion

1. Leachate pH

There is no significant increase in soil leachate pH for soil groups treated with basalt compared to untreated groups, as the pH increased in groups 1 and 3 and decreased in groups 2 and 4, shown in Figure 2. Therefore, the data does not support the hypothesis that EMW significantly increases the pH of soil leachate. The R² values for the treatment groups are low, indicating that time has little effect on the variation in pH values observed. A potential explanation for the pH drop observed in groups 2 and 4 could be due to the plants excreting organic acids to balance charge when they take up positively charged ions from solution, and or due to excreting organic compounds which are acidic²². The lack of any strong upwards trend could be explained by the short research period; insufficient HCO₃⁻ had been released by weathering during the four-week research period to alter the leachate pH. Over a longer research period, it is likely that the data would become more conclusive with a clear upwards or downwards trend and less variation by week; this is an area for further research. Some studies have questioned the efficacy of EMW as a geoengineering method due to the long timescale of weathering processes²³. Another potential reason why insufficient HCO₃⁻ was released could be due to particle size²⁴. The pulverised basalt used in this study was not finely ground, therefore the total surface area available for natural weathering processes is limited.

2. Leachate metal concentrations

There is no significant increase in leachate metal concentrations for soil groups treated with basalt compared to untreated groups. The data in Table 1 and Figure 3 displays that Si was the only metal that saw an increase in concentration over the four-weeks for the treated groups, but the Si concentration for the untreated groups also increased as well, therefore this increase cannot be assigned to the effects of EMW. Plus, the R² values were greater for the untreated groups, indicating a stronger upwards trend in the untreated groups contrary to

prediction. Aside from Si the only other increase in metal concentration for the treated groups was seen in group 3 for Fe. Unexpectedly, Al, Mn, Ca, Na, K, and Mg all displayed negative trends for the groups treated with basalt. This negative trend for treatment group 4 cannot be attributed to interactions with the plants as treatment group 2 displays positive trends for five of the eight metals (Si, Fe, Ca, Na, Mg). The relationship between basalt and plants on leachate metal concentrations is not clear and the highly variable data in Table 1 strongly suggests that treatment with basalt and plants has no effect on metal concentrations, the trends displayed are seemingly random. Therefore, the data does not support the hypothesis that EMW significantly increases the metal concentrations within soil leachate. As discussed previously, it should be questioned if these results would be the same over a longer research period, with a larger sample size, and using more finely ground basalt.

3. Soil microbial respiration rates and plant growth

There is no significant difference in soil respiration rates between groups treated with basalt compared to untreated groups. Therefore, the data does not support the hypothesis that EMW significantly increases soil microbial activity. However, the respiration rates calculated for each group are not mean values as no replicates were conducted so their accuracy should be questioned. Furthermore, whilst there was no significant difference between treated and untreated soil groups, the mean respiration rate for the groups treated with basalt was higher than for the untreated groups, $8.615 \times 10^{-10} \text{ g CO}_2 \text{ g}^{-1} \text{ air-dry soil s}^{-1}$ compared with $7.69 \times 10^{-10} \text{ g CO}_2 \text{ g}^{-1} \text{ air-dry soil s}^{-1}$, as shown in Table 2. Over a longer research period there is the potential that this difference would become significant; this is an area for further research. Based on the data in Table 2, plants do not have a clear effect on soil microbial activity. No plant growth was observed during the four-week research period due to its brevity, therefore this result neither proves nor disproves the research hypothesis so will not be discussed further.

Conclusion

The research hypothesis states that enhanced mineral weathering increases soil leachate pH, leachate metal cation concentrations, soil microbial activity, and plant growth. None of the experimental data obtained in this study supports this hypothesis. There is no significant difference in leachate pH, leachate metal concentrations, soil microbial activity, and plant growth between the soil groups treated with basalt and the untreated soil groups. Therefore, the proposed effects of enhanced mineral weathering were not observed in this study.

However, this is likely due to the length of the research period. The leachate measurements were made weekly over four-weeks, plant dimensions measured at the start and end of the research period, and soil samples were taken to calculate the respiration rates in the fourth week. But silicate mineral weathering can take many years^{25,26,27}. Therefore, the differences observed between the treatment groups over the research period were likely not a result of mineral weathering but of natural variation. This study is too brief to be conclusive. If these experiments were repeated across a substantially longer research-period, then there would be sufficient data to prove or disprove the hypothesis. Other studies have strongly indicated

that the data would support the original hypothesis and display the effects of EMW; this is an area for further research. Furthermore, a larger sample size should be utilised, which would be particularly useful for calculating the soil microbial respiration rates, and the elemental accuracies of the ICP-OES analysis should be improved. To conclude, whilst the results does not support the research hypothesis, due to factors such as time and sample size, this research does not disprove the hypothesis that enhanced mineral weathering increases soil leachate pH and metal cation concentrations, soil microbial activity, and plant growth.

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