# The potential of enhanced weathering as a CO2 removal

technique in UK agricultural soils

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## Thesis Abstract

Enhanced weathering (EW) is increasingly proposed as a promising negative emission technology that sequesters atmospheric carbon dioxide without substantially changing established agricultural practices. Current estimates suggest enhanced weathering could remove 0.5-4 GtCO<sub>2</sub> yr<sup>-1</sup> globally by the end of this century (Smith *et al.*, 2015) which equates to a substantial fraction of global anthropogenic emissions (49 GtCO<sub>2eq</sub> yr<sup>-1</sup>; IPCC, 2014). However, these estimates are based on limited experimental assessment of the complexities of the soil environment which inhibit alkalinity release, and existing pot and core studies do not consider the influence of natural hydrological conditions on dissolution rate and mineral saturation. In this thesis, I used two long-term, fully replicated soil core studies to comprehensively understand the geochemical dynamics of dissolution and carbon dioxide removal (CDR) in a soil environment. I used multiple, natural soil cores extracted from a typical UK agricultural site exposed to seasonal changes in weather and temperature to closely simulate field conditions.

I applied crushed basalt to agricultural soil cores at 100 t ha<sup>-1</sup> in a 14-month preliminary study (Chapter 3) and developed an innovative experimental method of extracting soil solution for geochemical analysis whilst minimising disruption to natural hydrology (Chapter 2). Assessment of soil solution sampled over five sampling events provided an initial insight into basalt dissolution and CO<sub>2</sub> drawdown in a soil environment. The experimental method established in this study formed the premise of a 16-month soil core study used to assess the dissolution of a range of proposed treatments applied

at 50 t ha<sup>-1</sup> (Chapter 4). Treatments included naturally occurring silicates (crushed olivine, crushed basalt, and volcanic ash), silicates produced from industrial processes (cement kiln dust, crushed steel slag) and agricultural lime (aglime).

High-resolution sampling provided a first look into the pathway of dissolution products through the soil-water system. Treatment dissolution elevated the pH of soil treated with basalt and steel slag, and the alkalinity of soil solutions increased following addition of all treatments, except olivine. Chemical changes to the soil-water system were most marked at the top of treated cores. The surface-area normalised ion-release rate varied from 10 <sup>-13.96 ± 0.03</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup> (aglime) to 10 <sup>-18.99 ± 0.01</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup> (basalt). This difference is partly attributed to the fast dissolution rate of Ca-carbonate relative to silicate minerals and rocks. The introduction of micro-porosity during crushing is also likely to have artificially elevated the BET surface area of crushed basalt, and, in turn, reduced the surface-area normalised ion release rate of basalt relative to uncrushed treatments. Soil processes, such as exchange and secondary mineral formation (measured with XRD and XRF, and modelled with PHREEQC), reduced the flux of alkalinity into solution, particularly in olivine-treated cores.

The carbon dioxide removal potential after a single application at 50 t ha<sup>-1</sup> was, in decreasing order: steel slag  $(20 \pm 3 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$  > cement kiln dust (CKD)  $(16 \pm 2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$  > basalt  $(5.0 \pm 0.7 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$  > volcanic ash  $(2.7 \pm 0.4 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$  > aglime  $(2.2 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$  > olivine  $(0.0 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$ . Industrial silicates were shown to be an effective source of alkalinity; however heavy metal

toxicity may limit addition of steel slag to arable soils, and availability of CKD will limit large-scale application. These findings demonstrate dissolution of aglime in alkaline soils is a previously unquantified negative flux of CO<sub>2</sub> that could influence national carbon accounting. Of the six treatments assessed, this research suggests basalt is the most promising treatment for nationwide enhanced weathering.

Scaling the CDR potential of basalt over UK cropland suggests basalt application will remove 1.2-1.3 MtCO<sub>2</sub> yr<sup>-1</sup>. This value takes into account hydrological variations, which this research indicates are a critical control on CO<sub>2</sub> removal potential. The resulting flux is equivalent to <3% of UK agricultural emissions, and is 5- to 25-fold lower than previous modelled estimates (Kantzas *et al.*, 2022); likely due to complexities of soil systems and to water limitation on alkalinity release. Further research is needed to fully understand the impact of water flux on the efficacy of enhanced weathering in a real-world setting across a range of hydrological and soil environments.

## Chapter 1. General Introduction

#### 1.1. The carbon cycle

Carbon is transported through different components of the Earth's systems, including: the atmosphere (~3000 GtCO<sub>2</sub>), the surface and deep ocean (~140,000 GtCO<sub>2</sub>), ocean floor sediments (6400 GtCO<sub>2</sub>), and the terrestrial environment (~11,100 GtCO<sub>2</sub>), of which ~80% derives from soil carbon (Ciais *et al.*, 2014). The annual flux of carbon from the atmosphere to land is equivalent to 10 GtCO<sub>2</sub> yr<sup>-1</sup>, and is similar to the scale of carbon uptake in the ocean (9 GtCO<sub>2</sub> yr<sup>-1</sup>) (Peters *et al.*, 2012). Anthropogenic activities annually release an additional 49 GtCO<sub>2eq</sub> into the atmosphere, globally, originating from: electricity and heat production (25%); agricultural, forestry and land use (24%); industry (21%); transport (14%); and buildings (6.4%) (IPCC, 2014). Transport and agriculture contribute 27% and 10%, respectively, of UK greenhouse gas emissions (0.435 GtCO<sub>2</sub> yr<sup>-1</sup>) and will be difficult to mitigate to achieve net-zero emission reduction targets (BEIS, 2019).

#### **1.2. Carbon dioxide removal**

To prevent global average temperature rise surpassing 2°C since pre-industrial temperatures, there is a consensus among several authors that both a global reduction in greenhouse gas emissions and active removal of greenhouse gases from the atmosphere is necessary (McLaren, 2012; Rogelj *et al.*, 2016; United Nations Environment Programme (UNEP), 2017; Fuss, 2018; IPCC, 2018; Minx *et al.*, 2018; The European Academies' Science Advisory Council, 2018). Negative emission

technologies (NETs) are defined as an "intentional human effort to remove carbon dioxide emissions from the atmosphere" (Minx *et al.*, 2018), and are heavily relied upon in modelled scenarios to limit global average temperature rise (figure 1.1). For example, Minx *et al.*, (2018) noted the 2°C target will require 320-840 GtCO<sub>2</sub> to be removed at a rate of 0.03-0.4 GtCO<sub>2</sub> yr<sup>-1</sup>, and Holz *et al.*, (2018) was unable to limit warming to 1.5°C in models which excluded CDR without changes in population growth or GDP. Moreover, the deployment of NETs will be essential to compensate for difficult to mitigate emissions, such as those from the aviation and agricultural industry which are predicted to reach 130 MtCO<sub>2</sub> yr<sup>-1</sup> in the UK by 2050 (The Royal Society, 2018)



**Figure 1.1.** The role of negative emission technologies in CO<sub>2</sub> emission pathways (Fuss et al., 2018). Global emissions turn net negative (blue hatched area) towards the end of the century following a substantial reduction in existing emissions (green area) and deployment of negative emissions technologies (blue area).

Carbon dioxide removal (CDR) technologies encompass NETs which remove and permanently store atmospheric carbon. A variety of CDR technologies have been suggested (Minx *et al.*, 2018, and references therein) and it is likely a plethora will be deployed synchronously to maximise carbon sequestration and minimise the scale of each technology. To understand the efficacy of CDR technologies, it is critical to understand their respective carbon removal potentials, the feasibility of large-scale deployment and associated environmental risk.

## 1.3. Enhanced weathering

Silicate weathering is an essential part of the global carbon cycle which removes ~0.35 GtCO<sub>2</sub> yr<sup>-1</sup> (Moon *et al.*, 2014). Strong silicate bonding kinetically limits weathering and dissolution occurs over geological timescales ( $10^5$  years) influenced by temperature, water supply, reactive mineral surface area and biota (Renforth and Henderson, 2017, and references therein). Enhanced weathering is a CDR technology which aims to accelerate the rate of silicate weathering and sequester carbon on a timescale relevant to anthropogenic change via the application of crushed rock or mineral treatments onto agricultural fields (Seifritz, 1990). This utilises a landscape which occupies 1200 Mha globally and is supported by existing infrastructure which spreads fertiliser and agricultural lime (Beerling *et al.*, 2018).

Eq.1.1. Dissolved inorganic carbon (DIC)

$$(1) DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] + [H_2CO_3]$$

Eq.1.2. Total alkalinity, TA, defined by the excess of proton acceptors over proton donors relative to an arbitrary zero point, as described by Zeebe & Wolf-Gladrow (2001).

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \pm \text{minor compounds} =$$
$$\Sigma(\text{conservative cations}) - \Sigma(\text{conservative anions})$$

Eq.1.3. Dissolution of  $CO_2$  and dissociation of carbonic acid into dissolved inorganic carbon

$$CO_{2(g)} \rightarrow CO_{2(aq)} + H_2O_{(aq)} \rightarrow H_2CO_{3(aq)} \rightarrow HCO_{3(aq)}^- + H_{(aq)}^+ \rightarrow CO_{3(aq)}^{2-} + 2H_{(aq)}^+$$

Eq.1.4.Dissolution of forsterite

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$$

Eq.1.5. Precipitation of Mg carbonate

$$2Mg^{2+} + 4HCO_3^- + H_4SiO_4 \rightarrow 2MgCO_3 + 2CO_2 + 4H_2O + SiO_2$$

Eq.1.6.Calcium carbonate dissolution and re-precipitation.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

Soil pore-water is moderately acidic as a result of root respiration and exudates (Manning and Renforth, 2013). During terrestrial chemical weathering, dissolution of minerals by carbonic acid in soil solution leads to the release of cations (such as Ca<sup>2+</sup>,

Mg<sup>2+</sup>, Na<sup>+</sup>) into solution which are transported to the ocean via rivers and runoff (Eq.1.4). The addition of conservative cations into the ocean increases total alkalinity (TA), as defined by Zeebe & Wolf-Gladrow (2001) (Eq.1.2). H<sup>+</sup> consumption therefore drives the forward reaction in Eq.1.3 and increases dissolved inorganic carbon (DIC). In turn, seawater becomes undersaturated with respect to dissolved CO<sub>2</sub>, and atmospheric CO<sub>2</sub> is transferred into solution to maintain equilibrium by air-sea gas exchange on a timescale of weeks to months (Hartmann et al., 2013 and references therein). Dissolved inorganic carbon in the ocean is stable for ~ 100,000 years, therefore carbon drawdown into DIC can be considered permanent on human-relevant timescales (Renforth & Henderson, 2017). The majority of DIC exists as bicarbonate ions (HCO<sub>3</sub>) in water of pH 6-9; whereby the input of one mole of divalent cation is balanced by the production of approximately two moles of bicarbonate ions and removal of approximately two moles of carbon from the atmosphere. This is reduced to a factor of 1.4 to 1.7 in alkaline waters, such as seawater, where an increasing fraction of the carbon is present as carbonate ion rather than bicarbonate ion (Renforth & Henderson, 2017). Depending on ocean chemistry, secondary carbonate minerals may precipitate from dissolved inorganic carbon (Eq.1.5); however carbonate precipitation may be limited by the presence of anions, such as sulphate and phosphate (Hartmann et al., 2013). Alternatively, carbon consumed during weathering may precipitate as pedogenic minerals in soils (Manning, 2008). Precipitation of carbonates drives the outgassing of CO<sub>2</sub> and reduces the sequestration potential from silicate dissolution by 50%. For example, dissolution of one mole of forsterite releases two moles of divalent Mg and four moles of carbon are drawdown into bicarbonate ions (Eq.1.4), but MgCO<sub>3</sub> precipitation releases two moles of carbon into the

atmosphere as CO<sub>2</sub> (Eq.1.5). The net effect of weathering on carbon drawdown is therefore greatest if sequestered carbon remains in a dissolved form.

In addition to silicate weathering, dissolution of carbonate minerals can also result in carbon drawdown. For example, the dissolution of one mole of CaCO<sub>3</sub> releases one mole of Ca<sup>2+</sup>; if this is transferred to the ocean the increase in TA and DIC will draw down one mole of CO<sub>2</sub>. However, re-precipitation of dissolved Ca<sup>2+</sup> as CaCO<sub>3</sub> (Eq.1.6) will release all carbon consumed during carbonate dissolution and result in no net drawdown. In this way, carbonate dissolution is less effective at removing CO<sub>2</sub> compared to silicate dissolution.

#### 1.4. Treatments proposed for enhanced weathering

The ideal treatment for enhanced weathering in cultivated agricultural soil will dissolve quickly to release alkalinity and contain minimal levels of heavy metals to avoid contamination of the soil-water system and the wider environment. As explained above, re-precipitation of dissolved carbonate results in no net drawdown, therefore the ideal EW treatment will not contain carbon itself. Nationwide application of EW onto UK cropland at a rate comparable to existing liming practices (0.1-10 t ha; Goulding 2016) will require ~0.6 to 60 Mt treatment. Therefore proposed treatments will need an abundant supply and will ideally be located proximal to cropland to minimise transport-related emissions. A large surface area accelerates the weathering rate of the dissolving grain/ mineral surface applied during EW; however comminution is estimated to be a significant sink of energy during EW and release 5-30% carbon consumed during dissolution (Renforth, 2012; Moosdorf *et al.*, 2014). Treatments with

an inherently fine particle size will negate crushing-related emissions and, in turn, increase the net CDR potential of EW.

A range of treatments have been proposed for EW, including naturally occurring silicates. Olivine dissolution has been studied in considerable detail over the past decade with many studies noting its fast abiotic dissolution rate, high Mg concentration, and large, accessible reserves within mafic and ultra-mafic rocks (Hartmann et al., 2013; Oelkers et al., 2018; Schuiling & Krijgsman, 2006; Strefler et al., 2018; ten Berge et al., 2012). Recent research has elucidated the potential of olivine dissolution to release harmful heavy metals, such as Ni and Cr, into the soilwater environment (ten Berge et al., 2012; Renforth et al., 2015; Amann et al., 2020) and suppress Ca plant-uptake through competition with Mg (ten Berge et al., 2012). Basalt, a cation-rich mafic silicate rock, is an alternative EW treatment and is responsible for the removal of 180 MtCO<sub>2</sub> yr<sup>-1</sup> via in-situ natural weathering (Dessert et al., 2003). Basalt has a lower heavy metal content than olivine and application to agricultural land is a well-established practice associated with the release of bioavailable plant-essential nutrients such as P, K, Ca, and Si (Shoji et al., 1993; Beerling et al., 2018). Basalt rocks are globally abundant, with extensive areas exposed in continental flood basalts and over 11 km<sup>2</sup> igneous rock formations exposed at the surface in the UK (Bryan and Ernst, 2008; Renforth, 2012). Basalt rock weathers more slowly than olivine as it is predominantly formed from plagioclase feldspar and pyroxene minerals which have greater SiO<sub>2</sub> polymerisation than olivine (Palandri and Kharaka, 2004). In comparison, naturally occurring felsic silicates, such as granite, are not as appealing for EW as they are comprised of slow-dissolving minerals, such as quartz and K-feldspar, and are not as cation-rich as mafic rock. Application of felsic

rocks would therefore release less alkalinity into solutions and remove CO<sub>2</sub> more slowly than basalt and/or olivine dissolution. Extracting, transporting and processing significant quantities of basalt and olivine from mafic and ultra-mafic formations will reduce the net CDR potential of EW. Application of volcanic ash therefore presents promise for EW as a cation-rich, fast dissolving silicate which is inherently fine-grained and will evade crushing-related emissions.

Silicates produced as a by-product from industrial processes present an alternative to naturally occurring silicates as they are cation-rich, fast-dissolving and fine-grained (Renforth, 2019). Examples of industrial silicates include steel and iron slag, cement kiln dust (CKD), red mud, demolition waste and mine tailings. Industrial silicates are less abundant than mafic rocks, whereby less than 10 Mt yr<sup>-1</sup> of slag and cement kiln dust (CKD) is produced annually in the UK and historical stockpiles are estimated to contain 566 Mt slag and 131 Mt CKD (Renforth, 2012). To date, there is no experimental evidence of industrial silicate dissolution in an agricultural setting; therefore the heavy metal risk of application in EW remains unknown. Some authors suggest CKD dissolution could release harmful heavy metals, such as Cd, Pb, Cr and Ti (van Oss & Padovani, 2003); and leaching experiments have noted the release of Cr, Ni and V from steel slag (Huijgen and Comans, 2006). In light of this, efforts to limit toxicity in the soil and freshwater environment may restrict the application of industrial silicate treatments and their associated carbon drawdown.

Aglime, formed predominantly from CaCO<sub>3</sub>, is regularly applied to cropland at a rate of 0.5-10 t ha<sup>-1</sup> to maintain an optimal soil pH for crop growth (Goulding, 2016). The

IPCC (Houghton *et al.*, 1997) view liming practices as a source of anthropogenic CO<sub>2</sub> assuming all carbon in carbonate lime is eventually released as CO<sub>2</sub> to the atmosphere following dissolution in the presence of a strong acid (Eq.1.7). However, these calculations do not consider the release of alkalinity following dissolution of aglime in moderately acidic soils (Eq.1.8). Although carbonate dissolution is 50% less efficient at removing CO<sub>2</sub> compared to silicate weathering, aglime spreading could be a previously unquantified sink of carbon in some agricultural settings.

Eq.1.7. Acidification of calcium carbonate with nitric acid

 $CaCO_3 + 2HNO_3 \rightarrow Ca^{2+} + 2NO_3^- + H_2O + CO_2$ 

Eq.1.8. Acidification of calcium carbonate with carbonic acid  $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{--}$ 

#### 1.5. Mineral dissolution rate

Laboratory-based studies demonstrate dissolution kinetics are controlled by temperature, mineral surface area, pH and mineral saturation (Palandri and Kharaka, 2004). Recent work has also illustrated the non-linear behaviour of dissolution associated with grain size and low reactivity minerals (Israeli and Emmanuel, 2018); heterogeneous reactivity of mineral surfaces (Oelkers *et al.*, 2018); non-stoichiometric release of cations (Bray *et al.*, 2015); and the formation of cation-depleted, Si-rich layers (Peters *et al.*, 2004; Oelkers *et al.*, 2018). The dissolution rate of forsterite, a magnesium-rich olivine, has been determined in laboratory-based experiments as 10<sup>-14</sup> mol cm<sup>-2</sup> s<sup>-1</sup> at 19°C, pH 7 (Palandri and Kharaka, 2004) and is consistent with modelled results (10<sup>-13.95</sup>–10<sup>13.77</sup> mol cm<sup>-2</sup> s<sup>-1</sup>; Strefler *et al.*, 2018). In comparison,

model-based studies suggest basalt dissolves considerably more slowly than olivine as a result of slow-dissolving mineral phases in mafic rock ( $10^{-16.63}-10^{-13.55}$  mol cm<sup>-2</sup> s<sup>-1</sup>) (Strefler *et* al., 2018).

Laboratory-determined dissolution rates have been shown to be up to three orders of magnitude faster than their field-based counterparts (Pačes, 1983; Velbel, 1985, 1993; Swoboda-Colberg and Drever, 1993) which is discussed extensively in White and Brantley (2003). Laboratory determined dissolution rates are inherently limited by their inability to capture the dissolution response to physical and chemical features of the soil environment, including: pH, temperature, soil structure, hydrological conditions, fluid macroflow, secondary mineral coatings, mineral-fluid interaction and mineral saturation (Velbel, 1993; Haren, 2017). A number of authors have also highlighted the influence of biotic factors which can accelerate dissolution 2-10 fold, such as: respiration, hyphae, and organic acid exudation (Adeleke *et al.*, 2017; Bonneville *et al.*, 2009; Bray *et al.*, 2015 and references therein; Hopf *et al.*, 2009; Kawano and Hwang, 2019; Pokharel *et al.*, 2019; Rosenstock *et al.*, 2019; Taylor *et al.*, 2012). Although field-based dissolution studies are more representative of mineral dissolution during enhanced weathering they are consuming in both time and space and are difficult to replicate or repeat under different conditions.

A small number of existing soil core studies (Renforth *et al.*, 2015) and pot studies (ten Berge *et al.*, 2012; Amann *et al.*, 2020; Kelland *et al.*, 2020) bridge the gap between laboratory and field studies by maintaining the complexities of the soil environment in a setting where variables can easily be isolated and measured. The rate of olivine dissolution was calculated from dissolved Mg in an olivine-treated pot  $(10^{-17.12} \text{ to } 10^{-17.12})$ 

<sup>17.75</sup> mol(Olivine)cm<sup>-2</sup>s<sup>-1</sup>; Amann *et al.*, 2020) and core study (10<sup>-16.7</sup> to 10<sup>-15.8</sup> mol(Olivine) cm<sup>-2</sup> s<sup>-1</sup>; Renforth et al., 2015). These findings are one to three orders of magnitude slower than olivine dissolution measured in simple laboratory experiments, and is thought to reflect the factors discussed above which limit dissolution in soil (Palandri and Kharaka, 2004) (figure 1.2). Kelland et al., (2020) conducted a "pot study" using individual weathering reactors containing plants. In this pot study, the dissolution rate of basalt was measured using a complete analysis of cations in the dissolved and exchangeable phase and by plant uptake (10<sup>-15.3</sup> to 10<sup>-16.2</sup> mol(Ca) cm<sup>-</sup>  $^{2}$  s<sup>-1</sup>; 10<sup>-16.1</sup> to 10<sup>-16.3</sup> mol(Mg) cm<sup>-2</sup> s<sup>-1</sup>). Cation release from basalt was one to two orders of magnitude faster than from olivine dissolution measured by Amann et al., (2020) (figure 1.2) and is thought to reflect the removal of dissolved cations by exchange onto soil surfaces which was not measured in the olivine-treated pot study. These early studies confirm that core and pot studies provide an insight into the geochemistry of dissolution and are a realistic proxy for catchment scale weathering rates. However, to date, pot and core studies are limited to the dissolution of a few silicates, including: olivine (ten Berge et al., 2012; Renforth et al., 2015; Dietzen et al., 2018; Amann et al., 2020); basalt (Kelland et al., 2020); and wollastonite (Hague et al., 2019; Haque et al., 2020); yet dissolution of industrial silicates, such as CKD and steel slag, in agricultural soils remains unstudied. Furthermore, different experimental set-ups introduce ambiguity when comparing dissolution between studies; for example some pot and core studies only measure the dissolved phase (Renforth et al., 2015; Amann et al., 2020), and therefore do not account for dissolution products held by exchange on mineral surfaces in the soil, or removed by secondary mineral formation. Other studies only sample effluent drained from the base of the core which conceals the distribution of dissolved cations (Renforth et al., 2015; Kelland et al., 2020).

Critically, all existing pot and core studies control temperature and irrigation, and therefore do not represent natural variations in hydrology - a key factor which influences the transport of solutes to and from the dissolving mineral surface. To date, the dissolution of a range of silicates proposed as enhanced weathering treatments has not been experimentally assessed in an experimental set-up which simulates natural field conditions using real agricultural soil.



*Figure 1.2.* The surface-area-normalised cation release rate of olivine and basalt (mol(cation) cm<sup>-2</sup>s<sup>-1</sup>), measured in existing laboratory-based, model-based, and pot and core mesocosm studies.

#### 1.6. Carbon dioxide removal potential of enhanced weathering

Existing theoretical calculations demonstrate promise for enhanced weathering as an effective means of removing CO<sub>2</sub>. Renforth (2019) estimated the CDR potential of a range of proposed treatments based on their total alkaline content using eq.1.9, including: basic rock (0.3 tCO<sub>2</sub> t<sup>-1</sup>), cement kiln dust (0.5 tCO<sub>2</sub> t<sup>-1</sup>), lime (1.2 tCO<sub>2</sub> t<sup>-1</sup>), steel slag (0.6 tCO<sub>2</sub> t<sup>-1</sup>), and ultra-basic rock (0.8 tCO<sub>2</sub> t<sup>-1</sup>). Basalt application over UK cropland could therefore theoretically remove 19 MtCO<sub>2</sub>yr<sup>-1</sup> following application at 10 t ha<sup>1</sup> (The Royal Society, 2018). This is aligned with a recent modelling study by Kantzas et al., (2022) who estimate basalt application at 40 t ha<sup>-1</sup> could draw down 6-30 MtCO<sub>2</sub> yr<sup>-1</sup> over UK cropland by 2050; akin to the scale of carbon drawdown associated with woodland creation. Carbon drawdown in the UK could be increased further to 44-180 MtCO<sub>2</sub> yr<sup>-1</sup> following the co-deployment of other land based NETs such as biochar, soil carbon sequestration, afforestation and reforestation (Smith et al., 2016). Furthermore, scaling basalt application over 2/3 global cropland (9x10<sup>8</sup> ha) has the potential to remove 0.5-4 GtCO<sub>2</sub> yr<sup>-1</sup> globally, by the end of this century (Smith et al., 2015). This is aligned with recent calculations by Lewis et al., (2021) who estimated the cumulative removal of 1.2 - 7.7 GtCO<sub>2</sub>, 15 years after a single basalt application at 50 t ha<sup>-1</sup> over the same area (900 Mha). Nevertheless, model estimations are based upon limited experimental evidence and therefore considerable uncertainty remains regarding the CDR potential of enhanced weathering on a largescale in a range of climate conditions, soil types and in a natural soil environment.

Eq.1.9. The EW potential of a proposed treatment ( $kgCO_2 t^1$ ), described by Renforth (2019);

$$E_{pot} = \frac{M_{CO2}}{100} \cdot \left( \alpha \frac{Ca0}{M_{Ca0}} + \beta \frac{Mg0}{M_{Mg0}} + \varepsilon \frac{Na_20}{M_{Na20}} + \varepsilon \frac{K_20}{M_{K20}} + \gamma \frac{SO_3}{M_{S03}} + \phi \frac{P_2O_5}{M_{P205}} \right) \cdot 10^3 \cdot \eta$$
where CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> are the elemental concentrations expressed as oxides; M<sub>x</sub> is the molecular mass of the respective oxide; coefficients consider the relative contribution of each oxide; and  $\eta$  is the molar ratio of CO<sub>2</sub> to divalent cation removed during EW.

Thus far, the CDR potential of alkaline waste materials in soils has not been experimentally determined, and equivocal results have been calculated from seven pot studies treated with either olivine (ten Berge *et al.*, 2012; Dietzen *et al.*, 2018; Amann *et al.*, 2020); basalt (Kelland *et al.*, 2020; Vienne *et al.*, 2022); or, wollastonite (Haque *et al.*, 2019; Haque *et al.*, 2020). The CDR potential of olivine, calculated from dissolved Mg in an olivine-treated pot study by Amann *et al.*, (2020) (0.023-0.049 tCO<sub>2</sub> ha<sup>-1</sup>) is one to two orders of magnitude slower than drawdown calculated by ten Berge *et al.*, (2012) (0.290 - 2.690 tCO<sub>2</sub> ha<sup>-1</sup>) and Dietzen *et al.*, (2018) (3.13-4.69 tCO<sub>2</sub> ha<sup>-1</sup>). In comparison, Kelland *et al.*, (2020) and Vienne *et al.*, (2022) estimated the CDR potential of basalt from the dissolved concentration of cations in soil solution as 2 - 4 tCO<sub>2</sub> ha<sup>-1</sup> and 1.83 - 4.48 tCO<sub>2</sub> ha<sup>-1</sup>, respectively, 1-5 years after a single application at 100 t ha<sup>-1</sup> and 50 t ha<sup>-1</sup>. When extrapolated to 2/3 global cropland (9x10<sup>8</sup> ha), this suggests basalt application could remove 1.8-3.6 GtCO<sub>2</sub> yr<sup>-1</sup>, which is equivalent to approximately 4-7% global anthropogenic emissions.

The net CO<sub>2</sub> removal potential of EW is determined from the difference between the flux of CO<sub>2</sub> sequestered into DIC and CaCO<sub>3</sub> via the release of alkalinity, and the flux of CO<sub>2</sub> emitted throughout the life-cycle of EW processes. Conventional mining, transport, comminution and spreading practices release CO<sub>2</sub> into the atmosphere, therefore EW will only result in net C drawdown if emissions from these processes are comparatively small. In a comprehensive life-cycle assessment of EW in Brazil, Lefebvre *et al.*, (2019) found transportation to be the primary process which reduced the CDR potential of EW whereby no net drawdown occurred when the road-distance between basalt quarry and field-site exceeded 990 ± 116 km (Lefebvre *et al.*, 2019). In addition, grinding basic and ultrabasic rocks to a fine grain size is expected to be a key source of C during EW (Renforth, 2012; Moosdorf *et al.*, 2014). EW using basic rocks is estimated to require 656-3502 kWh tCO<sub>2</sub><sup>-1</sup> (Renforth, 2012); therefore renewable energy sources will be relied upon to increase net C drawdown and improve the efficacy of EW.

#### 1.7. Co-benefits of enhanced weathering

The application of crushed treatments onto agricultural fields means that, unlike other proposed NETs, EW does not compete for land, energy, water or nutrients (Fuss, 2018; Minx *et al.*, 2018), and is estimated to only require <0.2% of the UK's power production (Kantzas *et al.*, 2022). In fact, several authors have commented on the potential of silicate application to increase crop productivity, reduce abiotic and biotic stress, supply comparable fluxes of P and K as conventional fertiliser, and reduce nitrous oxide emissions by ~0.1 MtCO<sub>2</sub>e yr<sup>-1</sup> (ten Berge *et al.*, 2012; Anda *et al.*, 2013, 2015; Dietzen *et al.*, 2018; Paula De Souza *et al.*, 2018; Kelland *et al.*, 2020; Swoboda

*et al.*, 2021; Kantzas *et al.*, 2022; Vienne *et al.*, 2022). Silicate application has also been shown to improve soil health by replenishing eroded soil, reducing soil acidity and increasing soil organic carbon, cation exchange capacity and negative charge (Gillman, 1980; Gillman *et al.*, 2002; Anda *et al.*, 2009; Anda *et al.*, 2013, 2015; Swoboda *et al.*, 2021). Similarly, some authors suggest steel slag application could enhance crop production by increasing soil alkalinity and releasing plant essential nutrients (Huijgen and Comans, 2006; Beerling *et al.*, 2018).

In addition to benefiting the soil environment and stimulating crop growth, enhanced weathering could influence the marine environment by increasing the pH of freshwater fluxes and supplying alkalinity. In turn, this would increase the carbonate saturation state, increase the oceans buffering capacity and counteract the effect of ocean acidification, particularly in coastal environments (Beerling *et al.*, 2018; Hartmann *et al.*, 2013; Renforth and Campbell, 2021). An elevated flux of silica to the oceans could also stimulate the growth of marine diatoms which transport carbon into the deep ocean via the biological pump (Hartmann *et al.*, 2013). Widespread EW deployment could therefore have a plethora of co-benefits on the terrestrial and marine environment.

#### 1.8. Thesis aim & research objectives

At a time when carbon dioxide removal technologies are becoming increasingly relied upon in carbon emission scenarios that limit global average temperature rise and reach net-zero commitments, this thesis aims to provide a comprehensive geochemical investigation of enhanced weathering in a soil environment

representative of UK cropland. This research provides a novel opportunity to investigate key factors which inhibit and/or accelerate enhanced weathering. Experimentally assessing the dissolution and CDR potential of a range of proposed enhanced weathering treatments in a representative agricultural setting will facilitate a system-wide understanding of the most suitable treatment for enhanced weathering and the associated impact on the terrestrial environment. In doing so, this thesis aims to further our geochemical understanding of the efficacy of enhanced weathering and inform plans for future deployment.

*Research objective 1* – to develop a robust method of extracting sufficient volumes of soil solution from soil cores for complete geochemical analysis, and to provide a framework for future soil core studies (Chapter 2)

*Research objective* 2 – to identify the geochemical and environmental impact of dissolution in the soil-water system (Chapter 3, 4)

*Research objective 3* – to calculate the cation-release rate and carbon dioxide removal potential of multiple proposed enhanced weathering treatments applied at different rates in a UK soil in conditions representative of the field environment (Chapter 3, 4)

## Statement of authorship

I am responsible for and led all the work included in this thesis. The contributions of co-authors, alongside the details of publication or planned manuscript submission, are given at the start of each chapter.

## Chapter 2. Methods

#### 2.1 Site description and experimental set-up

In August 2018, 36, 1.0 m length by 0.1 m diameter soil cores were removed from an agricultural field in North Oxfordshire (FAI Farm, 51.781°, -1.3141°). Soil cores were extracted in a 6 m x 6 m grid using a premier Compact percussion window sampler and taped at both ends (figure 2.1). The sampling site was covered in crop residue and had previously been used to cultivate Avena sativa (oats) and Hordeum vulgare (barley). The soil was a freely draining, lime-rich, loamy cambisol with pH 6.07, and is representative of some soil environments in SW England, E England and across Wales (Farewell et al., 2011). The soil core had a 20-30 cm loose, dark organic-rich layer of topsoil above poorly differentiated loamy soil. Soil cores were held in transparent acrylic tubing throughout the experimental work. Cores were transported five miles and stored in a custom-built rack on the roof of the Department of Earth Sciences, University of Oxford. Six soil cores were kept in a laboratory at room temperature for further analysis. Cores were covered with opaque, plastic sheeting and left undisturbed for two months. In October 2018, the tape covering both ends of the acrylic tubing was removed and an acrylic cap was placed on the bottom of each core. Each cap had a 1 cm hole to allow effluent water to drain through a 1 cm x 10 cm PVC tube into an acid-leached 250 ml sampling bottle beneath the core. The top surface of each core was exposed to the atmosphere and natural rainfall throughout the remainder of the experiment.

The aim of this research was to investigate dissolution in a setting representative of UK cropland. As only 2 % of UK cropland is irrigated (Weatherhead, 2007), soil cores were mostly unirrigated throughout the time-series, except for immediately before sampling to permit extraction of pore-water samples— see section 2.3. In this way, natural rainfall and mineral-fluid interactions were maintained throughout the majority of the study, and results from this research are assumed to be representative of enhanced weathering in UK arable soils.

Two soil core studies were conducted during this thesis. Six cores were used in a 14month preliminary experiment from November 2018 - January 2020 (Exp0), and 21 cores were used in a 16-month study from February 2020 - June 2021 (Exp1). An overview of the experimental design is illustrated in figure 2.1. In both studies, silicate or carbonate treatments were mixed into the top 13cm of three cores to replicate the ploughing process – see section 2.2.2 for further details. In both studies, three control cores experienced the same physical disturbance but remained untreated. In Exp0, crushed basalt was added to three cores at 100 t ha<sup>-1</sup>. In contrast, six different natural and anthropogenic silicate and carbonate treatments were applied in Exp1 at 50 t ha <sup>1</sup> to three cores, respectively. Treatments applied in Exp1 included: crushed basalt, crushed olivine, volcanic ash, crushed steel slag, cement kiln dust (CKD) and agricultural lime (aglime). In both studies, soil solution was sampled from the base of the core and from Rhizon CCS samplers (0.15 µm pore space, Rhizosphere Research Products) inserted horizontally into the soil core. In Exp0, Rhizons samplers were installed in 10 cm intervals into two cores and in 20 cm intervals into the remaining four cores. In contrast, Rhizon samplers were inserted every 10 cm into 21 soil cores during Exp1 to create a high-resolution data set. Herbaceous flowering plants naturally

grew in the cores and were neither tended to nor removed; this simulated the influence of biota on enhanced weathering in a field environment.

Eq. 2.1. Solution flux through the core ( $g s^{-1}$ ), where V is the volume of natural rainfall or evapotranspiration (ml), and T is the length of the study (seconds).

$$Q = \frac{V_{\text{natural rainfall}} - V_{\text{Evapotranspiration}}}{T}$$

Throughout the two experiments, rainwater was collected in a Palmex RS1B rainwater sampler located beside the soil cores. Rainwater volume was measured by mass during each sampling event and stored in acid-cleaned 20 litre cubitainers. Potential evapotranspiration was measured at Chimney Meadows, Oxfordshire (UKCEH, 2021) and was assumed to represent evapotranspiration from the plants that naturally grew in soil cores during the study. The flux of water into the soil cores was calculated from rainfall minus evapotranspiration over the duration of the study (Eq.2.1, g s<sup>-1</sup>). The water flux into the core was more tightly constrained than the water flux exiting the core in effluent and pore-water samples, therefore it is assumed the flux into the core.



**Figure 2.1.** Experimental set-up. (a) 6 x 6 m wide sampling site where 36, 1.0 x 0.1 m diameter soil cores were extracted; FAI Farms, Oxfordshire, UK. (b) Soil cores installed on the roof of the Earth Sciences Department after extraction, covered in black sheeting (Aug'18). (c) Syringes attached to rhizon samplers under vacuum during sampling. (d) An untreated soil core, Nov'18.



Figure 2.2. Schematic depiction of the experimental set-up.

### 2.2. Treatments

#### 2.2.1 Treatment description

Basalt used in Exp0 and Exp1 was obtained from the Cascade Mountain Range (Central Oregon Basalt Products; Oregon, USA) and was sourced from the same supplier as basalt applied in a mesocosm study by Kelland *et al.*, (2020). Basalt was crushed to a fine powder on a Tema mill (University of Oxford). Powdered olivine applied by Renforth *et al.*, (2015) was sourced from Western Norway (Minelco Ltd.) and used in Exp1. Volcanic ash from the December 2018 eruptions of Krakatau Kecil was collected in July 2019 from a 17 cm thick deposit in a vegetated area (S 6.08392°,

E 105.45415°) (Indonesia). Before sampling, the top layer of ash was discarded to remove weathered surfaces. Agricultural lime (aglime), steel slag and cement kiln dust (CKD) used in Exp1 were obtained from Pigdon Quarry in Cornwall (UK, E & JW Glendining Ltd.), Port Talbot Steelworks in West Glamorgan (Wales) and Tarmac Blue Circle Ltd, respectively. Steel slag was crushed using a Tema mill. Volcanic ash, aglime and CKD are inherently fine-grained and did not undergo further grinding.

The BET surface area of all treatments was determined by N<sub>2</sub> adsorption using Micromeretics Gemini VI (Oxford). The elemental composition of treatments was analysed using XRF (Rigaku ZSX Primus II) with a pre-calibrated EZ-scan semi quant program and calibrated using BCR-1 and 879-1 standards (Leeds University, October 2021). A detailed description of the physical properties and elemental composition of each treatment is provided in Chapter 3 and 4, and can be found in the Appendix C data repository.

#### 2.2.2 Treatment application

In Exp0, three 79 g subsamples of 125-250 µm powdered basalt were mixed into three cores, respectively (Feb' 2019). A high application rate was used (100 t ha<sup>-1</sup>) to ensure observable effects within the timeframe of the preliminary study. This application rate is considered within the upper limit of annual application (150 t ha<sup>-1</sup>) (Smith, 2016), is lower than olivine application by Renforth *et al.*, (2015) (127 t ha<sup>-1</sup>) and Amann *et al.*, (2020) (220 t ha<sup>-1</sup>), and is aligned with basalt application by Kelland *et al.*, (2020) (100 t ha<sup>-1</sup>). During treatment addition, the top 13cm of soil was removed from each core and placed into separate acid-leached plastic buckets. Crushed basalt was thoroughly
mixed with soil until it was no longer visible. The soil and basalt mixtures were then returned to their respective cores.

Before treatments were applied to cores in Exp1, soil solution was sampled twice over four weeks to establish background conditions. Treatments were added to soil cores in March 2020 using a similar process as described above; however a lower application rate was used (39 g per core; 50 t ha<sup>-1</sup>) as this compares with UK liming guidelines (0.5-10 t ha<sup>-1</sup>) (Goulding, 2016), and is aligned with the application rate used in a recent model-based study (40 t ha<sup>-1</sup>) (Kantzas *et al.*, 2022). To prevent cross contamination between soil cores and treatments the same treatment was added consecutively to different cores. In both studies, three control cores underwent the same ploughing process; however no treatment was added.

#### 2.3 Sampling protocols

One of the primary aims of Exp0 was to develop a means of extracting sufficient volumes of soil solution for complete geochemical analysis from unirrigated soils with a low natural water flux whilst minimising disruption to fluid dynamics through the soil. A number of sampling methods were trialled and modified over the course of the preliminary study (Exp0), these included: attaching syringes 24 hours after the addition of 400 or 500 ml fluorescent dye, and collecting samples the following day; attaching syringes 48 hrs after the addition of 700 ml fluorescent dye, and collecting samples the following day; attaching syringes immediately before the addition of 330 ml or 500 ml fluorescent dye, and collecting samples the following day; attaching syringes after 5 hrs. The final method proved most effective and was applied over five sampling weeks at the end of Exp0 (Oct'19 –

Jan'20) and throughout Exp1 (Feb'20 – Jun'21). This involved the application of 330ml fluorescent dye immediately before sampling to increase pore saturation - without such irrigation, natural pore saturation would not have permitted sample collection. Uranine, a photo-sensitive fluorescent dye (C<sub>20</sub>H<sub>14</sub>Na<sub>2</sub>O<sub>7</sub>), was selected as a passive tracer as it is chemically inert, has low adsorptive properties (Smart & Laidlaw, 1977; Davis *et al.*, 1980; Sabatini & Austin, 1991; Kasnavia & Sabatini, 1999; Flury & Wai, 2003), is non-toxic (Field *et al*, 1995; Behrens *et al*, 2001), is easy to measure, is inexpensive and is widely used (Cowie *et al.*, 2014 and references therein).

#### 2.3.1 Exp0 sampling protocol

Before each sampling event, the six soil cores used in Exp0 were irrigated with 330 ml fluorescent uranine dye (50 µg ml<sup>-1</sup>) to increase the saturation of pore spaces and permit the extraction of soil solution. Fluorescent dye was created from filtered rainwater mixed with uranine powder. Following this, 50 ml BD Plastipak amber luer-lock syringes were attached to Rhizon samplers under vacuum and left for five hours. Pore-water and effluent samples were collected in clear, 15 ml centrifuge tubes, and an aliquot of each sample was stored in an opaque, 1.5 ml centrifuge tube. Opaque centrifuge tubes were used to prevent photodegradation of the fluorescent solution. The fluorescence of soil solution samples stored in opaque tubes was measured immediately after sampling (see section 2.5.1). The cation concentration of each sample was measured using ICP-MS (section 2.5.3).

#### 2.3.2 Exp1 sampling protocol

The sampling method developed in Exp0 (section 2.3.1) formed the foundation of the sampling protocol applied throughout Exp1, with a few noteable exceptions. Soil solution was sampled twice over four weeks prior to treatment application in Mar'20 and subsequently sampled monthly until Jun'21. Sampling was not possible from Apr'20-Jun'20, inclusive, due to a COVID-19 building lockdown. An additional 330 ml of fluorescent dye (50 µg ml<sup>-1</sup>) was applied to cores 24 hours before sampling to mitigate the effects of high evapotranspiration and low rainfall during summer months. Thus, on two consecutive days per month, 330ml fluorescent dye was applied individually onto 21 soil cores. A total volume of 3.5 ml was required for compete geochemical analysis on the ICP-MS, IC, fluorimeter and auto-titrator; therefore sample priority alternated monthly between ICP-MS and IC analysis or pH and alkalinity measurements when sample volume was below 3.5 ml.

## 2.4 Soil core drainage study

Mineral-fluid contact time is a key factor which influences dissolution in soil. Fast macroflow (preferential flow) reduces mineral-fluid contact time and, in turn, minimises opportunities for dissolution. Conversely, poor drainage can lead to the accumulation of fluid within micropores and mineral saturation can inhibit dissolution. A drainage study is an efficient means of understanding individual drainage patterns and transit times within each core and was used to inform the sampling protocol.

A drainage test was performed on 18 of the 21 soil cores used in Exp1 from January'2020 to February'2020. The purpose of this drainage experiment was to

assess the pathway and retention of fluorescent dye through the core, and to understand whether irrigation increased pore saturation and permitted extraction of sufficient sample volume for full geochemical analysis.

#### 2.4.1. Method

In January 2020, a 49.2 µg ml<sup>-1</sup> solution of fluorescent dye was created by mixing 0.3689 g uranine powder with 7500 ml filtered rainwater in a clear, 10 litre acid-leached HDPE jerrican. 330 ml of fluorescent dye was measured by mass into 21 acid-leached amber LDPE bottles. Amber BD Plastipak 50 ml syringes were attached to Rhizon samplers immediately after the fluorescent dye was added, respectively, onto the 21 cores. At this stage in Exp1, Rhizon samplers had only been installed into cores 1-18, nevertheless all 21 cores were treated equally. Cores were covered with black, opaque plastic sheeting and left undisturbed for five hours before soil solution was collected from the syringes and effluent bottles. An aliquot of each soil solution sample was stored in a black, 1.5 ml tube and measured for its fluorescence - see section 2.5.1. The sampling process was repeated 14 days later with the addition of 330 ml filtered rainwater. Rainfall and evapotranspiration were taken into account to correct for changes in the uranine concentration of fluorescent dye during the five hour interval. An aliquot of fluorescent dye (49.2 µg ml<sup>-1</sup>) was also used in a precision test and photodegradation study. Data collected during the drainage study can be found in the Appendix A data repository.

The precision of fluorescence measurements was evaluated by measuring the fluorescence of 93 aliquots of fluorescent dye, diluted ten-fold to create a 4.9  $\mu$ g ml<sup>-1</sup> solution. This concentration is representative of uranine soil solutions collected on day

14 of the drainage study, which averaged 4.5  $\mu$ g ml<sup>-1</sup>. The standard error of 93 blank corrected fluorescence measurements was 0.3 %.



**Figure 2.3.** Fluorescence-concentration calibration curve used in the drainage study,  $r^2$  0.9984. An aliquot of fluorescent dye (49.2 µg ml<sup>-1</sup>) was progressively diluted with rainwater to create a series of standards with known uranine concentration. The uranine concentration of soil solution samples range between 0-49.2 µg ml<sup>-1</sup> (orange arrow). The precision of fluorescence was investigated using a 4.9 µg ml<sup>-1</sup> solution (star).

#### 2.4.2. Pathway of fluorescent dye

The concentration of uranine in soil solution samples indicates the extent fluorescent dye percolated through the core and increased sample volume. The presence of fluorescent dye in all cores from 80-90 cm in figure 2.4a suggests the fluorescent dye percolated to the base of the core within the five hour sampling window. This demonstrates that irrigation with 330 ml fluorescent dye five hours before sampling is an effective means of increasing pore saturation and sample volume along the entire length of the 1 m core. The proportion of samples retrieved with sufficient volume for

geochemical analysis is noted in table 2.1 and illustrated in figure 2.5. The volume of sample collected on both days of the drainage study was mostly greater than the sample volume collected during Exp0. This suggests the absence of irrigation for 17 months prior to Exp1 did not impair the saturation of cores in Exp1 relative to cores used in Exp0. These findings confirm that addition of 330 ml fluorescent dye before sampling permits the collection of a sufficient number and volume of samples to conduct a variety of geochemical analysis without the need for continual irrigation between sampling events.



*Figure 2.4.* Concentration of uranine in solution samples on (a) day 1 and (b) day 14 of the drainage study, Feb'20.



**Figure 2.5.** Volume of soil solution collected from cores 1-18 on (a) day 1 and (b) day 14 of the drainage study, Feb'20. Blue reference lines are dotted, dashed and solid for critical volumes for geochemical analysis (1.2 ml, 2.0 ml and 3.5 ml, respectively).

Analysis method	Sample volume	% of samples in drainage study		% of samples in Exp0
	required (ml)	Day 1	Day 14	
ICP-MS, IC, pH, alkalinity, fluorescence	>3.5	47	30	34
pH, alkalinity, fluorescence	>2.0	68	49	45
ICP-MS, fluorescence	>1.2	75	57	55
None	0	16	22	26

*Table 2.1.* The number of samples collected above a specified sample volume on day 1 and 14 of the drainage study.

The heterogeneity of flow pathways is illustrated in figure 2.4. Preferential flow is demonstrated in core 10, whereby a large volume (25 ml) of highly concentrated fluorescent dye (42 µg ml<sup>-1</sup>) was sampled at 90cm depth, five hours after irrigation (figure 2.4a). This suggests the fluorescent dye experienced minimal dilution as it flowed through the 1 m core. In contrast, the concentration of uranine in samples collected from the base of other cores was substantially lower than the initial concentration of added fluorescent dye. This indicates fluorescent dye was diluted with pore-water whilst slowly percolating downwards through the core.

The relationship between sample fluorescence and core depth provides an insight into the pathway of dye through the core. For example, the concentration of uranine was notably highest at the top of the cores five hours after the addition of fluorescent dye (26.3  $\mu$ g ml<sup>-1</sup>, 0-20cm; 12.2  $\mu$ g ml<sup>-1</sup>, 80-90cm) (figure 2.4a). It is reasonable to assume the tracer was initially concentrated at the top of the core because only a small fraction of the fluorescent dye percolated downwards where it would have been diluted with pore-water. In comparison, 14 days after the tracer was added, the uranine concentration of solutions was highest at the base of the core (3.3  $\mu$ g ml<sup>-1</sup>, 0-20cm; 4.2  $\mu$ g ml<sup>-1</sup>, 80-90cm), and the average concentration in the core reduced from 22.6  $\mu$ g ml<sup>-1</sup> to 4.5  $\mu$ g ml<sup>-1</sup> (figure 2.4b). The nature of percolation described above is consistent with observations of a "slug" of tracer through a body of water described by other authors (Cowie *et al.*, 2014 and references therein). This indicates the majority of fluorescent dye percolated through the core as a single pulse and did not significantly alter the chemistry of soil solution.

It is important, however, to consider the potential caveats of this assumption. For example, the addition of large fluxes of rainwater with a low cation concentration has the potential to impact exchange at the soil-fluid interface and elevate the concentration of dissolved cations. This could lead to inflated estimates of carbon drawdown. It is also possible small quantities of fluorescent dye that were retained within the core equilibrated with pore-water and, in turn, increased the dilution-corrected concentration of dissolved ions measured in subsequent sampling weeks. This is consistent with a heavy tailed distribution of transit times, and is common in dry conditions where subsequent precipitation is not sufficient to flush the tracer through the soil core (Heidbüchel *et al.*, 2020). Nonetheless, it is assumed these processes do not significantly alter the findings from this research as the mass of uranine retained within the transit tail is only a small fraction of the total mass of uranine added to the core (figure 2.4b).

#### 2.4.3. Uranine retention

The drainage study was interrupted by a COVID-19 related building lockdown. A second drainage study was therefore conducted on all 21 cores four weeks after the final sampling event of Exp1 (Jun'2021) to assess the retention of uranine in soil cores between sampling months. The same sampling method was applied as is described in section 2.4.1, with the exception that cores were irrigated with rainwater instead of fluorescent dye. This ensured that the fluorescence of soil solution samples could be attributed to previous uranine additions. The uranine concentration (figure 2.7) of these samples was calculated using the fluorescence-concentration calibration curve created during the final sampling event of Exp1 (figure 2.6).

The average concentration of uranine in 102 soil solution samples measured four weeks after cores were irrigated with fluorescent dye was 2.8 µg ml<sup>-1</sup>. The uranine concentration of 42% of these samples was <2.0 µg ml<sup>-1</sup> (figure 2.7), which is 6 % of the uranine concentration in the fluorescent dye added in Jun'21 (50 µg ml<sup>-1</sup>). This is also substantially lower than the average uranine concentration (14.8 µg ml<sup>-1</sup>) of 1878 soil solution samples measured during Exp1, which ranged between 0-50 µg ml<sup>-1</sup>. Furthermore, this study was conducted at a time when potential evapotranspiration was highest and rainfall was low (Jul'21); therefore it is likely the concentration of retained uranine would have been diluted in wetter and cooler months by additional rainfall and less evapotranspiration. In light of this, we assume the low concentration of uranine retained between monthly sampling negligibly influenced soil-solution measured in subsequent sampling months.



**Figure 2.6.** Fluorescence-uranine calibration curve used in the second drainage study ( $r^2 = 0.9951$ ), created in the final month of the Exp1 time series (Jun'21). The uranine concentration of soil solution samples measured in the drainage study ranged between 0-13.6 µg ml<sup>-1</sup> (orange arrow).



**Figure 2.7.** Uranine concentration of 102 soil-solution samples extracted from 21 cores, four weeks after the addition of fluorescent dye (dashed line, 50  $\mu$ g m<sup>1</sup>).

# 2.5 Solution analysis

# 2.5.1 Fluorescence

The fluorescence of 100  $\mu$ l aliquots of soil solution samples and uranine-standards were measured on a SPARK fluorimeter in a Greiner flat black 96-well plate using an excitation wavelength of 485 nm, emission wavelength of 505 nm, 30 flashes and a gain of 32. Uranine-standards were created from a 50  $\mu$ g ml<sup>-1</sup> fluorescent dye, progressively diluted with rainwater. The fluorescence of standards was used to create a fluorescence-uranine concentration calibration curve (figure 2.8, 2.11). The fluorescence of each soil solution sample was applied to the calibration curve to calculate the uranine concentration of each sample (data can be found in the Appendix data repository).



*Figure 2.8.* Calibration curves measured over five sampling events during Exp0, with an average  $r^2$  of 0.9961.



*Figure 2.9.* Calibration curves measured over 13 sampling events during Exp1, with an average  $r^2$  of 0.9925.

# Photodegradation of uranine solution

Uranine fluorescent dye is photo-sensitive (Wang *et al.*, 2008); therefore exposure to light reduces the fluorescence of dye solutions. During monthly sampling, fluorescent dye was exposed to direct light for a cumulative time of 35 minutes, whilst: the fluorescent dye was mixed in a clear jerrican, the fluorescent dye drained from the top of the core, and soil solution samples were pipetted into a black well plate. In addition, fluorescent dye was exposed to light indirectly through opaque bottles for five hours during sampling, between day 1 and 2 of sampling, and between monthly sampling events. To investigate the rate of photodegradation in fluorescent dye, the change in uranine concentration of a 49.9  $\mu$ g ml<sup>-1</sup> dye solution was assessed over 28 days. The fluorescence of the dye was measured immediately after mixing uranine powder with rainwater. An aliquot of the dye was subsequently transferred into a clear, 50 ml centrifuge tube and an opaque bottle. The clear tube and opaque bottle were placed

in front of a window where they were exposed to equal amounts of light. The fluorescence of solutions stored in the clear tube and opaque bottle was measured every 2, 4 and 8 hrs and then daily for a week. Subsequent measurements were made every other day until week 2, and then weekly until week 4 (figure 2.10).

The fluorescence of the dye stored in the clear tube and opaque bottle remained within error (0.3 %) of the starting concentration for 2 hrs and 2 days, respectively, before degrading over the remainder of the study. These findings indicate direct light exposure during sampling would not have degraded the fluorescent dye during 35 minutes of direct light exposure or when stored in opaque bottles between consecutive sampling days. However, these findings suggest effluent solutions collecting in opaque bottles in the 4-5 week interval between monthly sampling events are likely to have experienced photo-degradation. In light of this, effluent samples collected between monthly sampling events were not used for further analysis. Data collected during the photodegradation study can be found in the Appendix A data repository.



**Figure 2.10.** Photo-degradation of fluorescent dye (49.9  $\mu$ g m<sup>1</sup>) stored in a clear centrifuge tube (blue) and an opaque bottle (brown) for (a) 3 days (b) 28 days. Black dashed lines illustrate the uncertainty boundaries of the starting solution.

#### 2.5.2 Dilution correction

Cores were irrigated with fluorescent dye before sampling to increase pore saturation and permit sampling (see section 2.3). In doing so, soil solution samples were diluted and comprised of pore-water and fluorescent dye (Eq.2.2). The extent of dilution, α, was calculated from the ratio of the concentration of uranine measured in each soil solution sample relative to the concentration of uranine in the fluorescent dye (Eq.2.3). Samples collected in Exp1 and in the final five sampling weeks of Exp0 were corrected to calculate the concentration of dissolved ions in solution before dilution. In addition, pH and alkalinity measured throughout the Exp1 time series were corrected for dilution assuming pH and alkalinity acted conservatively when mixing two solutions.

Eq. 2. 2. The proportion of pore-water and fluorescent dye in a soil solution sample:

$$P = \frac{M - (\alpha) R}{(1 - \alpha)}$$

whereby M is the measured concentration of an element in a soil solution sample, R is the measured concentration of an element in fluorescent dye, P is the concentration of an element in pore-water prior to dilution,  $\alpha$  is the fraction of the sample comprised from the fluorescent dye, and (1- $\alpha$ ) is the fraction of pore-water in the sample

Eq. 2.3. Uranine dilution

$$\alpha = \frac{[uranine]_{sample}}{[uranine]_{fluorescent dye}}$$



**Figure 2.11.** The extent of dilution,  $\alpha$ , as a function of depth in six soil cores measured during Exp0. The extent of dilution in samples measured at the same depth varied between soil cores and between sampling weeks within the same core, which suggests the extent of dilution was unique to each soil-solution sample.

## 2.5.3 ICP-MS

The concentrations of major and trace elements in the soil solution samples were determined using a PerkinElmer NexION 350D inductively coupled plasma mass-spectrometer (ICP-MS) (University of Oxford), which was calibrated using externally prepared calibration standards (Merck Certipur ICP Standards), and corrected for any drift by internal standard additions of Rh, In, Re and Ir into all measured solutions. Accuracy was assessed by analysing the international reference standard for riverwaters (SLRS-6). Soil solutions were acidified before analysis using 2% HNO<sub>3</sub> in a metal-free laboratory. For the analysis of major elements, soil solutions were diluted 50-fold. For trace element analysis, a 1 ml aliquot of soil-solution sample was diluted

by weight to 3 ml with 2% HNO<sub>3</sub>. During Exp0, a total of 88 samples across five sampling weeks were analysed for their ion concentration with an ICP-MS accuracy of  $\pm$  6-11% (Appendix B data repository). During Exp1, a total of 1636 samples across 21 cores were analysed for their ion concentration with an instrument accuracy of  $\pm$  1 to 9% (Appendix C data repository). The concentration of dissolved ions sampled after treatment was averaged per depth section (top, 0-30cm; middle, 30-60cm; base, 60-100cm; whole core, 0-100cm), across three treated and three control cores (see Appendix data repository).

# 2.5.4 Ion Chromatography

The anion concentration of soil solution sampled during Exp1 was determined using lon Chromatography (IC) (Department of Geography, University of Oxford, Aug'2021). A 1 ml aliquot of sample was filtered to 0.2  $\mu$ m and analysed using the AS23 carbonate eluent to determine the concentration of sulphates, phosphates, nitrates, chloride, chloride, fluorides and bromide. A total of 130 samples across 21 cores were analysed for their anion concentration. The uncertainty of anion concentrations was calculated in quadrature from instrument error and equipment blanks (tube, syringes, Rhizon samplers). Anion accuracy varied from  $\pm 2$  to 40 %. High error derives from instrument error for bromide and fluoride ions, and chloride contamination whilst cleaning Rhizon samplers in HCl. Data can be found in the Appendix C data repository.

# 2.5.5 Titrated alkalinity & pH

The alkalinity and pH of 1321 samples collected during Exp1 were measured on a Metrohm 916 Ti-Touch auto-titrator with a flat head electrode and an eco-vessel

suitable for small sample volumes. Temperature was maintained at 21°C using a Julabo BC4 water bath. The flat head electrode was calibrated using buffer solutions of pH 4, 7 & 10 and rinsed with de-ionised water between measurements. The sample mass was measured to 5 significant figures (sf) and ~1.4 ml solution was pipetted into the eco-vessel. The flat-head electrode, temperature sensor and magnetic stirrer were submerged in the sample. The pH of the solution was measured before 0.01N HCl titrant was added in 5 µl increments until the solution reached pH 2.9, where the second end-point of titration was used to calculate sample alkalinity. A standard solution of 10 mmol L<sup>-1</sup> was measured every 50 samples to ensure measurements did not drift. Data can be found in the Appendix C data repository.

The precision of alkalinity measurements was assessed by repeatedly measuring a 10 mmol (alkalinity) L<sup>-1</sup> CaCO<sub>3</sub> standard solution 30 times using the method described above. The percentage difference between the standard and the average alkalinity was 0.3 %. The precision of the flat head electrode was assessed by repeatedly measuring a standard buffer solution of pH 8.00, 30 times. The percentage difference between the standard solutions.

#### 2.5.6. Combined uncertainty

The total uncertainty of the dissolved ion concentration in each sample was calculated in quadrature from error associated with the ICP-MS or IC, the fluorimeter, and from contamination during sample preparation from the centrifuge tube, Rhizon samplers and the syringe. The uncertainty associated with possible contamination from Rhizon samplers, syringes, sampling tubes and the dilution process was measured using a

blank, composed of mQ water, relative to the concentration of the respective ion in soil solution averaged across the dataset.

## 2.6 Soil chemical analysis

# 2.6.1 Soil core preparation

The composition of one of the soil cores extracted in Aug'2018 was measured in Nov'2018. The soil core was stored vertically in a laboratory for 10 weeks. During this time compression resulted in a 10 % change in volume, whereby no soil was visible in the top 10 cm of the acrylic tubing. A hand-held circular drill, made of serrated steel, was used to remove the acrylic tubing. The soil was divided into 10cm segments, weighed in a glass dish and dried at 60°C for 48 hrs (Nov'18, University of Oxford). Oven-dried soil segments were crushed <1 mm using a steel-plated jaw crusher and ground to a fine powder using a Tema mill; hereafter these samples will be referred to as "the initial core". All crushing equipment was operated in the Earth Sciences Department, University of Oxford and cleaned with ethanol and compressed air. Each sample of crushed soil passed through a 1mm sieve and was divided into eight subsamples using a rifle sampler to avoid sampling bias. Sub-samples were analysed for their specific gravity, total inorganic carbon content (TIC), total organic carbon content (TOC), elemental composition (XRF, University of Cardiff), bulk density, moisture content, and bulk mineralogy (XRD, University of Oxford). Data can be found in the Appendix B data repository.

Seven cores were removed from the roof at the end of Exp1 (Aug'21). Each soil core had been treated with one of the seven silicate or carbonate treatments. Soil was ovendried and crushed as described above. Sub-samples were analysed for TIC, TOC, XRD (University of Oxford), XRF (University of Leeds), cation exchange capacity (CEC) and soil exchangeable ions (Rothamsted Research). At the end of Exp1, plant growth in the seven cores was removed, dried overnight at 60°C, crushed to a fine powder (Rothamsted Research). Data can be found in the Appendix C data repository.

2.6.2 Bulk density

Eq.2.4. Soil Bulk density;

$$P_b = \frac{M_{sample}}{V_{sample}}$$

where  $P_b$  is the bulk density of the sample (g cm<sup>-3</sup>),  $M_{sample}$  is the wet mass of the soil sample (g),  $V_{sample}$  is the volume of the sample (cm<sup>3</sup>).

## 2.6.3 Moisture content

Soil was weighed in a glass dish and oven dried at 60°C. The combined mass of the dish and soil was regularly weighed until there was no change in mass. The total change in mass is equivalent to moisture loss and represents the initial moisture content of each soil sample.

Eq.2.5. Soil moisture content;

$$M_c = \frac{(\text{wt of wet soil} + \text{dish}) - (\text{wt of dry soil} + \text{dish})}{(\text{wt of dry soil} + \text{dish}) - \text{dish}}$$

# 2.6.4 Specific gravity

The specific gravity ( $G_s$ ) is a measure of the density of a sample relative to the density of water, and was calculated using eq.2.16 to eq.2.12. The mass of soil sample ( $M_{sample}$ ) was calculated from the difference between the mass of the pycnometer ( $M_p$ ) and the mass of the pycnometer filled  $\frac{2}{3}$  with soil sample ( $M_{p+s}$ ) (Eq.2.7). The pycnometer was subsequently filled with de-ionised water and placed in a vacuum desiccator overnight at 10kPa. The pycnometer was filled with de-ionised water and re-weighed ( $M_{p+s+w}$ ). The pycnometer was cleaned and filled with de-ionised water and re-weighed ( $M_{p+w+w}$ ). The total volume of water ( $V_{total_water}$ ) and the volume of water added to the soil ( $V_{water_added}$ ) were used to calculate the volume of soil sample ( $V_{sample}$ ), as shown in eq.2.12.

## Eq.2.6. Specific Gravity;

$$G_s = \frac{M_{sample}}{V_{sample}} \cdot P_w^{-1}$$

where  $V_{sample}$  is the volume of the soil sample (cm<sup>3</sup>);  $M_{sample}$  is the mass of the soil sampl e(g);  $P_w$  is the density of water, assumed to be 1 g cm<sup>-3</sup>

Eq.2.7. Mass of soil sample;

$$M_{sample} = M_{p+s} - M_p$$

Eq.2.8. Mass of water added;

$$M_{water\_added} = M_{p+s+w} - M_{p+s}$$

Eq.2.9. Volume of water added;

$$V_{water \ added} = \frac{M_{water \ aded}}{\rho_w}$$

Eq.2.10. Total mass of water;

$$M_{total water} = M_{p+w} - M_p$$

Eq.2.11. Total volume of water;

$$V_{total \ volume} = \frac{M_{total \ mass}}{\rho_w}$$

Eq.2.12. Volume of soil sample;

$$V_{sample} = V_{total volume} - V_{water added}$$

## 2.6.5 Porosity

Soil porosity (*P*) is the ratio of the volume of voids in a sample relative to the total sample volume. The specific gravity, moisture content and bulk density were used to calculate soil porosity as shown in eq.2.13 to 2.15.

## Eq.2.13. Specific Volume

$$V_s = G_s (1 + M_c) \frac{\rho_w}{\rho_b}$$

where  $V_s$  is the specific volume of the soil sample (cm<sup>3</sup> g<sup>-1</sup>), G<sub>s</sub> is the specific gravity of the soil sample,  $M_c$  is the moisture content of the sample,  $\rho_w$  is the density of water (cm<sup>3</sup>),  $\rho_b$  is the bulk density of the soil sample (g cm<sup>-3</sup>),  $V_R$  is the void ratio. Eq.2.14. Void Ratio

$$V_{R} = V_{s} - 1$$

Eq.2.15. Porosity

$$P = \frac{V_R}{V_S}$$

## 2.6.6 Total (in)organic carbon

The total inorganic carbon (TIC) and total organic carbon (TOC) content of oven-dried, powdered soil sampled from the initial core was measured at Cardiff University, Nov'18. A crucible  $\frac{2}{3}$  filled with soil was weighed, heated to 550°C overnight and reweighed the following day. The same sample was heated in a furnace at 1000°C overnight and re-weighed. The mass lost during the initial heating stage (550°C) was equivalent to the mass of soil organic matter (SOM) and was converted to soil organic carbon using a conversion factor of 0.56, as discussed by Hoogsteen *et al.*, (2015). The mass lost during the second heating stage (1000°C) equalled the mass of inorganic carbon. Water loss is unlikely to have contributed substantially to the reduction in mass as soil samples were dried thoroughly beforehand.

At the end of Exp1, the TIC and TOC of soil samples was measured at the University of Oxford (Sept'21). For each 10 cm depth interval, two oven dried, milled soil samples were weighed to 25.00 - 50.00 mg and 50.00 - 100.00 mg, respectively, on a Mettler Toledo microbalance. The heavier sample was heated to 420°C overnight in a furnace to remove organic matter. Following this, both the heavy and light samples were heated to 1220°C in a Coulomat 702 to measure the percentage of total carbon. TIC was calculated from the percentage of carbon contained within the pre-heated sample. The difference between TIC and total carbon was used to calculate TOC.

## 2.6.7 Mineral composition of soil

The mineral content of dried, crushed soil sampled in 10cm depth intervals from the initial core was analysed by x-ray diffraction (XRD) (Nov'18, University of Oxford). At the end of Exp1, milled, dried soil samples were collated into depth sections (top, 0-30cm; middle, 30-60cm; bottom, 60-100cm) and analysed for their mineralogy using XRD (Sept'21, University of Oxford). These results are semi-quantitative and were calculated using the RIR method using HighScore software.

#### 2.6.8. Elemental composition of soil

The elemental composition of the initial soil core was analysed shortly after extraction (Nov'18). Dried, milled soil samples were collated into 10cm depth sections and analysed using a hand-held XRF (Cardiff University). The instrument was calibrated with stainless steel and used a soil analysis and a mining analysis. At the end of Exp1, oven-dried powdered soil samples were collated into depth sections. The elemental composition of the soil was analysed at Leeds University using a Rigaku ZSX Primus II XRF using a pre-calibrated EZ-scan semi quant program (Sep'21).

# 2.6.9 Soil cation exchange capacity and exchangeable cations

At the end of EXP1, soil samples were analysed for their cation exchange capacity (CEC) using Co-Hex extraction and ICP-OES analysis. Soil exchangeable cations were measured using ammonium extraction. These analyses were performed by Rothamsted Research (Oct'21).

## 2.6.10. Plant material

At the end of Exp1, the stems and leaves of herbaceous flowering plants were harvested from one of each of the treated cores (Aug'21). Samples were analysed for their cation concentration using nitric/perchloric digestion and ICP-OES analysis (Rothamsted Research).

## 2.7 Geochemical modelling

A geochemical modelling programme, PHREEQC (Parkhurst and Appelo, 1999), was used to assess the saturation state of mineral phases in soil solution sampled at the end of Exp1, using the llnl.dat database. Data inputs include sample pH, alkalinity, [anions], [cations] and temperature. Outputs were discarded when error exceeded +/-5%. The saturation state of solid phases were grouped into: Mg silicates (forsterite, talc); Ca silicates (anorthite, gismondine); clay minerals (kaolinite, montmorillonite, illite, nontronite, beidellite); Fe minerals (hematite, magnetite, goethite, trevorite, ferrite, delafossite); alumina minerals (gibbsite, diaspore, boehmite); Ca-carbonate (calcite); Mg-carbonate (magnesite); Ca-Mg carbonate (dolomite).

**Chapter 3.** Soil core study indicates limited CO<sub>2</sub> removal by enhanced weathering in dry croplands in the UK

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# Authors' contributions

FB designed the study with help from GMH and PR. FB led the data collection with input from PH. FB directed the analysis with input from GMH and PR. FB led the writing with feedback from GMH, PH and PR. All authors contributed to the final version of the manuscript for publication.

## Abstract

The application of crushed silicate minerals to agricultural soils has been suggested as a route to enhance weathering rates and increase CO<sub>2</sub> drawdown. Laboratory and field studies have attempted to evaluate the potential of enhanced weathering as a carbon dioxide removal technique but do not simulate the geochemical complexity of a soil environment. To overcome these limitations, this study uses an experimental set-up which fully encapsulates field conditions in a controlled setting using soil cores removed from UK cropland and treated with crushed basalt. Cores were exposed to natural weather conditions throughout a 14-month time series and soil solution was sampled in 10 to 20 cm intervals in the core to provide insight into the fate of dissolution products with soil depth.

This study assessed the rate and chemistry of basalt dissolution 8 months after addition at a high application rate (100 t ha<sup>-1</sup>) using direct measurements from a UK soil. Assuming conclusions drawn from this study are representative of field-scale enhanced weathering, findings indicate that a set application of basalt to lime-rich, unirrigated UK soils releases alkalinity at a rate of 310  $\pm$  30 eq ha<sup>-1</sup> yr<sup>-1</sup> and could remove 10.2  $\pm$  0.8 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>. Accumulation of undissolved basalt may also lead to large and irreversible changes to soil compositions following repeated application. When considering variation in hydrology around the UK, we assess the drawdown potential of application of basalt to all UK arable land as 1.3  $\pm$  0.1 MtCO<sub>2</sub> yr<sup>-1</sup>, which is equivalent to 3% of current UK agricultural CO<sub>2</sub> emissions. This is 5- to 25- fold slower than previous modelled assessments, likely due to complexities of soil systems and to water limitation on alkalinity release. Further research is needed to fully assess

controls on the potential of enhanced weathering in the real-world environment, across a range of hydrological and soil environments, before the approach is substantively scaled-up for CO<sub>2</sub> removal.

**Key words:** enhanced weathering, terrestrial weathering, negative emissions, carbon dioxide removal

# Highlights:

- Crushed basalt was applied to a UK agricultural soil in a 14-month soil core study
- Five years of basalt application over UK cropland could remove  $1.3 \pm 0.1$  MtCO<sub>2</sub> yr<sup>-1</sup>
- Enhanced weathering removes CO<sub>2</sub> considerably slower than model predictions
- Low water flux limits drawdown from enhanced weathering in dry UK cropland

#### 3.1. Introduction

Carbon dioxide removal technologies, such as enhanced weathering, are heavily relied upon to meet the international target of limiting global average temperature rise to 2°C. These targets will require several hundred GtCO<sub>2</sub> to be removed by the end of the century (e.g., Fuss *et al.*, 2018; The Royal Society and Royal Academy of Engineering, 2018). Terrestrial enhanced weathering (EW) involves the application of crushed rocks or minerals to agricultural land to accelerate natural weathering and CO<sub>2</sub> drawdown via the release of alkalinity (Eq.1.4) (Seifritz, 1990; Hartmann *et al.*, 2013). Previous calculations suggest enhanced weathering could remove 0.5-4 GtCO<sub>2</sub> yr<sup>-1</sup> globally by the end of this century (Smith *et al.*, 2015). However, existing pot (ten Berge *et al.*, 2012; Amann *et al.*, 2020; Kelland *et al.*, 2020), core (Renforth et al., 2015), laboratory (Palandri and Kharaka, 2004) and modelling studies (Strefler *et al.*, 2018; Beerling *et al.*, 2020; Kantzas *et al.*, 2022) produce conflicting estimates for rock and mineral dissolution rates and the carbon dioxide removal (CDR) potential of enhanced weathering – see Swoboda, Döring and Hamer (2021) for a full discussion.

Field studies are inherently costly and time consuming, and it is difficult to isolate variables which impact the dissolution process. In comparison, laboratory dissolution experiments oversimplify the complexities of the soil environment and fail to represent factors which influence mineral-fluid interaction, such as: preferential flow, hydrological conditions, surface passivation and saturation in micropores (White and Brantley, 2003). Consequently, the rate of olivine dissolution calculated from laboratory studies ( $10^{-14}$  mol cm<sup>-2</sup> s<sup>-1</sup>,  $19^{\circ}$ ) (Palandri and Kharaka, 2004) is up to three orders of magnitude faster than olivine dissolution measured in treated pot studies ( $10^{-17.75}$  mol(Olivine) cm<sup>-2</sup> s<sup>-1</sup>, Amann *et al.*, 2020;  $10^{-16.7}$  to  $10^{-15.8}$  mol(Olivine) cm<sup>-2</sup> s<sup>-1</sup>,

Renforth *et* al., 2015). Furthermore, existing pot and core studies control temperature and irrigation rate and therefore fail to capture the extent to which natural drying/wetting cycles influence mineral saturation and dissolution rate. The lack of depth-resolution in previous pot and core studies make it difficult to understand the intricacies of dissolution in a soil environment where the distribution of dissolution products are influenced by downwards percolation, secondary mineralisation, adsorption and exchange.

Unlike the fast-weathering mineral olivine, which is known to release Ni and Cr into the soil (Renforth *et* al., 2015), basalt rock has been proposed as an ideal treatment for enhanced weathering as its application to agricultural soils is an established practice which provides essential nutrients (Beerling *et al.*, 2020). Although basalt has low levels of heavy metals, it is composed of a range of minerals with varying dissolution rates. It is therefore important to assess whether trace quantities of fastweathering, metal-rich minerals within basalt release heavy metals into the soil-water environment. The dissolution rate of basalt (10<sup>-15.3</sup> to 10<sup>-16.2</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>) has previously been measured in a comprehensive pot study by Kelland *et al.*, (2020). However, to date, the CDR potential of basalt has not been adequately assessed in an environment representative of natural soil and hydrological conditions.

In this study, we use soil cores removed from UK cropland and develop a robust method of extracting sufficient soil solution for geochemical analysis. Coarse-grained basalt was applied at a rate equivalent to 100 t ha<sup>-1</sup>, in-line with a recent mesocosm study (Kelland *et al.*, 2020). Soil solution was sampled at up to 10 depths through a

1.0 m length core, providing a high resolution insight into cation release and the fate of dissolved products in the soil. We simulate the field environment by exposing cores to real-time variations in weather and temperature, and overcome low pore-water saturation with a well-characterised irrigation regime. Chemical measurements of soil solution sampled 8 months after basalt application provide the rate of basalt dissolution, alkalinity release and the CO<sub>2</sub> sequestration potential of basalt in agricultural soils.

# 3.2. Methods

#### 3.2.1. Experimental design

Soil cores were used in this study to addresses the limitations of laboratory experiments, which simplify the complexity of the soil environment, and field studies, which are inherently costly, time-consuming, difficult to replicate, control and monitor. In August 2018, 36 soil cores of 1.0 m length and 0.1 m diameter containing lime-rich loamy soil were extracted from an agricultural field in North Oxfordshire (FAI Farm, Wytham, 51.781°, -1.3141°) that had most recently been used to cultivate *Avena sativa* (oats) and *Hordeum vulgare* (barley). Soil cores were held in transparent plastic core liners during transport and, in most cases, throughout the experimental work. The bulk mineralogy, elemental composition and physical properties of one soil core was measured at the beginning of the study. From August 2018 the remaining cores were stored vertically on the roof of the Earth Sciences Department at the University of Oxford and wrapped in black sheeting. The tops of all soil cores were exposed to local weather and temperature to permit continued soil weathering in an outside environment prior to soil solution sampling. Herbaceous flowering plants naturally grew in the soil cores and were neither removed nor measured.

Soil cores were left undisturbed for three months before six cores were used during this study from Nov'2018 to Jan'2020. Rhizon CCS samplers with a 0.15 µm pore size (Rhizosphere Research Products) were inserted horizontally every 10 cm to 20 cm along the profile of the core. Effluent collected into amber LDPE bottles at the base of the core and is hereafter reported as soil solution collected at 100 cm. In this way, soil solution could be sampled throughout the time series from a range of depths without disrupting the structure of the soil core (see section 2.3 for further details). Basalt was mixed into three soil cores in Feb'2019. The top 13cm of three cores was removed, mixed thoroughly with crushed basalt (125-250  $\mu$ m) at a rate equivalent to 100 t ha<sup>-1</sup>, and returned to the respective core. Three control cores were treated to identical mixing but without basalt addition. This high application rate is aligned with a basalttreated mesocosm study by Kelland et al., (2020) (100 t ha<sup>-1</sup>), is lower than used in an olivine-treated core study (127 t ha-1; Renforth et al., 2015), and is larger than applied in a modelling study (40 t ha<sup>-1</sup>) (Kantzas *et al.*, 2022). Changes in the dissolved soil water chemistry directly associated with basalt dissolution were isolated by comparing the concentration measured in the treated cores and control cores.

Water sampling commenced in October 2019, 8 months after basalt addition, and continued until January 2020. This interval allowed for equilibration of the basalt in the mixed layer. Sampling occurred approximately fortnightly, with a five week interval between Dec'2019 and Jan'2020. Immediately before sampling, cores were irrigated with 330 ml rainwater (collected immediately adjacent to the cores) with added uranine powder to create a fluorescent dye (50 µg ml<sup>-1</sup>). This increased pore saturation and

permitted recovery of fluid. Rhizon samplers were held under vacuum for five hours during sample collection. The concentration of dissolved ions in soil solutions samples were corrected for dilution experienced during irrigation using fluorescent uranine dye concentrations in extracted fluids (see Chapter 2 for a full description). Natural rainfall was the only additional flux through the core over the remainder of the study; therefore the infiltration flux was calculated from rainfall minus evapotranspiration (Eq.2.1) (1.2 ml day<sup>-1</sup>; 57 mm yr<sup>-1</sup>; 1.4x10<sup>-5</sup> g s<sup>-1</sup>). The cation concentration of rainfall was less than 5% of soil solution and was accounted for in the dilution correction (see section 2.5.2). It is possible rainwater added during sampling introduced acidity to the soil-water system. However, this is unlikely to have substantially enhanced mineral dissolution within the five hour window the additional rainwater took to percolate through the core

This experimental set-up aims to represent field conditions as much as possible; however conclusions are sensitive to the design of the core study. For example, CO<sub>2</sub> partial pressure and fluid drainage may differ between the core and field environment. In addition, TIC and pedogenic carbonate formation were not assessed within the scope of this study and could influence the net CDR potential of EW. This study examines carbon drawdown in soils extracted from a single field site exposed to local weather conditions; therefore appropriate caution should be applied when extrapolating findings to the field scale which include a range of soil types, hydrological and climate conditions. Further EW trials will be required to overcome these knowledge gaps and permit a robust understanding of the efficacy of EW across a range of environments. The experimental set-up developed in this study formed the foundation of a wider soil core study to assess a range of possible materials for enhanced weathering in addition to basalt (Chapter 4).

#### 3.2.2. Soil and basalt characterisation

An untreated soil core was cut into 10 cm sections at the beginning of the study (Nov'18), oven dried at 60°C for 48 hrs, crushed using a jaw crusher and powdered on a Tema mill (University of Oxford). Soil samples were analysed for bulk density, moisture content, total inorganic carbon content (TIC), total organic carbon content (TOC), bulk mineralogy (XRD) and elemental composition (XRF) (University of Cardiff, University of Oxford) - see Chapter 2 for further details. The characteristics of the soil core distinctly changed over the 1 m profile (table 3.2); for example, TOC was highest above 30cm (2.5%), compared to an average of 1.5% across the remainder of the core. XRD measurements of calcite were ~2-3-fold lower than TIC, and are thought to reflect the inaccuracy of semi-quantitative XRD analysis techniques. Nonetheless, both TIC and XRD calcite measurements exhibited a similar relationship with depth, whereby TIC reduced from 0.8% above 40cm to 0.4% between 40-60 cm, and increased to 3.3% below 80cm. Overall, these findings suggest soil horizon A was located above 30cm; with a zone of accumulation between 40-70 cm in which dissolved ions re-precipitated as secondary minerals; and below this soil horizon C was formed from calcite-rich parent material.

Basalt was obtained from the Cascade Mountain Range, Oregon (Central Oregon Basalt Products) and crushed to a fine powder on a Tema mill (University of Oxford). The 125-250µm size fraction was extracted with a series of dry sieves and used for this study to prevent fine particulates creating a respiratory risk. The BET surface-area  $(16.3 \pm 0.2 \text{ m}^2 \text{ g}^{-1})$  of the 125-250 µm size fraction was determined by N<sub>2</sub> adsorption using Micromeretics Gemini VI (Oxford). The geometric surface-area was calculated in accordance with Tester *et al.*, (1993) (0.011 m<sup>2</sup> g<sup>-1</sup>) (Eq.B1). XRF analysis was
conducted using a Rigaku ZSX Primus II with a pre-calibrated EZ-scan semi quant program, calibrated using BCR-1 and 879-1 standards (Leeds University). The mineralogy of the basalt applied in this study is comprehensively described in Kelland *et al.*, 2020.

	Crushed Basalt	Initial soil	
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	16.3 ± 0.2		
Geometric surface area (m <sup>2</sup> g <sup>-1</sup> )	0.011		
Particle size (µm)	125 – 250		
XRF analysis	Mass %		
Al <sub>2</sub> O <sub>3</sub>	13.1 ± 0.5	13.2 ± 0.5	
BaO	0.10 ± 0.04		
CaO	9 ± 1	15 ± 2	
Fe <sub>2</sub> O <sub>3</sub>	18.9 ± 0.5	12.0 ± 0.3	
K <sub>2</sub> O	2 ± 1	3 ± 2	
MgO	1.5 ± 0.9	0.9 ± 0.5	
MnO	0.29 ± 0.02	0.20 ± 0.01	
Na <sub>2</sub> O	1.8 ± 0.8	0.14 ± 0.06	
P2O5	0.46 ± 0.02	0.65 ± 0.03	
SiO <sub>2</sub>	49 ± 5	53 ± 5	
TiO <sub>2</sub>	$3.0 \pm 0.8$	1.1 ± 0.3	
V <sub>2</sub> O <sub>5</sub>	0.11 ± 0.02	$0.034 \pm 0.005$	

**Table 3.1.** Composition of basalt and the initial soil core. Soil samples were measured at the beginning of the study and averaged over the 1m soil core.

Depth	Bulk	Porosity	Moisture	TOC	TIC
interval	density	(%)	content	(%)	(%)
(cm)	(g cm⁻³)		(%)		
0 – 20	2.1	20.4	12.5	2.6	0.8
20 – 30	1.2	57.3	14.4	2.5	0.8
30 – 40	1.6	41.8	13.9	1.9	0.7
40 - 50	1.8	37.9	14.9	1.5	0.4
50 - 60	1.8	39.5	15.5	1.6	0.4
60 - 70	1.7	42.0	16.6	1.2	0.7
70 - 80	2.0	31.5	15.9	1.5	2.0
80 - 90	1.6	45.0	17.2	1.6	2.6
90 - 100	1.7	42.9	15.0	1.4	4.0

**Table 3.2.** Characterisation of the soil core, measured at the beginning of the study. Note, vertical compaction reduced the volume of the core by 10% before analysis.

Depth	Quartz	K-	Plagioclase	Calcite	Magnetite	Rutile	Muscovite/	Kaolinite
interval		feldspar					illite	
(cm)								
0 – 20	71	9	7	4			1	8
20 – 30	71	6	2	3			14	4
30 – 40	88	4	2	1	1			5
40 – 50	73	8	8				3	8
50 - 60	63	10	7				12	9
60 - 70	76	10		2	1			11
70 - 80	74	2		2			17	4
80 - 90	74	10		8			3	5
90 - 100	57	6	4	11	1	1	8	11

**Table 3.3.** Bulk mineralogy of the soil core (wt%), measured at the beginning of the study using XRD (Oxford University, Nov'18).

# 3.2.3. Sampling protocol

Throughout the study, the top surface of all six soil cores was exposed to natural rainfall. Rainfall was measured at the site (Department of Earth Sciences, University of Oxford; Feb'19-Jan'20) and is similar to that observed nearby at Chimney Meadows, Oxfordshire (1.8 mm day<sup>-1</sup>, 14 ml day<sup>-1</sup> core<sup>-1</sup>; UKCEH, 2021). After evapotranspiration, the cores normally contained insufficient water to recover soil solution samples from the Rhizons or from effluent at the base. To permit sampling,

each soil core was therefore also irrigated on each of the five sampling occasions (Oct'2019-Jan'2020) with an additional 330 ml of rainfall (collected adjacent to the core) with added fluorescent dye (see Chapter 2 for full details of this process). This irrigation rate was ~20-fold greater than natural daily rainfall based on data from Chimney Meadows, Oxfordshire (UKCEH, 2021). This sampling protocol proved the most efficient means of maintaining natural hydrological conditions throughout the majority of the time-series whilst increasing the number and volume of soil solution samples. Immediately after irrigation, 50 ml BD Plastipak amber luer lock syringes were attached to Rhizon samplers under vacuum. Cores were left for five hours before soil solution was collected. Based on time-series measurement of the fluorescent dye (Chapter 2) this is sufficient time for the added rainwater to increase pore saturation through the core.

The fluorescence and concentration of uranine in each soil solution sample was measured with a SPARK fluorimeter. The ratio of the concentration of uranine in the soil solution sample relative to the fluorescent dye was used to calculate the extent pore-water was diluted with fluorescent dye on a sample-by-sample basis. For further details see Chapter 2.

# 3.2.4. Soil solution analysis

The concentrations of major and trace elements in the soil solution samples were determined using a PerkinElmer NexION 350D inductively coupled plasma mass-spectrometer (ICP-MS) (University of Oxford), which was calibrated using externally prepared calibration standards (Merck Certipur ICP Standards), and corrected for any

drift by internal standard additions of Rh, In, Re and Ir into all measured solutions. Accuracy was assessed by analysing the international reference standard for river waters (SLRS-6), and varied from  $\pm$  6 - 11%. Soil solutions were diluted 50-fold in a metal-free laboratory with 2% HNO<sub>3</sub> before the analysis of major elements (Ca, Mg, K, Na). The remaining soil solution was diluted to 3 ml and analysed for trace metals.

### 3.3. Results

### 3.3.1. Basalt surface area

Comminution is believed to create internal micro-porosity in crushed samples which is unavailable for mineral-fluid reactions (Brantley and Mellott, 2000). This is known to increase the reactive surface-area measured with BET analysis by 1-2 orders of magnitude (Kelemen et al., 2020). Using the BET surface-area (SABET) can therefore lead to underestimation in the surface-area-normalised dissolution rate. Significant hysteresis was observed in the N<sub>2</sub> desorption isotherm (figure B1) and the SA<sub>BET</sub> of basalt (16.3  $\pm$  0.2 m<sup>2</sup> g<sup>-1</sup>) was five-fold greater than the SA<sub>BET</sub> of powdered olivine applied by Renforth et al., (2015) which had a similar particle size distribution (3.04 ± 0.03 m<sup>2</sup> g<sup>-1</sup>, 78% particles between 125-500 µm). Furthermore, the SABET was 1500fold greater than the geometric surface-area (SAGEO), calculated assuming spherical particles with a radius equivalent to the weighted average particle size (Tester et al., (1993); eq.B1). The high SABET of basalt indicates substantial micro-porosity was introduced during crushing, with the true surface area available for dissolution potentially lying between these extremes. The difficulty in assessing effective surface area introduces a limitation on surface-area normalised dissolution rates calculated in this and previous studies of enhanced weathering. We nevertheless follow such studies here and use BET surface areas for surface-area-normalisation, so our results

can readily be compared to previous studies (Renforth *et al.*, 2015; Amann *et al.*, 2020; Kelland *et al.*, 2020). This uncertainty in surface-area-normalisation does not influence the rate of alkalinity release per hectare for a given mass of basalt addition and therefore does not influence the calculation of efficiency of CO<sub>2</sub> sequestration.

### 3.3.2. Ion release

To prevent sampling depth biasing the concentration of dissolved ions averaged over the whole soil core, the concentration of dissolved ions were first averaged in depth sections corresponding to distinct soil zones (top, 0-30cm; middle 40-60cm; base, 70-100cm). The concentration of each ion was averaged for the three depth ranges for the five sampling events and for the triplicate cores (treated and control). The dissolved concentrations of Ca, Cr, K, Na, Mg and Sr averaged across the whole length of triplicate cores were significantly higher in basalt-treated cores (figure B3). This differs from results by Kelland *et al.*, (2020) who observed no significant increase in dissolved Ca and Si, which is attributed to accumulation in the soil-plant system.

Differences in the average values of dissolved ions between the treated and control cores are normalised to the percent concentration in basalt to assess the impact of basalt dissolution (figure 3.1). The dissolved concentration of Ca, K, Na and Mg were elevated in soil solutions, and was most notably elevated at the top of basalt-treated cores, localised to the area of basalt addition. In contrast, soil solutions averaged over the whole length of basalt-treated cores were depleted in Fe, Al, (-1 pbb/ wt%), Mn (-2 ppb/ wt%) and Si (- 20 pbb/ wt%). Ca was notably depleted at the base of the core, indicative of secondary carbonate formation following solution saturation.



**Figure. 3.1.** The difference in ion concentrations in basalt-treated and control cores. Shown is the average concentrations over five-sampling events in the top (0 - 30cm), middle (40 – 60 cm), base (70 – 100 cm) and whole core (0 - 100 cm) for the three treated cores, minus the average for the three control cores ( $\mu$ g L<sup>-1</sup>), normalised to the percent concentration of the respective element in basalt. Values above zero are attributed to basalt dissolution, with the magnitude indicating the relative release to the dissolved phase of each element. Uncertainty is based on the standard error over three treated and three untreated cores.

# 3.4. Discussion

### 3.4.1. Ion release rate

A key goal of this study is to assess the rate of release of elements from the added basalt into the pore-waters in the core; both those elements that will consume CO<sub>2</sub>, and those that may have negative consequences (e.g. through their toxicity). The surface-area-normalised ion release rate,  $Wr_{surface area}$ , of each element (mol(ion) cm<sup>-2</sup> s<sup>-1</sup>) was calculated using eq.3.1;

(3.1) 
$$Wr_{surface\ area} = \frac{([C]_{treated-control}). Q}{SA_{basalt} \cdot M_{basalt}}$$

where *Q* is the infiltration flux through the core, calculated from rainfall minus evaporation  $(1.4 \times 10^{-5} \text{ g s}^{-1})$ ; *C* is the dissolved molar concentration in soil pore-waters of each ion averaged across the whole length of triplicate cores for the five sampling events (mol g<sup>-1</sup>); *SA*<sub>basalt</sub> is the BET surface-area of basalt (16.3x10<sup>4</sup> cm<sup>2</sup> g<sup>-1</sup>); and  $M_{basalt}$  is the mass of basalt applied (79 g). Ions released from basalt dissolution were isolated by subtracting the concentration of ions in control cores from the concentration in treated cores. The overall uncertainty was calculated in quadrature by summing the errors from each component of eq.3.1 (see data repository for Appendix B).

	lon release rate		
	(mol cm <sup>-2</sup> s <sup>-1</sup> )		
Al	$-24x10^{-23} \pm 4x10^{-23}$		
Ba	6x10 <sup>-24</sup> ± 1x10 <sup>-24</sup>		
Ca	19x10 <sup>-20</sup> ± 1x10 <sup>-20</sup>		
Cr	30x10 <sup>-25</sup> ± 3x10 <sup>-25</sup>		
Fe	$-19 \times 10^{-24} \pm 6 \times 10^{-24}$		
K	6x10 <sup>-20</sup> ± 1x10 <sup>-20</sup>		
Mg	49x10 <sup>-21</sup> ± 3x10 <sup>-21</sup>		
Mn	$-8 \times 10^{-24} \pm 3 \times 10^{-24}$		
Na	$72x10^{-21} \pm 2x10^{-21}$		
Ni	26x10 <sup>-25</sup> ± 2x10 <sup>-25</sup>		
Р	$-9x10^{-21} \pm 3x10^{-21}$		
Si	$-18 \times 10^{-21} \pm 4 \times 10^{-21}$		
Sr	$42x10^{-23} \pm 2x10^{-23}$		
V	9x10 <sup>-25</sup> ± 1x10 <sup>-25</sup>		

**Table 3.4.** BET surface-area-normalised ion release rate (mol  $cm^{-2} s^{-1}$ ) of elements in basalt-treated cores. Negative rates indicate removal of the respective element from solution.

The release of ions from basalt in soil varies from 19x10<sup>-20</sup> mol(Ca) cm<sup>2</sup> s<sup>-1</sup> to -8x10<sup>-24</sup> mol(Mn) cm<sup>2</sup> s<sup>-1</sup>. The negative release rate of some ions implies removal of these elements from solution, presumably into secondary phases (table 3.4). For example, the concentration of dissolved Si is lower in basalt-treated cores, relative to the control, and is consistent with an olivine-treated pot study by Amann *et al.*, (2020). These findings suggests EW will not contribute to an elevated land-ocean Si flux as suggested by other authors (Hartmann *et al.*, 2013).



**Figure 3.2** BET surface-area-normalised cation release rate (mol cm<sup>-2</sup> s<sup>-1</sup>) of major elements in basalt, calculated from dissolved cations in this study (triangles) and cations in the soil-plant-water system in Kelland et al., (2020) (circles).

The surface-area-normalised release rate of Ca and Mg in Kelland *et al.*, (2020) was  $\sim$ 3 orders of magnitude faster than release into the dissolved phase in this soil core study (figure 3.2). Kelland *et al.*, (2020) sourced basalt from the same region as in this study (Cascade Mountain Range, Oregon) and also applied basalt at 100 t ha<sup>-1</sup>, so the discrepancy in ion release rate is thought to relate to other differences in the experimental set-up. For example, Kelland *et al.*, (2020) assessed dissolution by measurement of the soil-water-plant phase, therefore uptake into the exchangeable pool and plant phase may partially explain the difference. The Kelland *et al.* (2020) experiment also used a higher water flux (767 mm yr<sup>-1</sup>) than the natural flux of this study (57 mm yr<sup>-1</sup>) which will further contribute to high dissolution rates (as discussed in Section 3.4.5 below).

Basalt applied in this study contained ~30-fold less Mg (0.9 wt% Mg) than olivine applied in a core study by Renforth *et al.*, (2015). However the release of Mg in this study  $(10^{-19.31 \pm 0.02} \text{ mol}(\text{Mg}) \text{ cm}^{-2} \text{ s}^{-1})$  was 3 orders of magnitude slower than Mg dissolution calculated by Renforth *et al.*, (2015)  $(10^{-15.5} \text{ to } 10^{-16.4} \text{ mol}(\text{Mg}) \text{ cm}^{-2} \text{ s}^{-1})$  and ~2 orders of magnitude slower than Mg dissolution calculated in an olivine-treated pot study by Amann *et al.*, (2020)  $(10^{-16.8} \text{ to } 10^{-17.4} \text{ mol}(\text{Mg}) \text{ cm}^{-2} \text{ s}^{-1})$ . This indicates SiO<sub>2</sub> polymerisation in basalt minerals retards dissolution relative to fast-weathering olivine.

In summary, slower release of ions into the dissolved form is observed in this core study than in previous observation studies. This may be explained by several processes, including SiO<sub>2</sub> polymerisation, sorption, plant-uptake and by the lower water fluxes of this study, conducted under natural precipitation and evaporation.

# 3.4.2. Alkalinity flux

The flux of ions into solution during dissolution allows calculation of the flux of conservative alkalinity which, as this must be matched by carbonate alkalinity, is the driver of CO<sub>2</sub> removal and the key measure for the rate of enhanced weathering. Alkalinity flux represents the net effect of basalt dissolution and is unaffected by the inherently complex mineralogy of basalt which may undergo preferential phase dissolution (Kelland *et al.*, 2020). Alkalinity flux is calculated directly from dissolved ion-balance, and ions removed from solution by adsorption and precipitation do not contribute to alkalinity flux (Drever, 1997). Here we simplify conservative alkalinity by considering only the four most concentrated cations in basalt (Ca, K, Mg, Na). This is reasonable because other cations are present (and released) at much lower

concentrations, and because there is very limited release of free anions from weathering of basalt. Basalt used in this study contained trace carbonate minerals (<1 wt%) so it is assumed dissolved cations derived from silicate weathering.

The flux of alkalinity into solution,  $Alk_{surface area}$ , (eq cm<sup>-2</sup> s<sup>-1</sup>) was calculated using eq.3.2;

(3.2) 
$$Alk_{surface\ area} = \frac{Q.([Ca] + [Mg] + [K] + [Na])_{treated-control}}{M.SA_{basalt}}$$

The concentration of dissolved cations ([Ca], [K], [Mg], [Na]) in the soil pore-waters was averaged across the whole length of triplicate cores for the five sampling events (eq g<sup>-1</sup>). The sum of dissolved alkalinity in control cores was subtracted from the sum of dissolved alkalinity in treated cores, and multiplied by the infiltration rate (Q, 1.4x10<sup>-5</sup> g s<sup>-1</sup>). The alkalinity flux was normalised to the BET surface-area of basalt, whereby M is the mass of basalt added to each core (79 g) and  $SA_{basalt}$  is the BET site-specific-surface-area of basalt (16.3x10<sup>4</sup> cm<sup>2</sup> g<sup>-1</sup>). The surface-area-normalised alkalinity flux was 10<sup>-18.22 \pm 0.03</sup> eq cm<sup>-2</sup> s<sup>-1</sup>, 62% of which derived from Ca release. This is two to three orders of magnitude slower than the BET-normalised alkalinity flux of dissolved Mg (10<sup>-16.1</sup> to 10<sup>-15.2</sup> eq cm<sup>-2</sup> s<sup>-1</sup>) in a similar olivine-treated core study by Renforth *et al.*, (2015).

The alkalinity flux was also normalised to the area of land over which basalt was applied,  $Alk_{land area}$ , (eq ha<sup>-1</sup> yr<sup>-1</sup>) using eq.3.3. This normalisation circumvents the inherent uncertainty in measuring mineral surface areas, and is more directly useful for assessment of the impact of enhanced weathering on carbon fluxes.

(3.3) 
$$Alk_{land area} = \frac{Q.T.([Ca] + [Mg] + [K] + [Na])_{treated-control}}{SA_{land}}$$

where *T i*s the time in one year (s) and  $SA_{land}$  is the surface area of the soil core (7.9x10<sup>-7</sup> ha). The land-area-normalised alkalinity flux measured in this study was 310 ± 30 eq ha<sup>-1</sup> yr<sup>-1</sup>, for the application rate of 100 t ha<sup>-1</sup> used in this study. The overall uncertainty was calculated in quadrature by summing the errors from each component of eq.3.2 and eq.3.2, respectively (see Appendix B data repository).

# 3.4.3. Basalt dissolution

Ion and alkalinity fluxes into solution are the driver of CO<sub>2</sub> consumption, but it is also of interest to assess the rate at which applied basalt dissolves and accumulates in the soil. The rate of ion release is influenced by the relative abundance of each element in basalt. To constrain the surface-area-normalised dissolution rate of basalt,  $Wr_{basalt}$ , (g(basalt) cm<sup>-2</sup> s<sup>-1</sup>) the ion release rate of each element was normalised to the molar concentration of the respective element in basalt (Eq.3.4);

(3.4) 
$$Wr_{basalt} = \frac{Wr_{surface area(x)}}{M_{(x)}}$$

where  $Wr_{surface area(x)}$  is the surface-area-normalised ion release rate (mol(ion) cm<sup>-2</sup> s<sup>-1</sup>) and  $M_{(x)}$  is the molar concentration of the respective element in basalt (mol g<sup>-1</sup>). In doing so, remaining variation in the dissolution rate of basalt relates to mineral differences.

Assuming differences in soil solution are solely a consequence of basalt weathering, the dissolution rate of basalt in this soil core study calculated from dissolved Ca is 10<sup>-</sup>

<sup>15.93 ± 0.05</sup> g(basalt) cm<sup>-2</sup> s<sup>-1</sup> and is broadly consistent when considering the release of other major cations ( $10^{-15.9 \pm 0.2}$  g(basalt) cm<sup>-2</sup> s<sup>-1</sup>, Mg, K;  $10^{-15.8 \pm 0.2}$  g(basalt) cm<sup>-2</sup> s<sup>-1</sup>, Na). This suggests mineral phases in the basalt applied in this study dissolve at a similar rate. This differs from model results by Kelland *et al.*, (2020) which indicate preferential dissolution of olivine and diopside, and observations of incongruent basalt dissolution in Icelandic rivers (Gislason and Eugster, 1987). It is possible this discrepancy is, at least partly, related to the removal of dissolved cations into the sorbed, plant and mineral fraction which were not measured within the scope of this study. Basalt dissolution in this study is approximately 10 to 100 times slower than olivine dissolution recorded in a similar core study by Renforth *et al.*, (2015), based on the molecular mass of forsterite ( $10^{-13.7}$  to  $10^{-14.6}$  g(olivine) cm<sup>-2</sup> s<sup>-1</sup>), and is indicative of SiO<sub>2</sub> polymerisation.

To assess the timescale on which basalt will undergo complete dissolution, a shrinking core model (SCM) was applied to spherical basalt grains using the equation described by Hangx and Spiers (2009) (Eq.3.5);

(3.5) 
$$X(t) = \frac{D_0^3 - (D_0 - 2.Wr.V_m.t)^3}{D_0^3}$$

where X(t) is the amount of basalt to have dissolved (vol%),  $D_0$  is the initial particle diameter (cm), *t* is the dissolution time (s), and  $V_m$  is the molar volume (91.6 cm<sup>3</sup> mol<sup>-1</sup>). *Wr* is the molar dissolution rate of basalt grains (10<sup>-18.3</sup> mol(basalt) cm<sup>-2</sup> s<sup>-1</sup>), calculated from the dissolution rate of basalt described above (10<sup>-15.93 ± 0.05</sup> g(basalt) cm<sup>-2</sup> s<sup>-1</sup>) and the molecular mass of basalt weighted to the mineral composition described in Kelland *et al.*, (2020) (226.6 g mol<sup>-1</sup>).

The SCM indicates uniform dissolution of 125-250 $\mu$ m grains will undergo complete (100%) dissolution in 10<sup>6</sup> years, and slow basalt dissolution will require extensive comminution (0.02  $\mu$ m particles) for basalt to completely dissolve within 1000 years. In light of this, the accumulation of basalt in agricultural soil must be considered when planning basalt addition in multiple years.

# 3.4.4. Implications for agricultural soil

The co-benefits of basalt addition on long-term soil quality has been discussed by other authors (Swoboda et al., 2021). Here I highlight the short-term impact from the accumulation of undissolved residual basalt in the ploughed layer following repeated annual addition. Applying the dissolution rate observed in this study to the SCM discussed in section 3.4.3 indicates that, even if basalt were ground to 1 µm diameter, <1 % basalt would dissolve in one year. Consequently, most of the added basalt will remain in the soil and, if further basalt is added annually, progressively accumulate in the top soil of arable land to alter physical, chemical and biological soil properties. The addition of basalt at 100 t ha<sup>-1</sup> is the equivalent of a 4.8 mm yr<sup>-1</sup> layer (assuming 40%) porosity, as measured in the soil core). With a typical ploughed layer 20 cm thick, it would take only 20 years of sequential addition before half of the soil consisted of undissolved basalt. Considering the proposed addition of enhanced weathering to actively cultivated arable land, it is essential to prevent large-scale basalt application impairing soil structure, cation exchange capacity (CEC), soil microorganisms and overall soil quality. Conventional agricultural practices apply aglime to cropland at a rate of 0-10 t ha<sup>-1</sup> (Goulding, 2016), which is equivalent to the addition of <1 % of the depth of the ploughed layer per year. In light of this, we suggest annual basalt

application may need to be limited to ≈5 years to prevent the accumulation of residual basalt exceeding 10 % of the ploughed layer.

It is also important to consider the impact of secondary phase precipitation or changes in exchangeable ion chemistry in the soil as a result of basalt addition. Depleted Al, Ba, Fe, Mn, and Si in soil solution suggest dissolved ions were removed from solution via sorption or secondary formation of minerals such as clays and Al-, Fe- oxides (as seen in previous studies; Panhwar et al., 2016). The precipitation of clays and iron oxides from dissolved ions could impact physical and chemical properties of the soil core; for example, micronutrient availability, heavy metal exchange and/ or adsorption, and plant toxicity (Bradl, 2004; Berner, R. A.; Berner, 2012; Igbokwe, O.A.; Ugwu, 2018). In addition, the large, charged surface-area of clays increases the cation exchange capacity (CEC) of soil which improves nutrient retention, and the retention of K+ as an interlayer cation within secondary clays could provide a long term K supply, an essential macronutrient for plant growth (Basak et al., 2016). Precipitation of clays and metal oxides could also influence physical properties of the soil core, reduce soil erosion and improve water retention and soil organic carbon retention (Edwards et al., 2017). However, the precipitation of oxides on negatively charged sites has the potential to reduce soil CEC (Sumner, 1963; Durn et al., 2019).

Depending on the composition of the applied treatment, large-scale enhanced weathering deployment could elevate the heavy metal content of soil pore-water and pose an environmental risk (Beerling *et al.*, 2018). In this study, the concentration of dissolved heavy metals averaged across the treated core ( $2.4 \pm 0.1$  ppb, Ni;  $0.32 \pm$ 

0.02 ppb, Cr; 4.7  $\pm$  0.4 ppb, V) were not enriched beyond the safety threshold of drinking water (Gautam *et al.*, 2014), or freshwater (Environment Agency, 2009b). Moreover, the release of low levels of V and Cr has been shown to have beneficial effects on plant growth (Chen *et al.*, 2021) and soil microorganisms (Singh and Kalamdhad, 2011). Although basalt dissolution measured in this study does not pose an immediate contamination risk to surrounding ground- and fresh-water environments, large-scale EW deployment will require comprehensive monitoring practices to ensure residual basalt and secondary mineral formation do not impair the quality of arable soils.

# 3.4.5. CO<sub>2</sub> drawdown

The flux of alkalinity released to the dissolved phase by basalt dissolution provides a direct quantitative measurement of the carbon dioxide removal (CDR) potential of basalt. This was calculated, using eq.3.6, in terms of kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>;

(3.6) 
$$CDR = Alk_{land area} M_{Co2}$$
. n.  $\frac{1}{1000}$ 

where  $Alk_{land area}$  is the alkalinity flux normalised to land-area (310 eq ha<sup>-1</sup>yr<sup>-1</sup>, see Section 3.4.2);  $M_{Co2}$  is the molecular mass of CO<sub>2</sub> (44 g mol<sup>-1</sup>);  $\eta$  is the molar ratio of CO<sub>2</sub> removed from the atmosphere relative to alkalinity released during enhanced weathering. Here we used  $\eta$ =0.75, as in Renforth (2019), to account for the conversion of some HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup> in the river and ocean system. Pedogenic carbonate formation was not assessed within the scope of this study, therefore carbon drawdown relates to sequestration into dissolved forms. These calculations do not consider emissions released over the life-cycle of EW from mining, transport and comminution which have been previously estimated to reduce the net drawdown potential of EW by 10-30% (Moosdorf *et* al., 2014; Lefebvre *et al.*, 2019). The overall uncertainty was calculated in quadrature by summing the errors from each component of eq.3.6 (see Appendix B data repository).

After a single application, the CDR potential of basalt was  $10.2 \pm 0.8$  kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>. This rate of drawdown is ~200 fold slower than CO<sub>2</sub> uptake calculated in biotic basalttreated mesocosm studies, conducted at two rates of basalt addition: 100 t ha<sup>-1</sup> (2000 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>; Kelland *et al.*, 2020) and 50 t ha<sup>-1</sup> (1830 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>; Vienne *et al.*, 2022). Lower CDR observed in this study reflects the complexity of the soil-mineral-fluid system in the soil conditions used, and a substantially lower water flux under our natural conditions than used in previous studies. Water fluxes applied in previous mesocosm and modelling studies (Renforth *et al.*, 2015; Amann *et al.*, 2020; Kelland *et al.*, 2022; Vienne *et al.*, 2022) include irrigation and are over an order of magnitude greater than the flux of water measured through soil cores in this study.

Water is a primary requirement for weathering and dissolution, and the flux of water is known to limit both the dissolution of minerals and the transport of dissolution products. The extent to which water flux controls the slower dissolution and CDR potential in this study than in previous irrigated studies can be assessed by comparing rates of CDR normalised to the flux of water (i.e. kg of CO<sub>2</sub> uptake, per land-area, per mm of water flux). Values for this study, with a natural water flux through the cores of 57 mm yr<sup>-1</sup>, are 0.2 kgCO<sub>2</sub> ha<sup>-1</sup> mm<sup>-1</sup>, while those in the Kelland *et al.* (2020) study, with an irrigated flux of 767 mm yr<sup>-1</sup>, is 2.6 kgCO<sub>2</sub> ha<sup>-1</sup> mm<sup>-1</sup>. Even when normalising for water flux in

this way, CO<sub>2</sub> uptake rates in this study are  $\approx$ 15 times lower than in the earlier mesocosm studies. This indicates that other factors limit dissolution, perhaps indirectly related to water flux. These may include natural drying/wetting cycles creating a saturation limitation on dissolution at the mineral-water interface, increased secondary uptake of ions in the soil, or preferential flow of the limited water through channels in the natural soil environment. It is possible the regular irrigation regime applied in existing pot/core studies (Renforth *et al.*, 2015; Amann *et al.*, 2020; Kelland *et al.*, 2020; Vienne *et al.*, 2022) optimised mineral-fluid interaction, whereas real-time variation in rainfall patterns may have inhibited dissolution in this core study.

In summary, CDR rates assessed in the natural conditions of Oxfordshire are much lower than those assessed in previous lab and modelling studies, with the lower water flux observed in our natural settings a major control on these lower fluxes.

# 3.5. UK impact

The CDR potential of large-scale enhanced weathering deployment can be calculated by assuming the alkalinity flux derived in this study is representative of that in basalttreated agricultural fields more generally. We limit continuous annual application to five years to prevent accumulation of undissolved basalt in cultivated soils exceeding 10 % of the ploughed layer (Section 3.4.4). If all UK soils behave identically to those in this study, applying 100 t ha<sup>-1</sup> per year of ground basalt for five years to all UK croplands (6.1Mha; DEFRA, 2020) would remove  $0.31 \pm 0.02$  MtCO<sub>2</sub> yr<sup>-1</sup> from the atmosphere, with this level of removal continuing effectively indefinitely. Further application onto all farmland (17.1Mha; DEFRA, 2020), including non-ploughed

grazed land, may increase drawdown to  $0.87 \pm 0.07$  MtCO<sub>2</sub> yr<sup>-1</sup>, though the rate of weathering without mixing into the soil is not well constrained by this study.

Hydrological conditions vary significantly across the UK (Kay et al., 2013) and, given our conclusion that water-flux is a critical control on the rate of enhanced weathering, this variation should be considered in extrapolating nationally from our experiment. To do so, we use river flow data (m<sup>3</sup> s<sup>-1</sup>) from the National River Flow Archive (NRFA, 2022) to understand the net water flux available for EW following rainfall, evapotranspiration and irrigation. Using river fluxes for this purpose ignores groundwater recharge, but this is minor (<10%) relative to river fluxes (Jackson et al., 2013). Averaging UK river fluxes, normalised by crop-cover in catchment areas, indicates a weighted net water flux of 235 mm yr<sup>-1</sup> (NRFA, 2022). This is approximately four times greater than the water flux measured in Oxfordshire during this study (57 mm yr<sup>-1</sup>). Assuming a linear relationship between water flux and CDR potential, and increasing the flux above for all arable land accordingly, suggests 1.3 ± 0.1 MtCO<sub>2</sub> yr<sup>-</sup> <sup>1</sup> as a best estimate for the drawdown potential of EW in the UK when accounting for variation in hydrology. This is equivalent to 3% of current greenhouse gas emissions from UK agriculture (which were 46.3 MtCO<sub>2</sub>e yr<sup>-1</sup> in 2019; DEFRA, 2021a). It is likely that the relationship between water flux and CDR potential is not linear due to the complex interplay between dissolution, alkalinity release and natural drying/wetting cycles, particularly in dry conditions. Further research into this issue is required before a more accurate assessment of total UK EW potential can be made.

The rate of CDR calculated from this empirical study is 5- to 25- fold slower than derived in the detailed modelling study of Kantzas *et al.* (2022) (6 - 30 MtCO<sub>2</sub> yr<sup>-1</sup>). That study considered lower application rates of basalt (40 t ha<sup>-1</sup> yr-1), but with addition at this rate for multiple years with the annual CDR rate derived at a steady state condition. A large component of the higher CDR potential in Kantzas *et al.* (2022) is likely to be due to high water fluxes applied in that model for the UK (461-849 mm yr<sup>-1</sup>); rates significantly higher than net water fluxes derived from river flow.

Addition of silicates such as basalt to agricultural land has been practised in various parts of the world for many years, and can have important agricultural advantages for nutrient supply and retention (Swoboda *et* al.,2021). There may be benefit from expanding such application for agricultural reasons, but the capacity of this action for draw down of CO<sub>2</sub> from the atmosphere should not be overstated as a reason for such addition.

# 3.6. Conclusion

As negative emission technologies are increasingly relied upon to reduce atmospheric greenhouse gases, it is important to understand the contribution enhanced weathering could make to UK net-zero emission reduction targets. This soil core study revealed the fate of dissolution products at a range of depths within UK agricultural soil cores treated with crushed basalt and exposed to natural UK weather. Basalt dissolution elevated the dissolved concentration of major cations (Ca, Na, Mg, and K), and increased the alkalinity flux into the soil-water system at a rate of  $310 \pm 30$  eq ha<sup>-1</sup> yr<sup>-1</sup> when considering the high application rate used in this study (100 t ha<sup>-1</sup>). Assuming

findings in this core study are representative of the field scale, basalt dissolution in natural agricultural soil has the potential to draw down  $10.2 \pm 0.8 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$  after a single application. Slow, water-limited dissolution and accumulation of undissolved basalt in the ploughed layer could limit multiple additions. We calculate that five years of annual basalt application at 100 t.ha<sup>-1</sup> has the potential to sequester  $1.3 \pm 0.1 \text{ MtCO}_2$  yr<sup>-1</sup> over UK cropland. This value takes into account hydrological variations, which this study indicates are a critical control on CO<sub>2</sub> removal potential. The resulting flux is equivalent to <3% of UK agricultural emissions, and is substantially lower than previous modelled estimates. Given the importance of water flux demonstrated in this study, future work is needed to understand the interaction between these fluxes and enhanced weathering across a range of soil types.

**Chapter 4.** Experimental evidence constraining the enhanced weathering potential of a range of treatments in dry UK agricultural soils

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The chapter will be submitted to Science of the Total Environment

# Authors' contributions

FB led the development of the study, data collection, analysis and writing. GMH helped to design the study, influenced the analysis and provided feedback on writing.

### Abstract

Enhanced terrestrial weathering is a carbon dioxide removal (CDR) technology which aims to accelerate carbon drawdown associated with mineral dissolution through the spreading of crushed rock/mineral treatments onto agricultural fields. At present, the drawdown potential of EW remains uncertain. In this study, soil cores extracted from a typical UK agricultural site were used to geochemically assess the efficacy of EW whilst simulating field conditions. A range of "treatments" were applied to soil cores at 50 t ha<sup>-1</sup>, including: agricultural lime (aglime), basalt, cement kiln dust (CKD), olivine, steel slag, and volcanic ash. A diverse suite of chemistry was used to understand the pathway of dissolution products, and constrain the CDR potential and environmental impact of treatment addition.

After a single application, the CDR potential was, in decreasing order: steel slag ( $20 \pm 3 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > CKD ( $16 \pm 2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > basalt ( $5.0 \pm 0.7 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > volcanic ash ( $2.7 \pm 0.4 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > aglime ( $2.2 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > olivine ( $0.0 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ). Multiple steel slag addition is not advised as application raised the dissolved concentration of heavy metals, and availability will limit CKD application. Liming is currently considered a source of CO<sub>2</sub>, however this study suggests liming could reduce UK agricultural emissions in some conditions.

Assuming results are representative of EW on a field-scale, this research suggests 10 years of basalt application over UK cropland could remove  $1.2 \pm 0.2$  MtCO<sub>2</sub> yr<sup>-1</sup> when considering variation in hydrology. This is equivalent to <3% UK agricultural CO<sub>2</sub> emissions, and is 5- to 25- times slower than previously estimated. Slow rates of

drawdown are thought to reflect slow dissolution in a water-limited environment and limitations of soil degradation. Nationwide EW may therefore present limited potential as a practical means of contributing towards UK net-zero emission reduction targets.

**Key words:** enhanced weathering, basalt weathering, negative emissions, carbon dioxide removal, industrial silicates, liming

# Highlights:

- 16-month soil core study reveals impact of enhanced weathering (EW) in UK cropland
- Industrial silicates draw down CO<sub>2</sub> quickly but application will be limited
- Ten years of basalt application over UK cropland could remove  $1.2 \pm 0.2$  MtCO<sub>2</sub> yr<sup>-1</sup>
- Low water flux limits drawdown from EW in dry UK cropland
- Dissolution of lime could reduce UK agricultural emissions by ~0.6 MtCO2 yr<sup>-1</sup>

### 4.1. Introduction

To limit global average temperature rise to 2°C, existing research suggests we need to remove ~25% of the CO<sub>2</sub> emitted each year, equivalent to several hundred GtCO<sub>2</sub> over the 21<sup>st</sup> century (IPCC, 2018; The Royal Society, 2018). CO<sub>2</sub> is removed by silicate and carbonate mineral weathering, which are critical components of the global carbon cycle that stabilise Earth's climate (Eq.1.4-1.6). Such mineral weathering operates on a long-timescale, with consumption of atmospheric CO<sub>2</sub> by weathering of ≈0.35 GtCO<sub>2</sub> yr<sup>-1</sup> (Moon et al., 2014), compared to present global emissions of 49 ± 4.5 GtCO<sub>2</sub>eq yr<sup>-1</sup> (IPCC, 2014). Enhancing this rate of terrestrial weathering has been proposed as a CO<sub>2</sub> removal technology and involves the application of crushed rocks/minerals to agricultural land to accelerate the weathering process via the release of alkalinity and compensating removal of CO<sub>2</sub> to natural waters or secondary mineral formation (Seifritz, 1990; Hartmann et al., 2013 and refrences therein). Theoretical estimates suggests enhanced weathering (EW) could remove 0.5-4 GtCO<sub>2</sub> yr<sup>-1</sup> globally (Smith et al., 2015), which is a meaningful fraction of CO<sub>2</sub> removal (CDR) targets. However, these calculations are based on very limited experimental assessment of the physical, chemical and biological features of EW in agricultural soil, and of how this environment may control net alkalinity release.

Here we present a 16-month soil core study which analyses geochemically how dissolution of a range of silicates and carbonates, previously suggested as treatments for EW, operates in a soil environment. By comparing the chemistry of treated cores to untreated control cores at different depths in the soil, we isolate the geochemical impact of treatment dissolution on the soil and freshwater environment, and gain a novel insight into the fate and distribution of dissolution products. Together, these data

provide a comprehensive insight into the efficacy of enhanced weathering application over UK arable land.

### 4.2. Summary of previous experimental work

### Co-benefits

Application of crushed rock powder is an established agricultural practice with multiple rock powder studies demonstrating increased yield and nutrient supply, improved soil pH and microbiology, and reduced AI toxicity (Anda, Shamshuddin and Fauziah, 2013; Moretti *et al.*, 2019; Ramos *et al.*, 2019; Swoboda, Döring and Hamer, 2021 and references therein). A recent mesocosm experiment indicates basalt application reduces nitrogen leaching (Vienne *et al.*, 2022)(Vienne, A; Poblador, S; Portillo-Estrada, M; Hartman, 2022)(Vienne, A; Poblador, S; Portillo-Estrada, M; Hartman, 2022)(Vienne, A; Poblador, S; Portillo-Estrada, M; Hartman, 2022), and a model-based study suggests EW has the potential to replace conventional fertilisers and reduce UK nitrous oxide emissions (Kantzas *et al.*, 2022).

# Dissolution rate

A critical factor for assessment of EW is the rate of dissolution of fresh mineral surfaces in natural soil conditions. An extensive body of past work has used laboratory experiments to assess this rate. Olivine dissolution recorded in laboratory experiments typically give high rates ( $\approx 10^{-14}$  mol(Olivine) cm<sup>-2</sup> s<sup>-1</sup>, 19°C, pH 7; Palandri and Kharaka, 2004) but oversimplify the array of variables which influence mineral-fluid interaction in the soil environment. These dissolution rates are up to three orders of magnitude faster than olivine dissolution recorded in pot ( $10^{-17.12}$  to  $10^{-17.75}$  mol(Olivine) cm<sup>-2</sup>s<sup>-1</sup>, Amann *et al.*, 2020) and core studies ( $10^{-15.8}$  to  $10^{-16.7}$  mol(Olivine) cm<sup>-2</sup> s<sup>-1</sup>, Renforth *et al.*, 2015). However these pot and core studies underestimate olivine dissolution in the natural soil environment as they only account for dissolution products in soil solution. In contrast, Kelland *et al.*, (2020) measured the dissolution rate of basalt (10<sup>-15.3</sup> to 10<sup>-16.2</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>) in a comprehensive biotic mesocosm study considering the accumulation of dissolution products in the dissolved and exchangeable pool and by plant-uptake. Although pot and core studies are more representative of the soil environment than laboratory-based beaker studies, existing studies do not simulate the pattern or flux of natural rainfall - a key factor which can lead to mineral saturation and inhibit dissolution rate (see Chapter 3 for a full discussion). Furthermore, existing pot and core studies are based on low-resolution analysis of soil solution which conceals changes in soil-water chemistry with depth. To date, existing pot and core studies measure dissolution of one or two treatments in the same mesocosm set-up. As the experimental set-up can greatly influence dissolution rate, this prevents a direct comparison of the EW potential of multiple proposed treatments.

### Carbon dioxide removal

The release of alkalinity into soil solution is critical for CO<sub>2</sub> uptake, whereby an increase in total alkalinity (as defined by Zeebe and Wolf-Gladrow (2001)) accelerates the drawdown of atmospheric CO<sub>2</sub> into stable, dissolved and mineral carbon phases (Eq 1.1 to 1.5). The dissolution of ions described above is indicative of how quickly added treatments dissolve; however dissolved ions can be removed from solution by soil processes such as adsorption, exchange, secondary mineral formation and plant uptake. The remaining net flux of alkalinity contributes to carbon drawdown. A number

of recent modelling and theoretical studies have estimated promising drawdown potential for EW (Smith *et al.*, 2015, 2016; Renforth, 2019; Lewis *et al.*, 2021; Kantzas *et al.*, 2022). Kantzas *et al.*, (2022) used a vertical reactive transport model to estimate basalt application at 40 t ha<sup>-1</sup> yr-1 for multiple years over UK cropland could remove 6-30 MtCO<sub>2</sub> yr<sup>-1</sup>, which would compensate for a considerable proportion of UK agricultural emissions (which were 46.3 MtCO<sub>2</sub>e yr<sup>-1</sup> in 2019; DEFRA, 2021). UK drawdown could be further elevated to 44-180 MtCO<sub>2</sub> yr<sup>-1</sup> following the co-deployment of other land based NETs (Smith *et al.*, 2016). However, these studies are based on limited experimental assessment of EW in agricultural soils, and the land-ocean-transfer of alkalinity.

Thus far, seven studies have investigated the carbon dioxide removal (CDR) potential of soils in mesocosm pot experiments treated with olivine (ten Berge *et al.*, 2012; Dietzen *et al.*, 2018; Amann *et al.*, 2020); basalt (Kelland *et al.*, 2020; Vienne *et al.*, 2022); and wollastonite (Haque *et al.*, 2019; Haque, Santos and Chiang, 2020). For a detailed summary of these studies see Swoboda, Döring and Hamer (2021). The CDR potential of olivine remains equivocal and varies by two orders of magnitude when considering the dissolved concentration of Mg (0.023-0.049 tCO<sub>2</sub> ha<sup>-1</sup>, Amann *et al.*, 2020; 2.690 tCO<sub>2</sub> ha<sup>-1</sup>, ten Berge *et al.*, 2012; 4.16 tCO<sub>2</sub> ha<sup>-1</sup>, Dietzen *et al.*, 2018). Kelland *et al.* (2020) and Vienne *et al.*, (2022) applied the average cation concentration of leachate measured in biotic, basalt-treated pot studies to a geochemical model to predict 2.36 tCO<sub>2</sub> ha<sup>-1</sup> and 1.83 tCO<sub>2</sub> ha<sup>-1</sup> drawdown one year after application of 100 t ha<sup>-1</sup> and 50 t ha<sup>-1</sup>, respectively. However, existing mesocosm studies do not account for the reduction in net CO<sub>2</sub> drawdown related to anion dissolution or emissions released over the lifecycle of EW.

To date, the CDR potential and geochemical impact of alkaline-rich, industrial byproducts has not been experimentally assessed in agricultural soil. Recent research suggests alkaline-rich silicates produced from industrial processes, such as steel slag (a calcium and magnesium-rich silicate glass) or cement kiln dust (CKD), could provide an alternative source of cations without the need for extensive crushing (Renforth *et al.*, 2011; Renforth, 2012, 2019b). However, the EW response to industrial by-products may be heterogeneous as their chemical and physical properties depends on the production process (Renforth, 2019b), and heavy metal dissolution could pose a risk to the surrounding environment (van Oss & Padovani, 2003; Huijgen & Comans, 2006).

Aglime, formed predominantly from CaCO<sub>3</sub>, is regularly applied to cropland to maintain an optimal soil pH for crop growth. Aglime spreading is currently considered a source of greenhouse gas emissions based on the assumption that aglime reacts with strong acid and all C in lime is released to the atmosphere (IPCC, 1997) (Eq.1.7). However these calculations do not consider the reaction of aglime with carbonic acid in moderately acidic soils which releases alkalinity into solution and drives the drawdown of CO<sub>2</sub> (Hamilton *et al.*, 2007) (Eq.1.8). This means existing liming practices could be an unrecognised greenhouse gas removal mechanism which could significantly alter the accounting of agricultural emissions in the UK.

### Heavy metal release

The release of heavy metals from silicate-rich, industrial by-products remains understudied, and olivine dissolution in soils is associated with heavy metal toxicity in the soil-water environment. For example, elevated Ni was measured in soils after olivine application at 8.15 to 204 t ha<sup>-1</sup> in a pot study by ten Berge *et al.*, (2012); Renforth *et al.* (2015) estimated >99% dissolved Ni and Cr accumulated within olivine-treated soil; and Amann *et al.* (2020) measured elevated dissolved Ni and Cr in soil pore-water. In contrast, basalt is described as a promising enhanced weathering treatment with low heavy metal content (Renforth, 2012; Beerling *et al.*, 2020). Vienne *et al.*, (2022) observed an increase in Al availability and soil and pore-water Ni after amending soils with basalt at 50 tha<sup>-1</sup>, but Ni levels remained within environmental thresholds and potato growth was not impaired.

### 4.3. Experimental design

#### 4.3.1. Experimental set-up

A detailed description of the experimental set-up is provided in Chapter 2. Soil cores of 1.0 m length and 0.1 m diameter containing lime-rich, loamy soils were extracted from UK agricultural land (FAI Farm, N Oxfordshire, 51.781°, -1.3141°; Aug'2018). 21 cores were left undisturbed until the start of this study (Feb'2020) and six soil cores were used in a preliminary study (Chapter 3). Pore-water and effluent were sampled monthly over a 16-month time series (Feb'2020- Jun'2021) at a range of depths to investigate the pathway of dissolution products through the terrestrial environment. Soil solution was sampled twice over four weeks prior to treatment application in Mar'2020. Sampling of the core was not possible soon after treatment addition due to a COVID-19-related building lockdown (Apr'2020-Jul'2020). This period gave the cores opportunity to stabilise following treatment. Core sampling commenced in Aug'2020 and was undertaken for a complete annual seasonal cycle.

Six different treatments (agricultural lime, cement kiln dust, crushed basalt, crushed olivine, crushed steel slag, volcanic ash – see section 4.3.2 for details) were added to three soil cores, respectively, at a rate of 50 t ha<sup>-1</sup> (5 kg m<sup>-2</sup>) with an untreated triplicate control. This application rate compares with UK liming guidelines (0.5-10 t ha<sup>-1</sup>; Goulding, 2016), is aligned with a detailed modelling study (40 t ha<sup>-1</sup>; Kantzas *et al.*,, 2022), and is lower than the high application rate used in a recent mesocosm study (100 t ha<sup>-1</sup>; Kelland *et al.*, 2020).

Natural rainfall was the only source of irrigation throughout the majority of the timeseries to simulate the on-site water balance in an unirrigated agricultural setting. The exception to this was two doses of 330 ml rainwater applied to each core (84 mm/ core) immediately before sampling to increase pore-water saturation and permit sample collection. The impact of this irrigation flux on soil solution is accounted for using a dilution-correction – see Chapter 2 for further details. The infiltration flux (Eq. 2.1; 1.3 ml day<sup>-1</sup>, 60 mm yr<sup>-1</sup>;  $1.5x10^{-5}$  g s<sup>-1</sup>) was calculated from natural rainfall measured beside the cores, minus evapotranspiration measured in Chimney Meadows, Oxfordshire (UKCEH, 2021). This water flux is consistent with a similar unirrigated soil core study (57 mm yr<sup>-1</sup>, Chapter 3). The flux of water measured in this study was one to two orders of magnitude lower than the high infiltration rates applied in existing pot, core and modelling studies which include irrigation (Renforth *et al.*,

2015; Amann *et al.*, 2020; Kelland *et al.*, 2020, Kantzas *et al.*, 2022; Vienne *et al.*, 2022).

Chapter 2 provides a detailed description of the methods used to analyse soil and soil solution samples. Soil solutions collected during this study were analysed for their cation and anion concentration, pH and titrated alkalinity. Oven-dried, crushed soil sampled at the beginning and end of the study were collated into subsections representative of the top (0-30cm), middle (40-60cm) and base of the core (70-100cm). Soil mineralogy, elemental composition, exchangeable cations and total (in)organic carbon were analysed using methods described in Chapter 2.

# 4.3.2. Treatment characterisation

Details of the six applied treatments are provided in table 4.1. Basalt and steel slag were crushed to a fine powder using a Tema mill (University of Oxford), whereas the inherently fine particle size of volcanic ash, aglime and CKD required no further grinding. The particle size distribution of all treatments was measured using dry and wet sieving. The BET surface-area of all treatments was determined by N<sub>2</sub> adsorption using Micromeretics Gemini VI (Oxford). The geometric surface-area was calculated using the method by Tester *et al.*, (1993). XRF analysis of treatments was conducted using a Rigaku ZSX Primus II with a pre-calibrated EZ-scan semi quant program calibrated using BCR-1 and 879-1 standards (Leeds University, Oct'21). A detailed description of the physical properties and elemental composition of treatments are provided in the Appendix C data repository.

Aglime is a Ca-rich carbonate (92  $\pm$  10 wt% CaO), and the remaining treatments are Mg-rich silicates (olivine) or Ca-rich silicates (basalt, CKD, steel slag, volcanic ash). With the exception of CKD, all silicate treatments have >5wt% Fe<sub>2</sub>O<sub>3</sub>, and basalt and volcanic ash have >5 wt% Al<sub>2</sub>O<sub>3</sub>. Basalt, aglime, CKD and volcanic ash have low levels of heavy metals, whereas olivine is enriched in Ni (0.6 %) and Cr (0.3 %), and steel slag contains 0.3 wt% V and 0.1 wt% Cr. The lime-rich loamy soil used in this study was 53  $\pm$  5 wt% SiO<sub>2</sub>, with noteable Fe-oxide (12.0  $\pm$  0.3 wt% Fe<sub>2</sub>O<sub>3</sub>), Al-oxide (13.2  $\pm$  0.5 wt% Al<sub>2</sub>O<sub>3</sub>) and Ca-rich mineral phases (15  $\pm$  2 wt% CaO) (figure 4.1).

Treatment	Type of	Source	Key cations	Previous
	treatment		(wt% as	studies
			oxide)	
Agricultural	Carbonate	Pigdon Quarry,	CaO (91.9%)	
lime		Cornwall, UK (E & JW		
(aglime)		Glendining Ltd.)		
Cement	Silica-rich	(Tarmac Blue Circle	CaO (76.8%)	
kiln dust	industrial by-	Ltd.)		
(CKD)	product			
Crushed	Naturally	Cascade Mountain	Al <sub>2</sub> O <sub>3</sub>	Same source
basalt	occurring	Range, Oregon, US	(12.5%),	as basalt
	silicate	(Central Oregon Basalt	CaO (8.9%),	applied to pot
		Products)	Fe <sub>2</sub> O <sub>3</sub>	studies in
			(15.5%)	Kelland et al.,
				(2020)
Crushed	Naturally	Western Norway	Fe <sub>2</sub> O <sub>3</sub>	Applied to
olivine	occurring	(Minelco Ltd.)	(14.2%)	soil cores in
	silicate		MgO (37.1%)	Renforth et
	_			<i>al</i> ., (2015)
Crushed	Silica-rich	West Glamorgan,	CaO (50.8%),	
steel slag	industrial by-	Wales, UK (Port Talbot	Fe <sub>2</sub> O <sub>3</sub>	
	product	Steelworks)	(28.3%),	
Volcanic	Naturally	Lampung, Indonesia	Al <sub>2</sub> O <sub>3</sub>	
ash	occurring	(S 6.08392°, E	(14.9%),	
	silicate	105.45415°). 2018	CaO (11.6%),	
		eruption of Krakatau	Fe <sub>2</sub> O <sub>3</sub>	
		Kecil. Samples	(15.7%)	
		collected in Jul'2019.		

**Table 4.1**. Description of six applied treatments. A summary of the physical properties and
 elemental composition of all treatments are detailed in the Appendix C data repository.



*Figure 4.1.* Summary of key elements measured in the six applied treatments and an untreated soil core.

# 4.4. Results

In section 4.4.1, I describe the fate and distribution of dissolution products in soil solution, and changes in titrated alkalinity and pH. In section 4.4.2, I elucidate processes which remove dissolution products from solutions, including sorption in the exchangeable fraction and secondary mineral formation.

### 4.4.1. Soil solution chemistry

# pH and titrated alkalinity

The titrated alkalinity and pH of soil solutions was averaged over the full length of triplicate cores after treatment addition. Titrated alkalinity significantly increased in all treated cores, except those treated with olivine (figure 4.2). Titrated alkalinity increased most markedly in cores treated with steel slag (+1.5 meq L<sup>-1</sup>) and is consistent with the change in alkalinity caused by olivine addition at 40.7 t ha<sup>-1</sup> in a pot study by ten Berge *et al.*, (2012) (+1.4 meq L<sup>-1</sup>). Soil solution pH significantly increased in cores treated with basalt and steel slag by 0.11 pH and 0.20 pH units, respectively. This is similar to the increase in leachate pH measured in basalt-treated cores by Kelland *et al.*, (2020). Changes to soil solution alkalinity and pH were most marked in the top and middle sections of treated cores (Appendix C data repository).





### Dissolved ions

The dissolved concentration of ions (As, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Mg, Mn, Ni, NO<sub>3</sub>, P, Pb, Si, SO<sub>4</sub>, Sr, V, Zn) measured at different depths within the soil core provides an insight into geochemical interactions within the soil environment whereby their distribution is influenced by soil dissolution, treatment dissolution, percolation through the fluid phase and removal from solution via adsorption, exchange and secondary mineral formation. Dissolved Na was not measured during this study due to technical issues with the ICP-MS; however it is assumed dissolved Na did not significantly alter alkalinity flux as treatments contained negligible NaO (<1.7wt%). The concentration of dissolved ions was averaged over the top (0-30 cm), middle (40-60 cm) and bottom (70-100 cm) and whole length (0-100 cm) of triplicate cores (figure 4.3).


(b)



(a)



(d)





**Figure 4.3**. Dilution-corrected dissolved ion concentration of soil solutions averaged after treatment across (a) the whole length (b) top (c) middle (d) base (e) effluent solution, across three control (black) and three treated (coloured) soil cores. Uncertainty was calculated from the standard error of samples across the three treated and control cores.

The dissolved concentration of major ions was elevated at the top of treated cores, including: Ca (aglime, CKD, steel slag), K (aglime, basalt, CKD, olivine, volcanic ash), Mg (aglime, CKD, olivine, steel slag, volcanic ash); P (aglime, basalt, steel slag); Si (aglime, basalt, olivine, steel slag, volcanic ash) (figure 4.3b). This indicates treatment addition to arable soil will increase the bioavailability of nutrients localised to the area of plant/root growth and relieve nutrient limitation. Furthermore, the dissolved concentration of major ions was elevated in the effluent solution, including: Ca (aglime, CKD, steel slag); K (aglime, CKD, volcanic ash); Mg (aglime, CKD, volcanic ash), P (basalt), Si (basalt). This suggests addition of all EW treatments, except olivine, will

increase the land-ocean alkalinity flux and could alter the saturation index of carbonate and clay phases in the wider freshwater environment.

The dissolved concentration of Fe reduced in all treated cores, except those treated with volcanic ash, and is thought to reflect secondary mineral formation (section 4.5.3). Dissolved AI reduced in cores treated with aglime, basalt, and steel slag; and dissolved Mn reduced in cores treated with basalt and steel slag. These findings are consistent with reduced [AI], [Fe] and [Mn] in basalt-treated soils in Chapter 3 and reduced AI and Mn toxicity following basalt addition to weathered soils (Anda, Shamshuddin and Fauziah, 2013). The dissolved concentration of Cd, Co and Pb increased in all treated cores and is associated with an increase in metal hydroxide solubility at high pH (van der Sloot and Kosson, 2010; Król, Mizerna and Bożym, 2020). Although EW is often discussed as a means of reducing heavy metal toxicity in the soil-plant system, these findings suggest heavy metal toxicity depends on the initial pH of arable land, whereby increasing the pH of alkaline soils can increase heavy metal toxicity.

The combined dissolved positive and negative charge of solution was calculated from the concentration of dissolved major cations (Ca, K and Mg) and anions (F, Cl, Br, NO<sub>3</sub>, SO<sub>4</sub>), respectively (Eq.C2-C4). The combined positive charge largely derives from Ca release (figure 4.4a); and is significantly elevated at the top of all treated cores, except those treated with olivine and basalt (figure 4.4b). Moreover, the combined positive charge is significantly elevated in all cores except olivine when averaged across the whole length of three cores after treatment (figure 4.5a). Dissolution of negatively charged ions reduced the net alkalinity flux by an additional

4-7% in cores treated CKD, aglime and olivine (figure 4.5a). This is associated with elevated concentrations of dissolved nitrate and sulfate ions, and dissolved chloride ions in CKD-treated cores. Anion release is partly attributed to treatment composition, whereby CKD contains comparatively high levels of chloride ( $0.4 \pm 0.5\%$ ) and sulphide ( $0.28 \pm 0.01\%$ ) ions. In addition, elevated dissolved nitrate is associated with indirect changes to soil-water chemistry as discussed by Amatya *et al.*, 2011.

Conservative alkalinity is a direct indictor of CO<sub>2</sub> drawdown and is calculated from the net charge difference between the combined dissolved positive and negative charge, averaged after treatment addition across the whole length of triplicate cores (Eq.C4, figure 4.5a). The conservative alkalinity of soil solutions was significantly elevated in cores treated with CKD and steel slag, and falls within error of titrated alkalinity measured in soil solution samples from five of the seven treatments (figure 4.5b). It is possible titrated alkalinity is slightly higher than conservative alkalinity in almost all cores as it is a more thorough, direct measurement of the excess of proton acceptors relative to proton donors, which act to buffer changes in acidity.







**Figure 4.4.** (a) Dissolved [Ca] time-series, (b) the combined dissolved positive charge from  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ; (c) the combined dissolved negative charge from  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ . Data points average three cores over the top (0-30cm), middle (40-60cm) and base (60-100cm) of treated (coloured) and control cores (black). The concentration averaged after treatment addition is illustrated with a diamond on the right of the figures, separated from the time-series with a vertical black line. Uncertainty was calculated from the standard error over triplicate cores.



(b)



**Figure 4.5.** (a) The combined dissolved positive charge, negative charge, and net conservative alkalinity, averaged after treatment addition across three cores.(b) Comparison between conservative alkalinity (dark colours, left bar) and titrated alkalinity (light colours, right bar), averaged after treatment across the full length of three treated and untreated cores.

## 4.4.2. Exchangeable fraction & XRD

In most cases, treatment made little or no change to the fraction of sorbed cations (figure 4.6) or mineralogy of soil cores measured with XRD and XRF (Appendix C), with some exceptions. For example, exchangeable Mg was notably elevated at the top of olivine- and volcanic ash-treated cores, and exchangeable Ca, Mg and K was elevated in aglime-treated cores. A total of 0.4 g additional Mg was held in the exchangeable pool across the olivine-treated soil core, equivalent to 4 % of the total mass of Mg added in olivine (8.9 g). Exchange sites in the untreated soil were dominated by exchangeable Ca (78%, Appendix C), therefore it is possible the relatively high soil/liquid partition coefficient of Mg (Sheppard *et al.*, 2009) resulted in exchange between sorbed soil Ca and dissolved Mg in the olivine-treated core. These findings suggest the exchangeable pool acts as a critical sink of dissolved cations depending on the composition of the soil and treatment. These findings affirm conclusions by Pogge von Strandmann *et al.*, (2020) who related the retardation of dissolved cations through an olivine-treated soil core to exchange.



**Figure 4.6.** Soil exchangeable cations relative to total solid soil phase (mg/ g soil) measured in the top (0-30cm), middle (40-60cm) and base of soil cores (70-100cm) at the end of the 16-month study (Jun'21).

# 4.5. Discussion

# 4.5.1. Cation release rate

Quantifying the rate treatment addition releases cations into the soil environment is essential for understanding how addition will influence soil viability and the accumulation of residual treatment in soil. The cation release rate of each treatment was calculated from the additional concentration of dominant cation (Mg in olivine, Ca in all other treatments) in the dissolved and exchangeable phase, averaged after treatment addition. Dissolution of the dominant cation is used as a representative proxy for treatment dissolution as other major ions (Al, Fe, Si) are heavily influenced by removal processes (Chapter 3). Cation concentration was averaged over the full length of triplicate cores to account for dissolution products distributed across the soil profile. The impact of treatment dissolution was calculated by subtracting the concentration of cations in the dissolved and exchangeable phase in the untreated control core from the treated core. The flux of dissolved cations was calculated by multiplying the concentration of additional cations by the infiltration flux (1.5x10<sup>-5</sup> g s<sup>-1</sup>). The cation release rate was normalised to the BET surface-area of the applied treatment in accordance with existing literature (mol(cation) cm<sup>-2</sup> s<sup>-1</sup>) (Eq. C1). These calculations are conservative estimates as they do not include dissolved cations removed from solution by secondary precipitation or plant uptake (table 4.2). Results are sensitive to the experimental design of the core study and should be considered when applying findings to the field scale.

Treatment	Cation release rate	
	(mol(cation) cm <sup>2</sup> s ')	
Aglime	10 <sup>-13.96 ± 0.03</sup>	
Basalt	<b>10</b> -18.99 ± 0.01	
Cement kiln dust	10 <sup>-15.07 ± 0.03</sup>	
Olivine	10 <sup>-15.16 ± 0.04</sup>	
Steel slag	10 <sup>-15.30 ± 0.03</sup>	
Volcanic ash	10 <sup>-14.85</sup> ± 0.03	

**Table 4.2.** Cation release rate, normalised to the BET surface-area of treatments (cm<sup>2</sup>). The overall uncertainty was calculated in quadrature, by summing the errors from the components of eq.C1.



**Figure 4.7.** The cation release rate (mol(cation) cm<sup>-2</sup> s<sup>-1</sup>) of the dominant cation released from treatment dissolution in this study and in existing literature. Cation release rates in pot and core studies are calculated from the dissolved phase (ten Berge et al., 2012; Renforth et al., 2015; Amann et al., 2020; previous core study (Chapter 3); dissolved and exchangeable phase (this study); dissolved and exchangeable phase and plant uptake (Kelland et al., 2020).

The rate of cation release from treatment dissolution in this core study is compared to dissolution rates in existing laboratory, pot, core and model-based studies in figure 4.7. Aglime and olivine dissolved considerably slower in this study than recorded in simple laboratory experiments (Palandri and Kharaka, 2004). Slow cation release in a soil setting is thought to reflect the geochemical complexity of dissolution that cannot

be simulated in a controlled laboratory environment. For example, dissolution in soils is inhibited by secondary films, surface passivation, mineral saturation, preferential dissolution, and preferential flow – see White and Brantley (2003) for a full discussion. A significant fraction of Mg released in the olivine cores is adsorbed into exchangeable sites on mineral surfaces (section 4.4.2). Previous studies that have not accounted for this uptake have suggested dissolution rates significantly slower than in this study (Renforth *et al.*, 2015; Amann *et al.*, 2020) (figure 4.7).

Of the six treatments, basalt was the least effective at releasing cations  $(10^{-18.99 \pm 0.01} \text{ mol}(\text{Ca}) \text{ cm}^{-2} \text{ s}^{-1})$ . This is attributed to SiO<sub>2</sub> polymerisation in slow-dissolving basalt minerals and micro-porosity introduced during crushing which leads to underestimations in surface-normalised calculations (Brantley and Mellot, 2000). For example, the SA<sub>BET</sub> of crushed basalt (15.2 ± 0.2 m<sup>2</sup> g<sup>-1</sup>) is 11-fold greater than crushed olivine (1.435 ± 0.005 m<sup>2</sup> g<sup>-1</sup>) despite having a similar particle size distribution, whereby the p80 value (80% particles less than or equal to) of basalt was 355 µm and the p80 value of crushed olivine was 250 µm.

Ca release from basalt was three orders of magnitude slower than dissolution recorded in a mesocosm study  $(10^{-15.6 \pm 0.3} \text{ mol}(\text{Ca}) \text{ cm}^{-2} \text{ s}^{-1})$  by Kelland *et al.*, (2020). Basalt used in Kelland *et al.*, (2020) was sourced from the same region as in this study (Cascade Mountain Range, Oregon) and added at twice the application rate (100 t ha<sup>-1</sup>); therefore, most of the discrepancy in the rate of Ca-release is thought to relate to other differences in the experimental set-up, such as soil type and water flux. For example, Kelland *et al.*, (2020) irrigated cores every five days at a high infiltration rate

(~767 mm yr<sup>-1</sup>), whereas cores in this study were exposed to real-time variations in rainfall and a low natural water-flux (60 mm yr<sup>-1</sup>). In this way, the volume and pattern of water flux through the soil cores is likely to have restricted dissolution and promoted saturation at the mineral-fluid interface. It is also possible high background levels of dissolved Ca ( $62 \pm 1 \text{ mg L}^{-1}$ ) measured in this core study enhanced secondary mineral formation (see section 4.5.3) and diminished the rate of cation release compared to sandy soils used in Kelland *et al.*, (2020). In contrast, Ca release from basalt dissolution in this study is consistent with observations in a similar core study which used the same crushed-basalt and soil with an application rate of 100 t ha<sup>-1</sup> under comparable weather conditions (Chapter 3;  $10^{-18.22 \pm 0.03} \text{ mol}(Ca) \text{ cm}^{-2} \text{ s}^{-1}$ ).

# 4.5.2. Alkalinity flux

The flux of alkalinity into solution is a direct analogue for the rate of carbon drawn down from enhanced weathering. Alkalinity flux (eq ha<sup>-1</sup> yr<sup>-1</sup>) was calculated by multiplying the net alkalinity release (eq ml<sup>-1</sup>, section 4.4.1) (treated minus control) by the infiltration rate (ml yr<sup>-1</sup>), and was normalised to the land-area of treatment addition (ha) (Eq. C5). Note, alkalinity flux excludes cations removed from solution into the exchangeable pool and by secondary mineral formation.

Treatment	Alkalinity flux (eq ha <sup>-1</sup> yr <sup>-1</sup> )	
Aglime	130 ± 10	
Basalt	150 ± 20	
Cement kiln dust	480 ± 60	
Olivine	0 ± 7	
Steel slag	590 ± 90	
Volcanic ash	80 ± 10	

**Table 4.3.** Additional alkalinity flux, normalised to the land-area of treatment addition. The overall uncertainty was calculated in quadrature, by summing the errors from each component of eq.C5.



Figure 4.8. Additional alkalinity flux following treatment application at 50 t ha<sup>-1</sup>.

Alkaline-rich industrial silicates (CKD, steel slag) were most effective at releasing alkalinity into solution, whereas olivine addition resulted in negligible alkalinity flux (figure 4.8). This differs from elevated dissolved Mg measured in existing olivine-treated mesocosm studies (Renforth *et al.*, 2015; Amann *et al.*, 2020). The difference between the olivine response in this study and existing studies is thought to reflect slow-dissolution in a water limited environment, the preferential substitution of exchangeable Ca in lime-rich soils with dissolved Mg, and secondary formation of dolomite and calcite phases which reduces alkalinity (section 4.5.3). The extent to which exchange and secondary mineral formation influence the dissolved concentration of cations is likely to vary under different soil landscapes depending on soil composition, cation exchange capacity, soil-mineral-water interaction and hydrological conditions. In light of this, the CDR potential of enhanced weathering will

vary across different agricultural environments - a key factor when considering nationwide deployment of EW.

## 4.5.3. Implications for soil

## Accumulation of undissolved treatment

An important aspect of the viability of enhanced weathering is the impact on the soil after treatment. One component of this impact arises from residual treatment that has not yet dissolved or will not dissolve. Cation release rates calculated in this study allow us to assess the amount of treatment that will remain in the soil after addition of the six studied treatments.

The shrinking core model (SCM) described in Hangx and Spiers (2009) was used to calculate the extent of dissolution integrated over the particle size distribution of added treatments (Eq.3.5). Here we applied the cation release rate of the dominant cation (mol cm<sup>-2</sup> s<sup>-1</sup>) as a proxy for treatment dissolution. The SCM estimates >99.7 % all six treatments remain undissolved one year after application and undergo complete dissolution within  $10^3 - 10^7$  yrs. A single application at 50 t ha<sup>-1</sup> is the equivalent of 0.2-0.3 cm of soil thickness when accounting for soil porosity, therefore a coating equivalent to the depth of the ploughed layer (20cm) will accumulate after ≈100 years of annual addition. Consecutive application at 50 t ha<sup>-1</sup> may therefore be restricted to ≈10 years to ensure agricultural soil remains viable.

#### Heavy metal release and retention

As a consequence of slow dissolution described above, heavy metals present in the applied treatment will accumulate in the soil environment. It is therefore important to consider the maximum number of years treatment can be continuously applied to agricultural soils before soil safety thresholds are surpassed (Environment Agency, 2009a). Findings in this study suggest olivine addition will be limited by Cr and Ni toxicity within 1 year, and steel slag addition will be limited by Cr toxicity within 6 years (Appendix C data repository). In contrast, the low heavy metal content of the remaining treatments permit application of aglime, basalt, CKD and volcanic ash over the 10 year period suggested above. Increasing the depth of treatment addition and rotating crops with metal accumulators, such as legumes and biochar, will reduce heavy metal toxicity and prolong the number of years of application.

The dissolved concentration of heavy metals (As, Cr, Cu, Hg, Ni, Pb, V, Zn) averaged over the whole length of all triplicate treated cores stayed within the safety threshold for drinking water and freshwater (Environment Agency, 2009b; Gautam *et al.*, 2014; WHO, 2022) (Appendix C data repository). However, steel slag addition increased the concentration of dissolved vanadium and arsenic at the top of the core to 230% and 87%, respectively, of the safety threshold for V in freshwater (60 ppb; Environment Agency, 2009b) and As in drinking water (10 ppb; WHO, 2022). This suggests multiple steel slag additions could pose an environment risk to plant uptake and the surrounding freshwater environment. Extensive monitoring systems will therefore be essential to assess the impact of dissolution on ground- and fresh-water environments. Unlike olivine-treated soils in Amann *et al.*, (2020), the dissolved concentration of Ni

and Cr was not significantly elevated at the top of olivine-treated soil cores, and is thought to reflect slow release of trace metals in water-limited soils.

#### Secondary mineral formation

It is essential to understand the extent that ions released by dissolution precipitate as secondary minerals as this is a key factor which affects the composition of soils and groundwater, and the overall efficiency of C drawdown (whereby one mole of CO<sub>2</sub> is released for every mole of carbonate formation). A geochemical model, PHREEQC, (Parkhurst and Appelo, 1999 using IlnI.dat database) was used to assess the saturation state of mineral phases in soil solutions sampled at the end of the study (Jun'21). The saturation state was averaged across samples taken from the entire profile of three cores. Data inputs include sample pH, alkalinity, [anions], [cations] and temperature. Samples were used when the charge balance produced less than a 5% error. The saturation state of solid phases were grouped into: Mg silicates (forsterite, talc); Ca silicates (anorthite, gismondine); clay minerals (kaolinite, montmorillonite, illite, nontronite, beidellite); Fe minerals (hematite, magnetite, goethite, trevorite, ferrite, delafossite); alumina minerals (gibbsite, diaspore, boehmite); Ca-carbonate (calcite); Mg-carbonate (magnesite); Ca-Mg carbonate (dolomite).

The saturation index of Fe minerals in solutions sampled from treated cores was elevated relative to the control core (figure 4.9). This is consistent with the absence of appreciable Fe in the dissolved phase and elevated Fe<sub>2</sub>O<sub>3</sub> measured in the middle and/or base of soils treated with steel slag and CKD (Appendix C data repository). Solutions sampled from the control core were almost oversaturated with respect to

calcium carbonates, indicative of the high background levels of dissolved Ca in limerich soil. In comparison, solutions sampled from treated cores were oversaturated with respect to calcite and dolomite. This suggests dissolution of Ca and Mg from treatments increased solution saturation and promoted secondary carbonate formation. In turn, this will have reduced the dissolved alkalinity flux and decreased the CDR potential of EW. These findings suggest the efficacy of EW may be elevated in soil types with lower background levels of Ca.



*Figure 4.9.* Results from PHREEQC modelling, showing the saturation indices of mineral phases in soil solution, averaged over the whole core at the end of the study.

## 4.5.4. Carbon dioxide removal potential

In this section, I calculate the rate of CO<sub>2</sub> drawdown (kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) following a single addition of treatment to arable soil at 50 t ha<sup>-1</sup>, using the method described in Chapter 3 (Eq.3.6). The maximum drawdown potential (kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) was calculated by scaling the CDR potential over multiple annual additions. This was capped at 10 years for all treatments, except steel slag and olivine which were limited to a single application to prevent soil toxicity (figure 4.10a). Chapter 3 indicates water availability as a critical control on drawdown in dry croplands, therefore I scale drawdown to the average UK river flux, normalised to arable cover in catchment areas (235 mm yr<sup>-1</sup>; NRFA, 2022), to account for variation in hydrology across key agricultural areas in the UK. I follow such methods here to calculate the maximum CDR potential of EW in the UK (MtCO<sub>2</sub> yr<sup>-1</sup>) (figure 4.10b). The CDR potential calculated in this study is the gross drawdown and does not account for emissions released during the life-cycle of EW from mining, transport and comminution. The reduction in net CO<sub>2</sub> drawdown from these processes is expected to be greatest in crushed, naturally occurring silicates whereas life-cycle emission are expected to be lower for fine-grained volcanic ash and industrial silicates.

Treatment	(i) Single application	(ii) Maximum	(iv) UK CDR potential
	(kgCO <sub>2</sub> ha <sup>-1</sup> yr <sup>-1</sup> )	application	(MtCO <sub>2</sub> yr <sup>-1</sup> )
		(kgCO2 ha <sup>-1</sup> yr <sup>-1</sup> )	
Aglime	2.2 ± 0.2	22 ± 2	$0.52 \pm 0.06$
Basalt	5.0 ± 0.7	50 ± 7	$1.2 \pm 0.2$
CKD	16 ± 2	160 ± 20	$3.8 \pm 0.5$
Olivine	$0.0 \pm 0.2$	0 ± 2	$0.00 \pm 0.06$
Steel slag	20 ± 3	20 ± 3	$0.48 \pm 0.07$
Volcanic ash	2.7 ± 0.4	27 ± 4	0.67 ± 0.09

**Table 4.4.** The carbon dioxide removal potential of six treatments following annual application at 50 t ha<sup>-1</sup>. The (i) single and (ii) maximum CDR potential, calculated from the alkalinity flux normalised per land area (eq ha<sup>-1</sup>yr<sup>-1</sup>) multiplied by the molecular mass of CO<sub>2</sub> (44 g mol<sup>-1</sup>) and the molar ratio of CO<sub>2</sub> removed from the atmosphere relative to alkalinity released during enhanced weathering (0.75), as in Renforth (2019). The CDR potential of aglime was reduced by 50% to account for CO<sub>2</sub> released during carbonate dissolution. (iii) The UK CDR potential, calculated by scaling the maximum CDR potential across UK cropland (6.1 Mha; DEFRA, 2020a) and corrected for variation in hydrology, assuming a linear relationship between water flux and CDR. The overall uncertainty was calculated in quadrature, by summing the errors from each component.



**Figure 4.10.** The maximum carbon dioxide removal potential of six treatments following annual application at 50 t ha<sup>-1</sup> (a) normalised per ha, per year (b) scaled over UK cropland and corrected for variation in hydrology across the UK. The horizontal dashed line illustrates the lower bound of CDR calculated in a vertical reactive transport model by Kantzas et al., (2022) considering basalt application at 40 t ha<sup>-1</sup>.

The drawdown potential of six treatments applied in this study are detailed in table 4.4. Steel slag and CKD were the most efficient treatments at sequestering CO<sub>2</sub> after a single application, removing 20  $\pm$  3 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup> and 16  $\pm$  2 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>, respectively. This reflects the high flux of Ca into solution from fast-dissolving industrial silicates. The CDR potential of aglime after a single application (2.2  $\pm$  0.2 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) was markedly slower than industrial silicates despite dissolving an order of magnitude faster. This reflects the reduced efficiency of CO<sub>2</sub> drawdown from carbonate dissolution compared to silicate dissolution, as discussed in Chapter 1, and the removal of dissolved cations by exchange (figure 4.6). Of the three naturally occurring silicates applied in this study, basalt was the most efficient at consuming carbon  $(5.0 \pm 0.7 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$ . In comparison, olivine addition resulted in negligible  $CO_2$  drawdown (0.0 ± 0.2 kg $CO_2$  ha<sup>-1</sup> yr<sup>-1</sup>) despite releasing Mg into solution at a rate comparable to industrial silicates (section 4.5.2). This incongruence is associated with the high proportion of dissolved Mg retained by sorption on soil surfaces which were dominated by exchangeable Ca (section 4.4.2). Sorbed ions do not contribute towards dissolved alkalinity, therefore this process constrains C drawdown in olivine-treated soils. These findings demonstrate how treatment composition and soil type influence the drawdown potential of EW and highlights the importance of assessing the impact of EW in different soil landscapes.

Water availability is a critical factor which inhibits alkalinity release in soils with a low natural water flux (Chapter 3). After a single application, the CDR potential of basalt was ~400 fold slower than estimated by Kelland *et al.*, (2020) (2000 kgCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>). This is largely associated with the high infiltration rate and regular irrigation regime applied in Kelland *et al.*, (2020) in addition to other components of the experimental set-up in that study which promote dissolution, such as soil type and plant growth.

The maximum drawdown potential of each treatment was scaled over UK cropland to consider the contribution of each treatment to national carbon accounting. Cement kiln dust presents the most promise as an enhanced weathering treatment with the potential to remove  $3.8 \pm 0.5$  MtCO<sub>2</sub> yr<sup>-1</sup> over UK cropland, assuming an infinite supply of CKD (figure 4.10). However, historical CKD stockpiles (131 Mt, Renforth, 2012) and annual production rates (2 Mtyr<sup>-1</sup>, Renforth, 2012) fall short of the amount of treatment required for EW over UK cropland for ten years at the high application rate used in this study (305 Mt yr<sup>-1</sup>). CKD is therefore a promising treatment for EW when applied on a small scale and/ or at a low application rate. In comparison, extensive mafic rock formations in the UK (Renforth, 2012) make basalt a favourable treatment for nationwide EW application.

Scaling the CDR potential of basalt over UK cropland, and accounting for national variations in hydrology, suggests application of basalt at 50 t ha<sup>-1</sup> for 10 years could consume  $1.2 \pm 0.2$  MtCO<sub>2</sub> yr<sup>-1</sup>. This rate of drawdown is equivalent to 3% of current greenhouse gas emissions from UK agriculture (which were 46.3 MtCO<sub>2</sub>e yr<sup>-1</sup> in 2019; DEFRA, 2021a), and is consistent with a similar basalt-treated soil core study following application at 100t ha<sup>-1</sup> ( $1.3 \pm 0.1$  MtCO<sub>2</sub> yr<sup>-1</sup>) (Chapter 3). These findings affirm EW in dry croplands is considerably slower than CDR predicted in a recent model-based study (6-30 MtCO<sub>2</sub> yr<sup>-1</sup>; Kantzas *et al.*, 2022) which applies basalt at 40 t ha<sup>-1</sup> with a high water flux (461 – 849 mm yr<sup>-1</sup>). UK croplands are largely located in the English Lowlands (based upon UKCEH Land Cover Plus Crops; UKCEH, 2007), which has an average annual total runoff of 273 mm yr<sup>-1</sup> (Blyth *et al.*, 2019) that is comparable to

the UK water normalisation applied in this study (235 mm yr<sup>-1</sup>). Assuming runoff is representative of the water flux available for EW (from precipitation, evapotranspiration and irrigation) and that drawdown responds linearly to water flux, we conclude Kantzas *et al.*, (2022) over-estimate the drawdown potential over large areas of water-limited croplands in the UK. Instead, there is greatest potential for UK EW in areas with a high on-site water balance such as Scotland (972 mm yr<sup>-1</sup>; Blyth *et al.*, 2019) and Wales (945 mm yr<sup>-1</sup>; Blyth *et al.*, 2019) where acidic conditions could further accelerate drawdown.

# 4.5.5 Impact of liming

Conventional carbon accounting assumes all carbon in lime is eventually released as CO<sub>2</sub> to the atmosphere and does not consider CO<sub>2</sub> drawn down from the release of alkalinity (IPCC, 1997). Approximately 7% of the total tilled cropping area in Great Britain (4.4 Mha) was limed in 2020 at an average rate of 4.4 t ha<sup>-1</sup> (The British Survey of Fertiliser Practice, 2021). Assuming agricultural lime is predominantly formed of CaCO<sub>3</sub>, this equates to ~0.6 MtCO<sub>2</sub> emitted per year from lime dissolution in Great Britain.

In this study a set application of aglime to alkaline soils increased the flux of alkalinity into solution (+0.4 meq L<sup>-1</sup>) and, in turn, consumed CO<sub>2</sub> at a rate of 0.0022 tCO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>. The nationwide applicability of this finding depends on the pH of soils, particularly acidic soils treated with N<sub>2</sub> based fertilisers; nevertheless, extrapolation of these results over existing UK cropland could reduce conventional accounting of UK agricultural emissions by ~0.6 MtCO<sub>2</sub> yr<sup>-1</sup>. These findings suggest aglime dissolution

in alkaline soils is a temporary carbon sink, rather than a source of emissions, and represents a previously unquantified contribution to the UK's net-zero emissions target

# 4.6. Conclusion

The experimental design used in this soil core study closely simulates EW in a UK agricultural setting. Complete geochemical analysis and high resolution sampling along the profile of soil cores reveals how alkalinity flux and associated CO<sub>2</sub> drawdown is diminished by the accumulation of sorbed cations in the exchangeable pool and secondary carbonate precipitation, particularly in cores treated with olivine.

Of the six treatments applied in this study, cement kiln dust, an alkaline-rich industrial silicate, was most effective at removing CO<sub>2</sub> on a small scale ( $16 \pm 2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ), however application will be limited by availability. Basalt presents promise for large-scale EW deployment and had minimal impact on the soil-water environment, whereas the CDR potential of steel slag application was limited by heavy metal toxicity. Conclusions from this core study are sensitive to the experimental design; however assuming findings are representative of field-scale application, this research suggests spreading basalt to UK cropland land for 10 years could remove  $1.2 \pm 0.2 \text{ MtCO}_2 \text{ yr}^{-1}$  when considering variation in hydrology. This rate of CDR is equivalent to <3% UK agricultural emissions and affirms EW in dry croplands is considerably slower than recent modelled estimates (Kantzas *et al.*, 2022). Since UK cropland is largely located in dry regions, EW presents considerably less promise at removing CO<sub>2</sub> in the UK than previously thought, and EW deployment should initially focus on wetter regions.

Together, these findings demonstrate CO<sub>2</sub> drawdown during enhanced weathering is a helpful co-benefit of an established agricultural practice, but will not contribute substantially to UK net-zero emission reduction targets. Future work should focus on understanding the EW potential of basalt and selected industrial silicates in a range of agricultural settings, with different soil types and hydrological conditions.

# Chapter 5: General Discussion

**Research objective 1** - to develop a robust method of extracting sufficient volumes of soil solution from soil cores for complete geochemical analysis, and to provide a framework for future soil core studies

The experimental set-up designed in this thesis closely simulates enhanced weathering (EW) in a typical UK agricultural setting by using UK arable soil exposed to natural changes in weather and temperature. Low pore-water saturation was the biggest limitation to fluid extraction and multiple sampling methods were trialled and iteratively improved over the course of a preliminary study. This culminated in an innovative sampling method which successful increased soil-pore saturation whilst minimising disruption to soil structure and natural hydrological conditions (Chapter 2). Immediately before sampling, soil cores were irrigated with fluorescent uranine dye and the fluorescence of individual soil solution samples was used to correct for dilution. A drainage study demonstrated the fluorescent dye largely percolated as a single pulse through the core, and a small fraction of the initial mass of uranine was retained within the core between monthly sampling. This transit time distribution indicates rainwater and evaporation were the primary factors that influenced water flux over the majority of the study. As a result, research in this thesis simulates the on-site water balance in an unirrigated agricultural landscape and directly represents the potential of EW across large areas of UK cropland (Chapter 3 and 4).

The preliminary study (Chapter 3) highlighted a number of critical interactions to be considered for further soil core studies. For example, inter-core heterogeneity between

treated cores identified the need for at least three replica soil cores in future studies. In addition, three orders of magnitude difference between the geometric and BET surface area of crushed basalt demonstrated the difficulty in measuring the effective reactive surface area of crushed treatments which limits the application of surfacearea-normalised calculations. Dissolution rates in Chapter 3 and 4 were therefore normalised to both treatment surface area and land-surface-area to allow comparison with existing literature and to overcome uncertainty in surface-area. The preliminary study also highlighted the retention of dissolved ions in the soil core. This prompted the use of high depth-resolution sampling of ions and soil exchangeable cations in Chapter 4 to fully capture the fate of dissolution products. In this way, the preliminary study led to the development of a robust experimental set-up which formed the foundation of another soil core study (Chapter 4).

**Research objective 2** – to identify the geochemical and environmental impact of dissolution in the soil-water system

The pathway of dissolution products through the soil-water system is influenced by an interplay of geochemical interactions, these include: dissolution at the mineral-water interface, surface passivation, exchange onto soil particle surfaces, secondary mineral formation, physical percolation and changes to soil-water pH. In Chapter 4, a diverse suite of chemistry was used to understand geochemical changes in the soil-water system at a high depth-resolution through the core.

A range of geochemical techniques revealed consistent changes to the chemistry of the soil and soil solution across treated cores. The increase in titrated alkalinity was highest in steel slag- (+1.5 meq L<sup>-1</sup>) and CKD-treated cores (+ 0.6 meq L<sup>-1</sup>), and is indicative of rapid cation release from fast-dissolving industrial silicates. In comparison, olivine was the only treatment which did not raise soil solution alkalinity despite dissolving at a rate in-line with industrial silicates. This is consistent with sorption of dissolved Mg on soil particle surfaces, whereby soil exchangeable Mg was notably elevated at the top of olivine-treated cores (Chapter 4). It is possible dissolved Mg substituted with exchangeable Ca and promoted carbonate precipitation. In this way, dissolution of Mg-rich silicates in Ca-rich soils inhibits the flux of alkalinity into solution. Furthermore, PHREEQC simulations showed all treated cores were oversaturated with respect to Ca-carbonate phases, and changes in core chemistry were most marked at the top/ middle of treated cores. Research in this thesis indicates secondary mineral formation and cation exchange on soil particle surfaces are critical factors which retard the flow of cations through a core, reduce solution alkalinity and, in turn, decrease the CDR potential of enhanced weathering.

Enhanced weathering has the potential to geochemically alter soil and groundwater through the release of dissolution products. If these signals are translated to the oceans via rivers and run-off, large-scale enhanced weathering deployment could influence the geochemistry of freshwater and marine environments. High resolution analysis of soil and solution samples in Chapter 3 and 4 elucidate the previously unknown geochemical risks and co-benefits of enhanced weathering in an agricultural setting. The pH of soil solution was elevated in cores treated with steel slag and basalt on a scale consistent with pH change measured in Kelland *et al.*, 2020. It is possible

the absence of a statistically significant rise in pH in other treated cores reflects slow dissolution of Ca-rich silicates and carbonates into Ca-rich solutions in water-limited alkaline soils. Together, these findings indicate that application of most treatments to alkaline soils will not substantially alter the pH of run-off into streams and rivers; however the extent to which EW alters pH may vary following application in different environmental settings.

The dissolved concentration of major ions (Ca, Mg, K, P, Si) was elevated at top of all treated cores, which could relieve nutrient limitation at a depth relevant to plant and root growth. However, it is possible raised concentrations of dissolved Si localised to the depth of treatment addition could create a mineral-saturation limitation on dissolution, as discussed by other authors (Maher et al., 2016). With the exception of olivine addition, effluent solution from all treated cores was enriched in major cations. This indicates treatment addition could enhance the nutrient flux to freshwater (and marine) systems, and alter the saturation state of carbonate and clay phases in surrounding freshwater environments. In addition, the dissolved concentration of Cd, Co, Pb increased in all treated cores, and is associated with increased solubility of metal hydroxides in alkaline conditions. The high heavy metal content of steel slag also increased the As and V toxicity of soil pore-water after a single application. Multiple additions of steel slag therefore present an environment risk and should be limited and closely monitored. In accordance with existing literature, basalt dissolution did not elevate the dissolved concentration of heavy metals beyond safety thresholds (Chapter 3, 4). Interestingly, olivine addition also did not elevate the dissolved concentration of Ni and Cr, which differs from findings in an existing pot study (Amann et al., 2020). Soil solution in both olivine-treated studies had a similar pH, therefore it is unlikely heavy metal mobility influenced the dissolved concentration of Ni and Cr; rather the difference between heavy metal release in these two studies is thought to reflect slow dissolution of heavy metals from olivine in water-limited soils.

Changes to solution chemistry has the potential to influence secondary mineral formation in soils. PHREEQC simulations indicate solutions from treated cores were oversaturated with respect to Fe- minerals which aligns with depleted dissolved Fe and elevated soil Fe<sub>2</sub>O<sub>3</sub> observed in Chapter 3 and 4. As discussed in Chapter 3, formation of Fe-oxides in soils has the potential to reduce heavy metal availability by adsorption and exchange which could prove advantageous to crop and soil health in cultivated soils. In contrast, secondary formation of clay and Al-mineral phases, measured with XRD and predicted with PHREEQC simulations, was negligible over the timescale of the study relative to the mass of the soil.

Together, results from this research convey the direct and indirect impact of EW on the soil-water environment, which was most marked localised to the depth of treatment addition. These findings suggest the geochemical and environmental impact of EW is likely to vary in different agricultural settings, depending on the soil type and treatment composition, and will require close monitoring to minimise deleterious effects in the wider environment.

**Research objective 3** - to calculate the cation-release rate and carbon dioxide removal potential of multiple proposed enhanced weathering treatments applied at different rates in a UK soil in conditions representative of the field environment

In this thesis, I calculated the ion release rate and carbon dioxide removal potential of a novel range of proposed treatments in a soil environment representative of EW in a typical UK agricultural setting. The core study in Chapter 3 provided an initial insight into basalt dissolution and elucidated the impact of water-limitation on cation release and CDR. This research was extended in Chapter 4 where a diverse suite of geochemical data provided a comprehensive assessment of the EW potential of a range of treatments in UK soils.

The cation release rate of six treatments was calculated in Chapter 4 from the flux of dominant cation in each treatment into the dissolved and exchangeable pool, normalised to the BET surface area. Aglime was the fastest treatment to release Ca (10  $^{-13.96 \pm 0.03}$  mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>) attributed to fast weathering carbonate phases; however the rate of cation release from aglime (and olivine) was up to four orders of magnitude slower than measured in simple laboratory-based studies (Palandri and Kharaka, 2004). This is thought to reflect the complexity of dissolution in soil, and is discussed extensively by others authors (White and Brantley, 2003). The surface-area-normalised Ca release rate from basalt was consistent over two soil core studies (10<sup>-18.22 ± 0.03</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>, Chapter 3; 10<sup>-18.99 ± 0.01</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>, Chapter 4); however this rate of Ca release was four to five orders of magnitude slower than from aglime (10<sup>-14.0 ± 0.1</sup> mol(Ca) cm<sup>-2</sup> s<sup>-1</sup>). This difference is attributed to slow-dissolving basalt minerals and the impact of comminution on the BET surface area of crushed basalt which can lead to underestimations in surface-area-normalised calculations.

The net flux of alkalinity into solution is a key driver of C drawdown during enhanced weathering. The net alkalinity flux (eq ha<sup>-1</sup> yr<sup>-1</sup>) was calculated in each soil core study following a single application at 50 t ha<sup>-1</sup> (Chapter 4) and 100 t ha<sup>-1</sup> (Chapter 3) considering the release of dissolved cations (and anions in Chapter 4). Nitrate, sulphate and chloride release was found to reduce the net alkalinity flux by an additional 4-7 % in soils treated with CKD, olivine and aglime. This is thought to relate to the high concentration of chloride and sulphate ions in industrial silicates, and indirect changes to soil chemistry. In light of this, it will be critical to monitor anion release in future research on the EW potential of industrial silicates. In contrast, the net alkalinity release from basalt weathering was not affected by anion release. This suggests the absence of anion data in Chapter 3 and previous basalt weathering studies does not reduce the applicability of drawdown calculations. The flux of alkalinity from basalt in Chapter 4 (150  $\pm$  20 eq ha<sup>-1</sup> yr<sup>-1</sup>) was approximately half the alkalinity flux measured in Chapter 3 (310  $\pm$  30 eq ha<sup>-1</sup> yr<sup>-1</sup>). These findings suggests the high application rate applied in Chapter 3 increased mineral-fluid interactions almost linearly, with minor differences attributed to the inclusion of Na<sup>+</sup> in Chapter 3, negative charge considered in Chapter 4, and the difference in particle size distribution of crushed basalt.

The CDR potential of the six treatments applied in Chapter 4 was, in decreasing order: steel slag ( $20 \pm 3 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > CKD ( $16 \pm 2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > basalt ( $5.0 \pm 0.7 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > volcanic ash ( $2.7 \pm 0.4 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) > aglime ( $2.2 \pm 0.2 \text{ kgCO}_2$ ) ha<sup>-1</sup> yr<sup>-1</sup>) > olivine ( $0.0 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ). These findings demonstrate fastdissolving industrial silicates were most effective at releasing alkalinity into solution, whereas the alkalinity flux from olivine dissolution was inhibited by soil processes which remove dissolved cations from solution. This research demonstrates carbonate dissolution is less effective at consuming  $CO_2$  compared to silicate dissolution. Nonetheless, aglime dissolution in this soil core study was a sink of  $CO_2$  and contrasts current convention which considers dissolution of aglime a source of  $CO_2$ . The nationwide applicability of this finding depends on the pH of soils, particularly acidic soils treated with N<sub>2</sub> based fertilisers. Nevertheless, extrapolation of these results over existing UK cropland could reduce conventional accounting of UK agricultural emissions by ~0.6 MtCO<sub>2</sub> yr<sup>-1</sup>.

The maximum drawdown potential of proposed treatments was calculated considering limitations to application which could influence soil viability. In light of slow dissolution measured in a water-limited soil environment, annual application at 100 t ha<sup>-1</sup> or 50 t ha<sup>-1</sup> should be limited to 5 or 10 years, respectively, to prevent the accumulation of residual treatment exceeding 10% of the ploughed layer (Chapter 3, 4). Chromium and nickel toxicity from undissolved olivine further limit olivine application at 50 t ha<sup>-1</sup> to one year, and dissolution of high levels of As and V from steel slag limit application to one year (Chapter 4).

Water supply is known to be a key theoretical control on mineral dissolution (Chapter 1), however the impact of hydrology on EW has been overlooked in recent modelbased studies (Kantzas *et al.*, 2022). In contrast, findings from both core studies in this thesis indicate water flux is a critical process which influence alkalinity flux and CDR in dry soils. Slow supply of reactants restricts the mass transfer of cations into solution, and the long contact-time between water and mineral surfaces introduces a saturation limitation on dissolution and promotes surface passivation and secondary mineral

formation. These processes inhibit dissolution and remove alkalinity from solution which, in turn, reduce carbon drawdown. To calculate the UK CDR potential of each treatment, drawdown was scaled over UK cropland and adjusted for the spatial variation in hydrology across arable land. Of the six treatments, CKD was the most efficient at removing CO<sub>2</sub> ( $3.8 \pm 0.5 \text{ MtCO}_2 \text{ yr}^{-1}$ ); however limited resources will restrict application. In light of this, CKD addition will be effective on a small-scale, whereas basalt has the most potential for large-scale EW deployment. Application of basalt over UK cropland was consistently shown to remove <3% UK agricultural emissions when considering variation in hydrology ( $1.3 \pm 0.1 \text{ MtCO}_2 \text{ yr}^1$ , Chapter 3;  $1.2 \pm 0.2 \text{ MtCO}_2 \text{ yr}^1$ , Chapter 4). These findings are markedly slower than recently modelled estimates ( $6-30 \text{ MtCO}_2 \text{ yr}^1$ ; Kantzas *et al.*, (2022). This disparity is largely attributed to the high water flux applied in Kantzas *et al.*, (2022) in addition to other factors that are indirectly linked to water flux and act to limit alkalinity release, such as natural drying/wetting cycles creating a saturation limitation on dissolution at the mineral-fluid interface, secondary mineral formation, and preferential flow.

UK cropland is largely located in dry regions in England; therefore, water flux is likely to limit the nationwide drawdown potential of EW. With this in mind, EW is likely to prove most successful in regions with a high on-site water balance, such as Scotland and Wales. Overall, this research suggests EW is a helpful co-benefit of an established agricultural practice; however water-availability in key arable areas will limit the contribution of EW to UK net-zero emission reduction targets.
### Future work

This thesis presents a high resolution insight into the pathway of dissolution products through a real soil environment and provides a first look at the carbon dioxide removal potential of a range of proposed treatments in unirrigated agricultural soil. This research concludes water flux and soil type are critical, and previously understudied, controls on the efficacy of EW in an arable soil environment. Future work is needed to understand the interaction between water flux and enhanced weathering in a range of soil environments and to reduce uncertainty when scaling the potential of EW as a negative emission technology across UK cropland. Furthermore, future studies should investigate the impact of EW deployed synchronously with other land-based NETs, such as biochar, on the soil-plant-river system to elucidate the full potential of EW in the UK.

# Conclusions

As negative emission technologies are increasingly relied upon to reduce atmospheric greenhouse gases, it is important to understand the contribution enhanced weathering could make to ambitious UK net-zero emission targets. In this thesis I have used two long-term, fully replicated soil core experiments to geochemically determine the efficacy of enhanced weathering as a carbon dioxide removal technology in a soil environment representative of unirrigated UK cropland using a range of proposed treatments (agricultural lime, basalt, cement kiln dust, olivine, steel slag, volcanic ash). I developed a novel method of sampling soil pore-water at a high resolution whilst minimising disruption to the natural soil environment, and a suite of geochemistry was used to assess the pathway of dissolution products through the soil-water system.

My results indicate exchange and secondary mineral formation are key sinks of dissolved cations which reduce the land-ocean transfer of dissolved cations and diminish carbon drawdown. The carbon dioxide removal potential after a single application at 50 t ha<sup>-1</sup> is, in decreasing order: steel slag  $(20 \pm 3 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}) >$  cement kiln dust  $(16 \pm 2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}) >$  basalt  $(5.0 \pm 0.7 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}) >$  volcanic ash  $(2.7 \pm 0.4 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}) >$  aglime  $(2.2 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1}) >$  olivine  $(0.0 \pm 0.2 \text{ kgCO}_2 \text{ ha}^{-1} \text{ yr}^{-1})$ . Slow dissolution and accumulation of residual treatment will curtail multiple additions at 50 t ha<sup>-1</sup> to 10 years to ensure soil remains viable, and steel slag and olivine application will be further restricted to 1 year to avoid heavy metal toxicity. Of the six treatments, CKD was most efficient at releasing alkalinity, however application will be restricted by resource availability. This research therefore suggests large-scale EW deployment should apply crushed basalt with small additions of CKD

when possible. Findings presented in this thesis estimate basalt application at 50-100 t ha<sup>-1</sup> over UK cropland will remove ~1.3 MtCO<sub>2</sub> yr<sup>-1</sup>, which is equivalent to <3% UK agricultural emissions. This rate of carbon drawdown is considerably slower than recent model predictions, which is thought to reflect water-limited dissolution and restricted application in agricultural land. This thesis indicates water flux is a critical control on the CDR potential of EW which will limit drawdown over large areas of cropland in dry regions in the UK. In light of this, EW is not likely to contribute substantially to UK net-zero emission reduction targets. More work is needed to fully understand the interaction between water flux and C drawdown during enhanced weathering in a range of agricultural environments.

The future deployment of enhanced weathering as a negative emission technology requires a rigorous understanding of the efficacy of carbon drawdown and the implications on the wider terrestrial, freshwater and marine environment. My thesis contributes to this by providing a robust methodology for future EW studies; a unique assessment of the carbon dioxide removal potential of a range of proposed treatments; and a novel insight into the fate of dissolution products in the soil-water system. To fully comprehend the potential of enhanced weathering as a negative emission technology in the UK, future research should take a whole system approach to understanding the impact of enhanced weathering on the soil-plant-river-ocean system in a range of UK agricultural settings.

# Appendix A. Supplementary information for Chapter 2

# A.1. Description of Appendix A data repository

Please refer to the data repository for further information

A.1.1. Volume of samples extracted in the Exp1 drainage study

A.1.2. Uranine-fluorescence calibration curves applied during drainage studies (a) Exp0 (b) Exp1

A.1.3. Exp0 drainage study. The uranine concentration of soil solution sampled in 6 cores over 21 days

A.1.4. Exp1 drainage study, Jan'20. The volume and uranine concentration of soil solution sampled in 18 cores over 14 days.

A.1.5. Exp1 drainage study, Jul'21. The uranine concentration of soil solution samples measured 4 weeks after uranine addition

A.1.6. Photo-degradation of a 49.9µg/ml uranine-rainwater solution stored in a clear centrifuge tube and an opaque bottle over 28 days.

A.1.7. The extent of dilution,  $\alpha$ , as a function of depth in six soil cores measured during Exp0.

#### A.2. Equipment cleaning

Equipment was cleaned using the principle that equipment should be cleaned with either a stronger reagent or for longer or at a higher temperature than the equipment would be used for. All equipment was required to be trace metal free to ppb level unless otherwise stated. Cleaning took place in a metal free laboratory (University of Oxford). Reagent grade 12M = 43%; 6M = 22%; 3M = 11% of the specified acid.

#### Bottles - amber

Amber, 1 litre LDPE plastic bottles were used from September 2019-July 2021 to store fluorescent dye for up to 4 hours during sampling. Before use, amber bottles were rinsed with mQ water three times and filled with 3M reagent grade HCl for 48hrs at room temperature, then rinsed thoroughly with mQ water three times. Amber bottles were rinsed 3 times with de-ionised water between monthly sampling

#### Bottles - clear

Clear, 1 litre LDPE plastic bottles were used throughout Exp0 and Exp1 and were used to store either 6M reagent grade HCl for 24hrs; mQ water for 48hrs; or 3M HCl for 1 week. Before use, bottles were refluxed with concentrated sub-boiled HCl at 60°C for 6 hrs, filled with 6M reagent grade HCl for 48hrs at 30°C and filled with mQ water for 48hrs at 30°C.

#### Centrifuge tubes - opaque

Opaque, 1.5ml centrifuge tubes were used to store soil-solution samples during Exp0 and Exp1, which were analysed for their fluorescence, pH and alkalinity. Opaque centrifuge tubes were used directly from packaging and discarded after use.

#### Centrifuge tubes - clear

Clear, 15 ml centrifuge tubes were used to store soil-solution samples throughout Exp0 and Exp1. Centrifuge tubes were certified metal-free to ppb level and were used directly from packaging and discarded after use. Samples were stored in centrifuge tubes for up to 3 months in a cold room before analysis. A centrifuge tube blank was taken during each sampling event by filling a 15ml centrifuge tube with mQ water in a metal free laboratory. These samples were parafilmed and stored alongside soil solution samples in a cold room until further analysis.

### Cubitainers

20 litre, LDPE Cubitainers were used from October 2019- July 2021 to hold rainwater for a maximum of 5 months at any one time. Before use, cubitainers were rinsed with mQ water three times and leached with 3M reagent grade HCl for 24hrs by submerging one side of the cubitainer with acid and rotating every 24hrs. The cubitainer was thoroughly rinsed with mQ water three times.

### Effluent sampling bottles

250ml, LDPE opaque plastic bottles were installed at the base of each soil core from September 2018- July 2021. Before use, bottles were wiped with acetone and rinsed with detergent and mQ water three times before being filled with 10% HNO<sub>3</sub> for 4 weeks. Bottles were then rinsed with mQ water three times and air dried in a laminar flow hood, parafilmed and stored in a plastic bag before use.

### Jerrican

A 10 litre HDPE jerrican was used throughout Exp1 to create fluorescent dye from filtered rainwater and uranine powder. The fluorescent dye was held in the jerrican for a maximum of 30 minutes during each sampling event. Prior to use, the jerrican was leached with 3M reagent grade HCl for 24hrs and rinsed with mQ water three times.

#### Pipette tips

Eppendorf pipette tips were leached in 3M HCl at room temperature for 7 days in a 1 litre acid-leached clear LDPE plastic bottle. Pipette tips were thoroughly rinsed with mQ water three times and left to air dry overnight in a laminar flow hood.

#### Rainwater sampling bottle

Rainwater collected in a 3-litre HDPE plastic bottle within a Palmex RS1B rainwater sampler. The sampling bottle was installed on the roof of the Earth Sciences Department in September 2018 and used at ambient temperature throughout Exp0 and Exp1 until July 2021. Prior to installation, the rainwater sampling bottle was leached with 3N HCl for 4 weeks and rinsed with mQ water 3 times

#### Rhizon samplers

Rhizon samplers are a hydrophilic, microfiltration membrane composed from an inert polymer blend. In October 2018, 38 rhizon samplers were inserted into the six cores used in Exp0. From January- March 2020, 189 rhizon samplers were inserted into 21 cores used in Exp1. Rhizon samplers remained in the cores throughout the respective time-series. Prior to insertion, each rhizon sampler was submerged in 6M reagent grade HCl for 24 hrs in an acid-leached, clear LDPE plastic bottle. Following this, 20 ml 1% sub-boiled HCl was extracted through the rhizon sampler using an acid-leached BD Plastipak syringe and clear LDPE plastic bottle. This process was repeated two further times with HCl and three times with mQ water. Rhizon samplers were then submerged in mQ water for 48hrs in an acid-leached clear plastic bottle until they were inserted into soil cores. This cleaning process ensured the membrane and tubing were leached with a reagent stronger than fresh water, and ensured samplers were thoroughly rinsed and conditioned with mQ before use.

Rhizon blanks were sampled during each sampling event. To do so, a rhizon sampler was submerged in mQ water in an acid-leached, clear, 1 litre LDPE bottle at the beginning of the study. The bottle was parafilmed, double bagged and stored on the roof of the Earth Sciences Department. During each sampling event, a rhizon blank was collected by extracting mQ water from the storage bottle through a rhizon sampler using an acid-leached syringe. Rhizon blank samples were stored in a certified metal free 15 ml centrifuge tube, parafilmed and stored in a cold room until further analysis.

#### Syringes- amber

Amber, 50 ml luer lock BD Plastipak syringes were used to collect soil pore-water samples during Exp0 between August 2019- December 2019 and throughout Exp1 (January 2020-July 2021). Prior to use, syringes were dissembled and submerged in 2% reagent grade nitric acid in a large Pyrex beaker for 24 hrs at room temperature. Syringes were rinsed thoroughly with mQ water three times, dried in a laminar flow hood and stored in a plastic sampling bag. Between monthly sampling, amber syringes were rinsed with mQ water three times, dried in a laminar flow hood and stored in a plastic sampling bag. Between monthly sampling, amber syringes were rinsed with mQ water three times, dried in a laminar flow hood and stored in a plastic bag.

Amber syringe blanks were collected throughout Exp0 and Exp1 by leaving a syringe filled with mQ water horizontal in a metal free laboratory for 6 hrs. This is representative of the time syringes were exposed to soil pore-water during sampling. The syringe blank was stored in a certified metal-free 15 ml centrifuge tube, parafilmed and stored in a plastic bag in a cold room until further analysis.

### Syringes - clear

Clear, 10 ml luer lock BD Plastipak syringes were used to collect soil pore-water samples during Exp0 from October 2018- July 2019. Syringes were used directly from packaging and disposed of after use.

#### A.3. Exp0 drainage study

An additional drainage study was conducted in Sept'2019 on the six cores used during Exp0. A 50 µg ml<sup>-1</sup> fluorescent dye was created by mixing 0.3000 g uranine powder with 6000 ml filtered rainwater. 700 ml of fluorescent dye was measured by mass into six, acid-leached amber LDPE bottles and poured individually onto soil cores. Amber BD Plastipak 50 ml syringes were attached to Rhizon samplers one hour after irrigation and held in vacuum for 5 hours. Soil pore-water and effluent samples collected after this interval were stored in opaque, 1.5 ml centrifuge tubes. 100 µl aliquots of each sample was pipetted into a Greiner flat black 96-well plate along with a 100 µl blank composed of rainwater. A SPARK fluorimeter was used to measure the fluorescence of soil solutions samples and a series of standards of known uranine concentrations. Standards were created by progressively diluting the fluorescent dye with filtered rainwater, and ranged from 0-50 µg ml<sup>-1</sup> (figure A.1). 300 ml filtered rainwater was added to cores on subsequent sampling days to ensure soil pores were sufficiently saturated for daily sampling. On subsequent days, amber syringes were attached to Rhizon samplers 1 hour after the addition of rainwater and held in vacuum overnight. Soil solution samples were collected the following morning and their fluorescence measured alongside a series of standards. This process was repeated 11 times over 21 days to assess the change in sample fluorescence as the fluorescent dye percolated through the core. Note, no natural rainfall occurred during this drainage study therefore the flux of fluorescent dye and added rainfall represents the total flux of water through the cores.



**Figure A1.** Twelve calibration curves created during the Exp0 drainage study, with an average  $r^2$  value of 0.97915. The uranine concentration of soil pore-water samples ranged between 0-47.4 µg m<sup>1</sup>. The precision of fluorescence was investigated using a 5 µg m<sup>1</sup> solution (star)



**Figure A2.** Concentration of uranine in soil solution samples collected from six cores over 21 days during the Exp0 drainage study. Sampling is labelled as a time interval e.g. "Day 2-3" whereby syringes were attached on day 2 and collected 24 hrs later, on day 3.

# Appendix B. Supplementary information for Chapter 3

# B.1. Description of Appendix B data repository

Please refer to the data repository for further information

- B.1.1. Characterisation of basalt and the initial soil core
- B.1.2. Uranine-fluorescence calibration curve
- B.1.3. Precision of uranine concentration
- B.1.4. Fluorescence of soil solution samples
- B.1.5. Water flux
- B.1.6. Uncertainty
- B.1.7. Raw dissolved ion concentration
- B.1.8. Dilution-corrected dissolved ion concentration
- B.1.9. Dilution-corrected dissolved ion concentration, averaged per section
- B.1.10. Ion release rate, basalt dissolution rate, alkalinity flux, CDR
- B.1.11. Safety thresholds for dissolved heavy metals
- B.1.12. Shrinking core model: dissolution of basalt grains
- B.1.13. Height of residual basalt, using a shrinking core model

## **B.2.Basalt characterisation**

Service).

**Eq.B1**. Geometric SSA ( $m^2 g^{-1}$ ), calculated according to Tester et al., (1993), where d is the diameter of spherical grain (m) and  $\rho$  is the density (g  $m^{-3}$ ).

Geometric SSA = 
$$\frac{6}{d.\rho}$$



**Figure B1**. The N<sub>2</sub> adsorption (bright red) and desorption (dark red) isotherm recorded whilst measuring the BET surface area of crushed basalt (Oxford Materials Characterisation

## **B.3.Dissolved ion concentration**



**Figure B2**. Dilution-corrected dissolved concentration of major cations in soil solutions averaged over five sampling weeks across the top, middle, base and whole length of individual control (grey) and basalt-treated (blue) soil cores, demonstrating the scale of inter-core heterogeneity. Empty data bars correspond to samples which were unable to be collected due to unsaturated pore spaces. Uncertainty was calculated from the standard error of samples across the length of each core.



**Figure B3.** Dilution-corrected dissolved ion concentration of soil solutions averaged over five sampling weeks across the whole length of three control (grey) and three basalt-treated (blue) soil cores. Uncertainty was calculated from the standard error of samples across the three treated and control cores.

# Appendix C. Supplementary information for Chapter 4

# C.1. Description of Appendix C data repository

Please refer to the data repository for further information

- C.1.1. Treatment characterisation
- C.1.2. Soil core properties measured at the end of the study (Jun'21)
- C.1.3. Water flux
- C.1.4. Uranine-fluorescence calibration curve
- C.1.5. Uncertainty of fluorescence
- C.1.6. Fluorescence and concentration of uranine in soil solution samples
- C.1.7. Titrated alkalinity and pH
- C.1.8. Raw dissolved ion concentration
- C.1.9. Raw dissolved anion concentration
- C.1.10. Uncertainty in dissolved anion concentration, pH and alkalinity
- C.1.11. Dilution-corrected dissolved ion concentration
- C.1.12. Dilution-corrected dissolved anion concentration
- C.1.13. Cation exchange capacity of soils, Jun'21
- C.1.14. Soil exchangeable cations measured in soil cores, Jun'21
- C.1.15. Cation release rate
- C.1.16. Release of positive charge into solution
- C.1.17. Dissolved conservative alkalinity
- C.1.18. Alkalinity flux and carbon dioxide removal potential
- C.1.19. Composition of herbaceous flowering plants, Jun'21
- C.1.20. The number of years treatment can be applied at 50t/ha (5kg/m2) before exceeding soil safety thresholds
- C.1.21. Dissolved concentration of heavy metals
- C.1.22. PHREEQC output

### C.2. Additional equations

**Eq. C1.** Cation-release rate,  $Wr_{surface area}$ , of the dominant cation normalised to treatment surface-area (mol(cation) cm<sup>-2</sup> s<sup>-1</sup>). Mg is the dominant cation in olivine-treated cores, Ca is the dominant cation in all other treated cores. Q is the infiltration flux through the core (g s<sup>-1</sup>, 1.5x10<sup>-5</sup> g s<sup>-1</sup>). Cation<sub>dissolved</sub> is the molar concentration (mol g<sup>-1</sup>) of dissolved cation averaged over the whole length of treated cores after treatment in the treated core minus control core. Cation<sub>exchangeable</sub> is the molar concentrated cores after treatment in the treated core, minus control core. Mass is the mass of treatment added (g, 39). SA<sub>treatment</sub> is the BET surface area of the treatment (cm<sup>2</sup> g<sup>-1</sup>)

$$Wr_{surface\ area} = \frac{Q.([Cation_{dissolved}] + [Cation_{exchangeable}])_{treated-control}}{Mass.\ SA_{treatment}}$$

**Eq.C2.** The total dissolved negative charge,  $\Sigma(Anion_{dissolved})$ , (eq g<sup>-1</sup>).

 $\Sigma(Anion_{dissolved}) =$ 

$$\Sigma([Br] + [Cl] + [F] + [NO3] + [PO4] + [SO4])$$

**Eq. C3.** The total dissolved positive charge,  $\Sigma(Cation_{dissolved})$ , (eq g<sup>-1</sup>).

$$\Sigma (Cation_{dissolved}) = \Sigma ([Ca] + [Mg] + [K])$$

## **Eq. C4.** Dissolved alkalinity, $Alk_{dissolved}$ (eq $g^{-1}$ ).

$$Alk_{dissolved} = \Sigma (Cation_{dissolved}) - \Sigma(Anion_{dissolved})$$

**Eq. C5.** Alkalinity flux  $Alk_{land area}$ , normalised to the land-area over which treatment was applied (eq ha<sup>-1</sup> yr<sup>1</sup>). Q is the infiltration flux through the core (g yr<sup>1</sup>, 462),  $SA_{land}$  is the area over which treatment was applied (ha, 7.9x10<sup>-7</sup>).  $Alk_{dissolved}$  is the dissolved alkalinity (eq g<sup>1</sup>), averaged over the entire length of triplicate cores, in the treated cores minus the control cores.

$$Alk_{land area} = \frac{Q. \ (Alk_{dissolved})_{treated-control}}{SA_{land}}$$

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