Roinn Cumarsáide, Gníomhaithe ar son na hAeráide & Comhshaoil
Department of Communications, Climate Action & Environment

Geological Survey
Suirbhéireacht Gheolaíochta
Ireland | Éireann

Research Programme
- Short Calls, Final Report -

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Host Organisation name	University College Dublin
Project Title	Geological GHG emission mitigation: A preliminary investigation of crushed basalt as a soil amendment to sequester atmospheric CO_2
Contract Number	2017-sc-019

Date: 12th Nov. 2018

This report covers the period November 1st 2017 to October 31st 2018

2. (a) Project information:

Final project report (*max **2500**words, excluding figures and headings*):

(i) *Progress* of objectives and scientific/engineering targets beyond the state of the art & *methods* used

2.1 Introduction and background information

Preliminary field- and laboratory-based weathering experiments were conducted to evaluate the potential use of Tertiary basalt 'quarry dust, a waste product from a commercial quarry in N. Ireland (Budore, Co. Antrim) as:

(i) a CO_2 sequestering soil amendment for large scale removal of CO_2 from the atmosphere
(ii) an alternative to ground limestone for pH regulation in agricultural soils.

Most of our experiments used crusher fines (referred to in the industry as 'quarry dust'), a waste product with a limited market that is currently being stockpiled at quarries in Ireland. While we investigated the effects of additional crushing, our preference was to focus on 'quarry dust' that was obtained directly from the quarry, without any additional crushing, because real-world applications that require further crushing/grain size reduction would incur significant energy and GHG emission penalties. Because of the short duration of the project, the weathering results are preliminary, and additional supplementary work will be completed by the PI in the coming months at no cost to the project in order to further verify the laboratory results and to expand and bolster the field-based study with additional data following the recent restoration of soil-moisture surpluses after months of water deficits during the dry summer of 2018.

2.2 Methods used

Basalt was sourced in N. Ireland (McQuillan's Budore Quarry, Co. Antrim) in collaboration with Dr Mark Cooper (GSNI). Quarry dust was sieved to remove the coarsest fraction and was spread on the soil surface at one plot at each of the sites (Table 1). In order to assess the role of grain size, a smaller number of experiments utilised a finely crushed (<200 micron) basalt powder, manufactured in the UCD laboratory by crushing several kilograms of the 'quarry dust' in a tungsten carbide Tema® mill, and these are referred to hereafter and in Table 1 as the 'finely crushed basalt' amendment. This 'finelt crushed basalt' amendment was applied by spreading it on the soil surface on metre-scale plots at the Feighcullen (Co. Kildare) and on two plots at the UCD Lyons Research Farm (Co. Dublin). Application rates at all sites were designed to mimic typical ground limestone application rates to agricultural soils, equivalent to 15 tonnes/hectare.

Twelve soil-water samplers (vacuum tension lysimeters manufactured by Soilmoisture Equipment Corp. Santa Barbara, USA) were installed at the field sites (see Table 1 for details of field sites, plots and amendments). Four samplers were installed in a circum-neutral pH (pH=7.46) mineral soil at Feighcullen, Co. Kildare, comprising grassland and a bare-soil plot (two treated plots and with two adjacent non-treated control plots). An additional two soil suction samplers were installed in a low-pH organic-rich peaty soil at Killinthomas Wood, Co. Kildare to investigate the role of low pH and naturally occurring organic matter content on basalt weathering kinetics (Table 1). The remaining six samplers were installed at the UCD Lyons Research Farm on May 9th 2018, (3 on the tillage (spring barley) sites, and 3 on the adjacent managed grassland; Table 1). Installations at this site were delayed by very poor spring weather and difficult soil conditions that had delayed spring cereal planting at UCD Lyons Farm and installation could not be done until ploughing and other farm operations involving heavy machinery had been completed. Tiny-tag soil temperature loggers were also installed at all sites. These units are programmed to log shallow (c. 10cm depth) soil temperature variations hourly which will aid in the interpretation of the geochemical data and were still logging data at the time of writing of this report (November 2018). At the time of writing, all of the field experiments are still operational and soil water sampling will continue at least through winter 2018 and into spring 2018 to complete a full annual hydrological cycle.

In addition to these field experiments, a series of laboratory-based microcosm batch weathering experiments were carried out at UCD over a period of 125 days. These experiments consisted of water-saturated mixtures of top-soil from the UCD Lyons Farm (selected from both grassland and tillage fields), with fine (Tema crushed) basalt amendment (10:1, soil to basalt by weight). The experiments were conducted in a closed batch system using 50 ml centrifuge tubes that were regularly agitated (5 times per week) and sampled for cation (weathering) yield, pH and alkalinity at intervals to track the weathering response of the basalt. Results from these experiments are shown in Figures 4 to 8 below.

Plot number	Land use and soil type	Amendment
Plot 1 (Killinthomas, Kildare)	Woodland, organic peaty soil, low pH (pH 6.3 to 6.5)	Sieved quarry dust
Plot 2 (Killinthomas, Kildare	Woodland, organic peaty soil, low pH (pH 6.3 to 6.5)	None. Control plot for P1.
Plot 3(Feighcullen, Kildare)	Grassland, mineral soil, circum-neutral pH	Sieved quarry dust
Plot 4 (Feighcullen, Kildare)	Grassland, mineral soil, circum-neutral pH	None. Control plot for P3
Plot 5 (Feighcullen, Kildare)	Bare mineral soil, circum-neutral pH	Finely crushed basalt
Plot 6 (Feighcullen, Kildare)	Bare mineral soil, circum-neutral pH	None. Control plot for P5
Plot 7 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Cereal crop, mineral soil, neutral pH	Sieved quarry dust
Plot 8 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Cereal crop, mineral soil, neutral pH	Finely crushed basalt
Plot 9 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Cereal crop, mineral soil, neutral pH	None. Control plot for P7 & 8
Plot 10 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Grassland, mineral soil, neutral to high pH	Sieved quarry dust
Plot 11 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Grassland, mineral soil, neutral to high pH	Finely crushed basalt
Plot 12 (UCD Lyons Farm, Rathcoole, Co. Dublin)	Grassland, mineral soil, neutral to high pH	None. Control plot for P10 & 11

***Table 1**: Summary of study sites, plots and amendments applied (July 2018). Note that all sites have control plots in which suction soil-water samplers have been installed, but no amendments have been added. In total 12 soil water samplers are in operation.*

Figure 1. Overview of experimental sites at UCD Lyons Research Farm (A) grass soil and (B) crop soil immediately after finely crushed basalt was spread. The soil-water suction sampler is visible near the centre of the treated area. Shallow soil samples were also taken from these sites for the laboratory experiments described below.

2.3.1 Results – quarry dust characterisation: Three basalt flows are exposed in Budore Quarry with a combined thickness in excess of 50 metres. In general, the flows comprise fresh to very slightly altered massive basalt with sparse amygdales. However, each flow has visible lateritic alteration confined to the upper 1 to 2 metres, with abundant clear crystalline zeolites and primary porosity (Cooper, 2018; pers. comm.). The stockpile of 'quarry dust' that was sampled (c. 300 kgs) from the quarry floor in March 2018 appeared somewhat heterogeneous (Figure 2), presumably reflecting on the state of alteration of the basalt being fed to the crusher when the waste batches were successively added to the stockpile. The material was homogenised using cone and quartering techniques at UCD and was subsequently sampled for geochemical analysis, along with hand specimens of visibly fresh and altered samples taken from recently blasted quarry faces. The objective of this part of the work was to assess the extent to which the 'quarry dust' stockpile that we sampled in the quarry for our weathering experiments represented predominantly fresh or weathered (lateritic) material, because this in turn could affect the weathering kinetics when used as a soil amendment.

Figure 2: General view of Budore Quarry working face, showing the reddish lateritic top of flow 2 in the middle background. Note that the 'quarry dust' stockpile in the middle foreground that was sampled and used in all of the weathering experiments contains patches of reddish material, indicating the presence of altered/lateritic basalt. When sampling this stockpile to obtain material for the weathering experiments, we tried to avoid the altered material. Subsequently, bulk geochemical analysis of the material taken from of this stockpile confirmed that its major element chemistry is dominated by unaltered basalt (Fig. 3).

The unbound water content of the quarry-dust stockpile was measured at 8.20 ± 0.58 Wt. % (n=5, ± 2 σ) and this water content was factored into subsequent mass calculations when the material was used as a soil amendment.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	TiO_2	K_2O	Cr_2O_3	MnO	P_2O_5	LOI	Total
Fresh basalt	45.3	15.75	10.75	10.55	7.58	1.73	1.24	0.29	0.020	0.21	0.07	5.60	99.11
Lateritic basalt	40.1	12.50	13.60	8.71	8.47	0.85	1.46	0.10	0.024	0.26	0.09	14.2	100.37
Quarry 'dust'	45.3	16.55	11.55	10.80	8.42	1.77	1.23	0.25	0.013	0.21	0.08	4.47	100.65

Table 2: *Major element oxide data (wt %) for representative samples of fresh and lateritic basalt compared with a sample of material from the 'quarry dust' stockpile.*

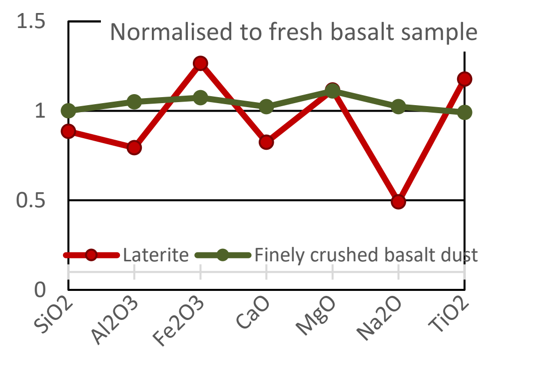


Figure 3: Comparison of the major element oxides in a representative sample of 'quarry dust' relative to a red lateritic sample from a flow top. Both profiles are normalised to the major element chemistry of a fresh basalt sample collected from a working quarry face at Budore . In general, the quarry dust has a major element chemistry similar to the fresh basalt sample for most major elements, indicating that is relatively free of altered lateritic basalt. The lateritic sample from the flow-top by contrast is depleted in Si, Al, Ca and Na relative to the fresh basalt sample.

2.3.2 Results –Laboratory weathering experiments: Results from the laboratory weathering experiments on soil/basalt mixtures using grassland and crop soil from UCD's Lyons Farm are shown below in Figures 4 to 8 below. Soil solution electrical conductivity (indicative of total dissolved ions) were significantly higher at the end of the 125 day experiment in the treated soils from both the grass-land and crop-land soils, although the difference had developed close to the end of the experiment only in the case of the grassland soil. Similarly, pH values were robustly higher by approximately 0.12 pH units for both soils, maintained for the duration of the experiment. Alkalinity values are substantially higher for the treated crop soil compared with the control, but minimal differences were observed in the case of the grassland soil.

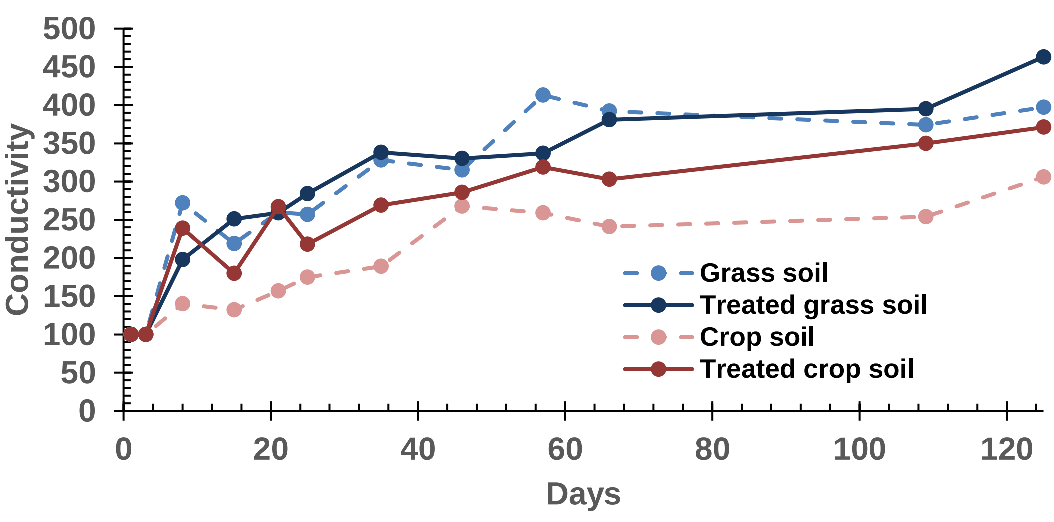


Figure 4: Changes in electrical conductivity (mS) over the course of the 125-day laboratory weathering experiment for treated soils and controls

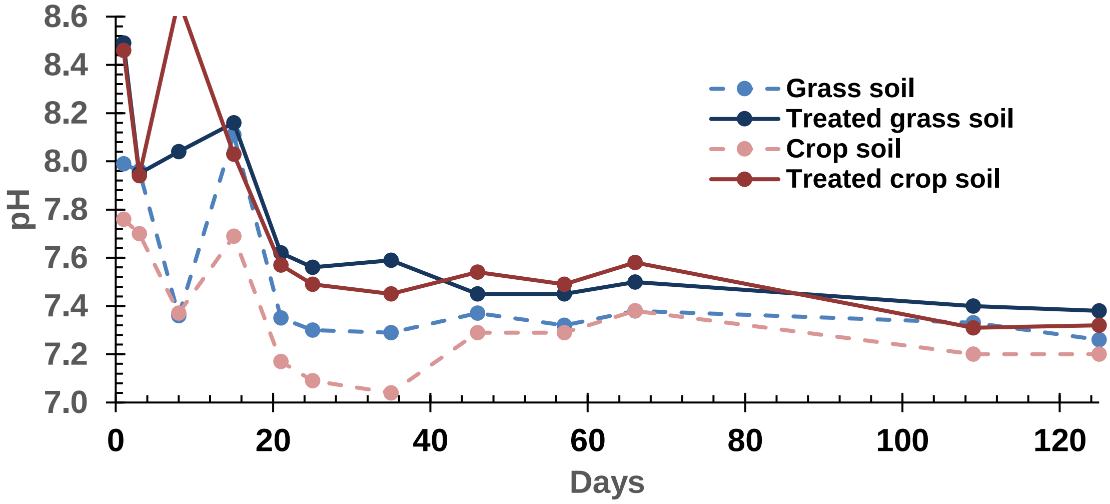


Figure 5: Changes in pH over the course of the 125-day laboratory weathering experiment for treated soils and controls. In both soils, pH values were higher in the treated (basalt amended) soils.

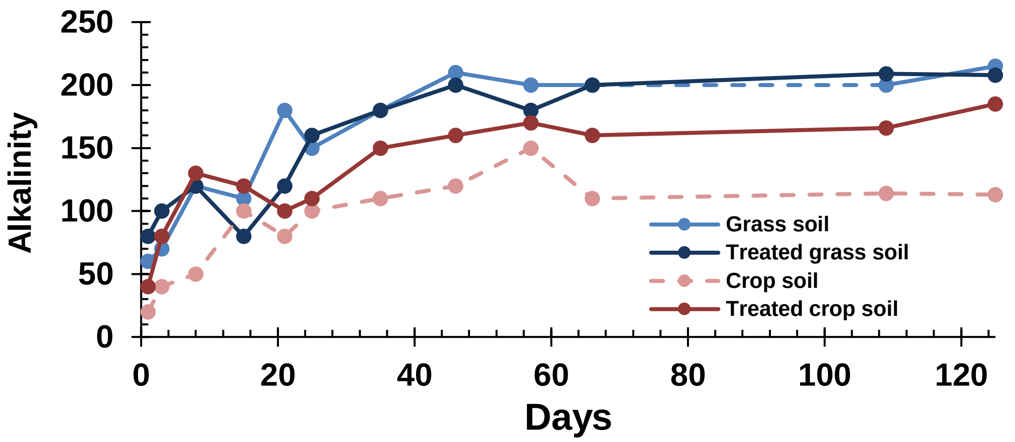


Figure 6 (above): Changes in alkalinity (as mg $CaCO_3$/L) over the course of the 125-day laboratory weathering experiment for treated soils and controls.

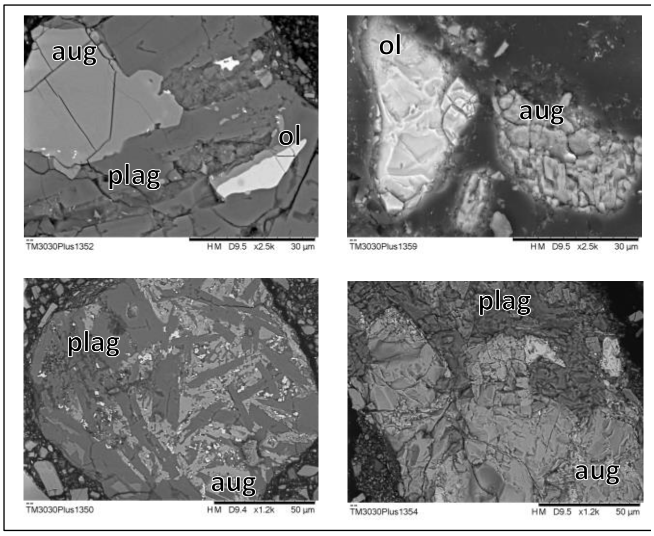


Figure 7: SEM images of augite (aug), olivine (ol), plagioclase feldspar (plag) in the 'quarry dust' ***before*** (left) and ***after*** (right) the laboratory weathering experiments. Note the fresh appearance of the augite, olivine and plagioclase before the experiments, compared with their pitted appearance after the 125 day weathering experiments in the presence of deionised water and soil. It should be noted that secondary clay minerals that sequestered Al, Fe and Mg were produced in these batch experiments after 60 days (not shown – please see poster by McDermott et al. (2018) presented at the Geoscience 2018 conference).

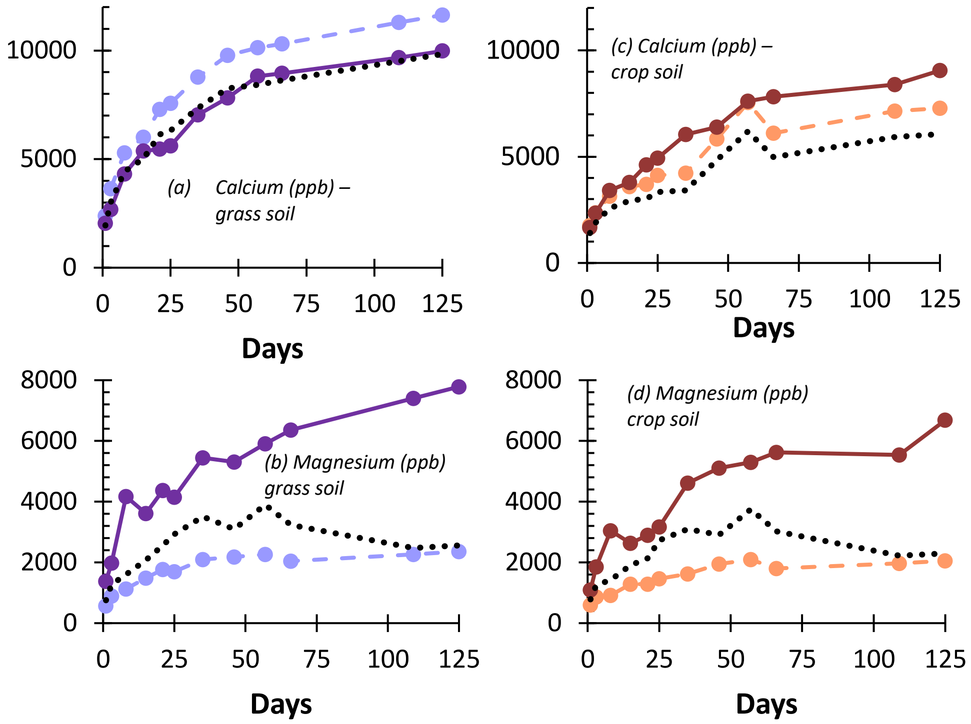
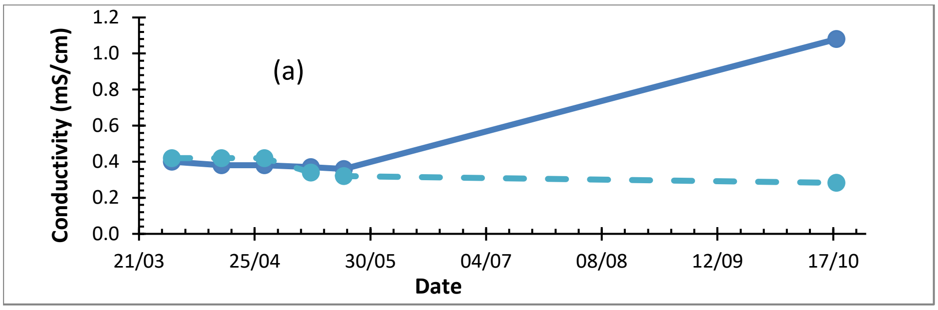


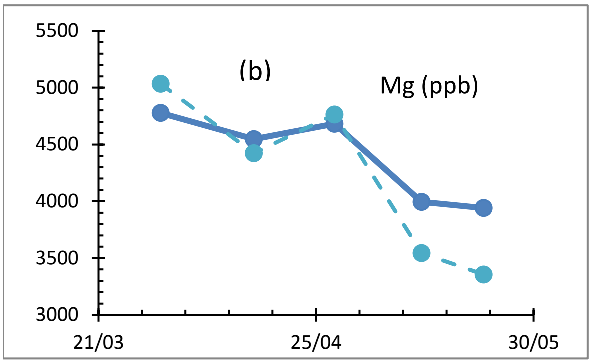
Figure 8: Ca (upper) and Mg (lower) concentrations (ppb) in soil solutions as a function of time (days) in the laboratory weathering experiments. The plots on the left-hand side (a & b) are for grass-land soil and those on the right (c & d) are for crop soils from UCD Lyons Research Farm. The dashed line represents the concentrations of Ca and Mg predicted to be present in the soil solutions based on data from basalt-only and soil-only experiments, i.e. for simple mixing with no additional leaching of the basalt as a result of the presence of soil. Coloured dashed lines (purple and orange) show Ca and Mg concentrations from soil-only (control) weathering experiments. The solid coloured lines (purple for grass soil, orange for crop soil) show Ca and Mg yields for treated (basalt amended) soils. For both soils, Mg concentrations in the soil/basalt mixtures are very substantially higher (c. by a factor of 3 at the end of the experiment) compared with either the untreated soils (dashed coloured lines) or the theoretical values based on simply mixing. In other words, the presence of soil very significantly increased the Mg yields from basalt weathering. The same is true for Ca in the crop soil (top right diagram), but no measurable increase in Ca yield from the grassland soil (top left) occurred when basalt was added.

2.3.3 Results –Field weathering experiments:

Figure 9: Installed soil water suction samplers (centre of photographs) at the tillage and grass-land (perennial ryegrass) sites at UCD Lyons Research Farm (Newcastle, Co. Dublin). For much of the summer these sites suffered substantial soil moisture deficits and sampling of soil pore waters was not possible. At the time of writing (November 2018), deficits are close to zero and soil pore-water sampling has recommenced. Geochemical results from the Feighcullen site in Co. Kildare are more complete as summer moisture deficits were less severe compared to the Lyons and Killinthomas sites.

Preliminary data from the Feighcullen site are shown in Figure 10 below.





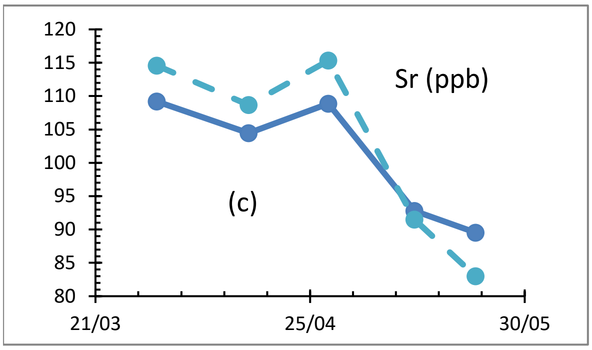


Figure 10:
(a) Electrical conductivity (mS/cm) in soil pore waters in a basalt treated (solid line) and an untreated soil (dashed line).
(b) Magnesium concentration (ppb) in soil pore waters in a basalt treated (solid line) and an untreated soil (dashed line).
(c) Strontium concentration (ppb) in soil pore waters in a basalt treated (solid line) and an untreated soil (dashed line). Sr isotope measurements have been completed for these waters but no significant differences in $^{87}Sr/^{86}Sr$ ratios between treated and untreated sites have been detected so far.

All data in Figure 10 are from the Feighcullen field site (Co. Kildare). Regular sampling at these sites is continuing at the time of writing to improve the dataset, now that soil pore water is available again in the suction samplers after the strong summer soil moisture deficits. Water was not available at the field sites from May until October 2018.

The preliminary field weathering results indicate that Mg (and to a lesser extent Sr and Ca) concentrations in the soil porewaters at the Feighcullen site have become higher in the treated sites, consistent with weathering of olivine, and to a lesser extent plagioclase from the basalt amendment. These field-based results are broadly consistent with those from the laboratory-based study discussed above (e.g. Figure 8), although more data are required to confirm weathering rates and the longevity of these effects at the basalt-amended field sites.

***2.3.4 Results –Mass balance calculations and quantification of weathering rates*:**

The 'quarry dust' basalt amendment contains 8.42 wt% MgO and 10.80 wt% CaO (Table 1). These divalent cations are of particular interest for CO_2 sequestration, because they have the potential to precipitate magnesium and calcium carbonates in the oceans, following transport in fluvial systems from the weathering zone. The laboratory batch weathering experiments utilised 0.2-1.5 grammes of basalt per experiment. The basalt-only experiment for example, comprised 1.5g of basalt in contact with 15 mls of deionised water and contained approximately 76 mg of Mg and 116 mg of Ca. After 66 days (before the precipitation of secondary Mg-Ca-Al clays in these closed-system experiments) about 1.62% of the available Mg and 0.2% of the available Ca had been removed in the weathering solutions. However, when soil/basalt mixtures were used (0.2g basalt mixed with 1.3g soil in 15 mls of water to retain solid/water ratios), there was a dramatic increase in the amount of basalt-derived Mg leached (5.9 % by mass of the rock-available Mg in the added basalt was removed in 125 days for the grass-land soil mixture, after correction for exchangeable Mg derived from the soil component of the mixture). The equivalent figure for the crop-soil/basalt mixture is somewhat lower; approximately 4.7 % by mass of the available Mg in the added basalt was removed in 125 days, but this represents an approximately three-fold increase in removal rates of Mg, relative to the basalt-only control.

In contrast, calcium yields by weathering solutions were much lower. In the case of the basalt-treated grass-land soil for example, there was little or no detectable Ca removal from the basalt and almost all of the dissolved Ca could be accounted for by exchangeable Ca from the soil. Minor proportions of basalt-derived Ca could be detected in the weathering solutions in basalt amended crop soil (c. 1.6% of the available basalt Ca was removed after 125 days).

The fresh basalts at Budore Quarry contain approximately 8 wt% MgO (Table 2). Assuming that about 15% of their available Mg could be mobilised from soil/basalt mixtures on an annual basis (scaled up from the 4 month laboratory weathering experiments), approximately 1.2% of the mass of applied basalt could be available to form MgO. Taking a simple 1:1 molar stoichiometry for $MgO:CO_2$ to form $MgCO_3$ and a conservative value 1% for the proportion of amendment basalt available to form MgO, and a plausible application rate of 10 tonnes basalt/hectare, leads to estimates of c. 1 tonne CO_2 sequestered per hectare, per year, requiring 10 Mt of crushed basalt/year. Thus, one million hectares (c. 12% of Ireland's land surface) could sequester c. 1 million tonnes of CO_2 in this scenario. For context, approximately 7 Mt of basalt is quarried annually in N. Ireland, mainly for aggregate. In the UK, 47Mt per year of igneous rock are quarried annually. In summary, while the required quantities (10 Mt/annum) are large, they are plausible, given a quarrying infrastructure similar to that existing at present.

2.3.5 Summary and Recommendations

- Basalt 'quarry dust' sampled at Budore Quarry is compositionally similar to fresh or only weakly altered basalt and contains minor amounts of lateritic weathering only.
- ~15% of the quarry dust is below 63 µm, facilitating accelerated weathering when added to spoils without any need for additional crushing.
- In most cases, treated soils show a **small but significant increase in pH and soil solution conductivity**.
- Weathering experiments show **strong dissolution of olivine, moderate dissolution of plagioclase**, and some dissolution of augite and ilmenite as early as ~60 days.
- Ca^{2+} and Mg^{2+} concentrations in soil solutions increase over time in the laboratory experiments. Field experiments are still ongoing to assess if this is true for field conditions. Field weathering experiments are also continuing to assess the longer term effects of the basalt amendment on soil-water Ca^{2+} and Mg^{2+}, soil pH and soil nutrient status.
- Release of Mg^{2+}, and to a lesser extent Ca from the basalt during the laboratory weathering experiments is higher than predicted in a simple mixing model based on weathering data for the basalt and soils in isolation, likely due to naturally organic acids and microbes present in soils that enhance basalt leaching rates.
- Both field and laboratory experiments show encouraging results for the suitability of crushed basalt as soil amendment to sequester atmospheric CO_2 and **buffer soil pH. There may be opportunities to use basaltic 'quarry dust' for Aglime substitution which would directly reduce CO_2 emissions from soils.**
- Precipitation of Mg(Ca)-Al-Fe bearing clay minerals and Fe-oxyhydroxide minerals occurred in the basalt amended spoils after 66 days in the closed-system batch laboratory weathering

experiments. This process would be detrimental to CO_2 sequestration in a natural system at the weathering Mg and Ca would become locked up in the soil and would not be available for transport via drainage to the oceans for carbonate precipitation. It is less likely to occur in flow-through experiments or in well-drained field conditions, but it could be an issue for heavy water-logger soils and is a process that requires further investigation.

- Further work is required to assess the effect of basalt amendment on soil nutrient status, particularly with respect to phosphorus availability.
- The science is now at the stage where larger-scale field trials (multi hectare scale) should be conducted in instrumented catchments to assess increases in Mg and Ca fluxes from amended soils relative to controls. An intermediate step could be to conduct flow-through experiments (e.g. on basalt amended soils in pots) to measure Ca and Mg fluxes.

(ii) Implementation (please include any issues with timelines, milestones, management etc. or deviations from the original implementation plan)

Both field- and laboratory based experiments were conducted. In the initial project proposal, the emphasis was on field experiments. However, the unusually wet spring of 2018 led to delays in field deployment of the soil moisture tension lysimeters at the UCD Lyons Research Farm (deployment had to be until the spring barley crop was planted in early May to avoid damage by farm machinery). Additionally, the unusually dry summer of 2018 led to large soil moisture deficits at all of the study sites in Co. Dublin and Co. Kildare, further hindering the progress of the experiments. As a contingency (as explained in the Interim Report of June 2018), a suite of additional laboratory-based weathering experiments were undertaken during the summer of 2018 to augment the delayed field experiments. At the time of writing (October 2018), soil moisture deficits are slowly reducing and regular collection and analysis of soil waters from the amended sites has resumed at most, but not all of the field amended sites.

(iii) Outputs (please provide a short description *and* complete the table below)
Poster presentation at Geoscience 2018, Dublin Castle, November 2018 on 'A preliminary investigation of crushed basalt as a soil amendment to sequester atmospheric CO_2'.

Task No.	Deliverable description	Planned delivery (as per proposal)	Date of delivery
1	Manuscript for publication on rates of basalt weathering (copy to be supplied to GSI)	Month 12	Month 12
2	Poster at Irish Geological Research meeting to highlight ongoing work	Month 12 (poster at Geoscience Ireland)	Month 12
3	Final Report to GSI	Month 12	Month 12

Publications to date: *Please use format below and provide a copy of the presentation*

McDermott, F., Barros, R., Cooper, M., van Acken, D. (2018) A preliminary investigation of crushed basalt as a soil amendment to sequester atmospheric CO_2. *Geoscience 2018*, Dublin, Ireland, 06-Nov-18.

4. Data/outputs submitted with final report *(please list the documents, presentations, datasets etc. submitted with this report)*

a. Poster presentation at Geoscience 2018 Conference, Dublin Castle, November 2018.
b. Excel file containing geochemical data for laboratory and field experiments.

SUPPLEMENTARY MATERIAL

(This section will be included in your published report unless otherwise instructed. If you have a published report, publication, etc. you may include it here).