Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: An opportunity for passive carbon sequestration☆

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ABSTRACT

The proportions of different carbon pools within artificial soils prepared by blending composts with dolerite and basalt quarry fines has changed over a period of 7 years, accumulating inorganic carbon as carbonate minerals newly formed within the soils. With no artificial energy inputs following construction, this is regarded as a passive mineral carbonation process. Carbon isotope data show that up to 40% of the carbon within the soil carbonate is derived from photosynthesis, mixed with carbon from geological sources (limestone present in the quarry fines). Organic matter within the soils shows very variable composition, with an apparent increase with time in the relative proportion of labile carbon relative to more stable forms, reflecting a change in the soil organic matter composition associated with the establishment of new plant communities. The rate of accumulation of inorganic carbon as carbonate minerals is estimated to be equivalent to $4.8\,t\,C\,ha^{-1}$ annually to a depth of 0.3 m, consistent with rates observed for accumulations of carbonate carbon in urban soils containing demolition wastes (annually $3.0\,t\,C\,ha^{-1}$ to 0.3 m). There appears to be substantial potential for artificial soils to be designed expressly for the purpose of carbon capture. The process is analogous to the use of reed beds for the removal of pollutants from contaminated waters.

1. Introduction

There is little doubt that atmospheric concentrations of CO_2 and other greenhouse gases have increased as a consequence of human activity, possibly dating back to the dawn of agriculture (Kutzbach et al., 2010) as well as through the comparatively recent combustion of fossil fuels since the industrial revolution (Denman et al., 2007). It is widely accepted that the increase in atmospheric greenhouse gas concentrations is responsible for a change in climate; the geological record suggests that our present interglacial period has extended for longer than previous interglacials (Kutzbach et al., 2010), and global temperatures overall are rising with implications for sea level and the frequency of extreme weather events (Denman et al., 2007).

In the context of climate change mitigation, there is a need to improve our understanding of natural processes that remove atmospheric CO_2 in ways that begin to compensate for artificial emissions. Work of this type provides a basis for decisions to be made that enable sustainable carbon dioxide removal systems to be trialled, and possibly then implemented. In this context, the 'excess' CO_2 that needs to be removed in order to compensate for anthropogenic emissions and so maintain atmospheric levels at a target of 500 ppmv is of the order of $8\,Gt\,C\,y^{-1}$ by 2050 (Pacala and Socolow, 2004). These authors envisage that no single technique or approach will achieve this, and suggest that individually some approaches may potentially remove a 'wedge' of $1\,Gt\,C\,y^{-1}$.

Near complete elimination of anthropogenic greenhouse gas emissions is the only long-term sustainable solution. However, the intrinsic relationship between fossil fuel energy and developed economies, and the slow progress that has been made to decouple this dependency, suggests that atmospheric CO_2 concentration will continue to rise, beyond a current value of approximately 400 ppmv. Even if emissions were drastically reduced to zero today, it would take hundreds of years before atmospheric CO_2 would stabilize back to pre-industrial concentrations (Lowe et al., 2009). In

these circumstances it is prudent to develop mitigation technologies that remove CO_2 from the atmosphere.

It is well known that the coupled plant–soil system plays a fundamental role in the global carbon cycle (e.g. Lal, 2004). Although its size as a reservoir is small compared with the ocean, the coupled plant–soil system contains 2261 Gt C (1990s figures; Denman et al., 2007), of which approximately 600 Gt C is in plants and 1600 Gt C in soil. This is well in excess of the atmospheric reservoir (762 Gt C; Denman et al., 2007). Most importantly, the fluxes of carbon to and from the coupled plant–soil system are greater than those between the atmosphere and the ocean (approximately 150 Gt C y^{-1}). An amount equivalent to all atmospheric CO_2 will pass through the coupled plant–soil system in 7 years. In these circumstances, and given the recent geological record of agricultural influence on atmospheric CO_2 concentrations (Kutzbach et al., 2010), it seems self evident that any influence that humans may wish to have should be based on ways in which we can intercept and preserve in soils carbon that has been removed from the atmosphere by photosynthesis.

Many studies have investigated the application of organic matter to soils, as composts, manures etc. (Diacono and Montemurro, 2010). It takes many years to build soil carbon stocks using this approach. For example, Triberti et al. (2008) report annual increases in soil organic carbon of 0.16–0.26 t C ha^{-1} over a 30 year period in a cropped soil system. It is equally well known that soil organic matter turns over at rates that vary for different SOM pools (Jones et al., 2005; Smith, 2004, 2008 and references therein). Large-scale studies have shown that, overall, as much as 90% of carbon input as compost is lost from a soil system within 10 years (Lin et al., 1997). Overall, where data are available, loss of organic matter from soil over time is potentially a serious problem (Smith et al., 2005). Restoration of organic carbon concentrations in modified soils (agriculture and urban environments) has the potential to be an important tool for mitigating anthropogenic climate change (Lal, 2003), as long as organic inputs are maintained to compensate for turnover. Organic carbon in soils is controlled largely by land management practices, and these may change depending on a number of social and economic drivers (e.g. feeding the increasing global population).

The formation of pedogenic carbonates offers a sink for plant-derived carbon that is effectively permanent from a human perspective (Manning, 2008; Pustovoytov, 2003). Globally, the amount of inorganic carbon held within soil carbonates is estimated to be between 720 Gt (Batjes, 1996) and 950 Gt (Schlesinger, 1985). Pedogenic carbonates readily form in specific environments with appropriate conditions that relate (for example) to depth and rainfall as well as the availability of calcium (Jenny, 1941). In general, the occurrence of pedogenic carbonates may have been underestimated, partly because of the scale of the task of mapping soils to greater depths than is conventional (typically 1 m), and partly because of the need for rigorous chemical or mineralogical determination of carbonate and its carbon and oxygen isotopic composition (Cerling, 1984).

We have recently shown (Renforth et al., 2009; Washbourne et al., 2012; Manning and Renforth, 2013) that pedogenic carbonate formation commonly occurs within urban soils that carry a burden of fine-grained mineral matter derived ultimately from concrete and Portland cement (in the UK, this type of soil is sometimes known as 'made ground'). Total inorganic carbon (TIC) contents of such soils may achieve 300 t C ha^{-1} to a depth of 3 m, compared with 175 t C ha^{-1} to a depth of 1 m for TOC within agricultural soils (e.g. Smith et al., 2005), the majority of which is in the top 0.3 m. What is more, urban soils accumulate TIC very rapidly (i.e. within 5–10 years) following demolition or landscaping, after which restoration may involve initial seeding of an installed topsoil followed by opportunistic revegetation. Washbourne et al.

(2012) have shown that the 10 ha Science Central site in Newcastle removed 36,000 t CO_2 from the atmosphere in 3 years following demolition. This is equivalent to 100 t CO_2 ha^{-1} monthly, for a site with no restoration following demolition.

A key control on the formation of pedogenic carbonates in urban soils is the availability of calcium. Arisings of artificial calcium silicates with the potential to undergo carbonation are estimated by Renforth et al. (2011) to have an annual global sequestration potential equivalent to 190–332 million t C (a sixth to a third of a wedge; Pacala and Socolow, 2004) which would have the potential to mitigate 4–7% of emissions over the next 100 years (Allen et al., 2009).

In the context of considering ways in which soils can be managed to enhance the accumulation of inorganic carbon derived ultimately from the atmosphere, this paper describes artificial plots that have developed significant pedogenic carbonate within a blend of compost and finely ground basic igneous rock. It is important to note that the plots were originally constructed with other purposes in mind, as part of a semi-commercial study designed to assess the potential for blending quarry fines (a by-product of primary aggregate production) with composts in the formulation of artificial soils. Unexpectedly, the experimental plots have provided evidence of rates and mechanisms of carbon mineralization through reaction between compost and the calcium silicate minerals present within the quarry fines, and because of the importance of these observations they are reported here. The work presented in this paper augments reports of carbonation of synthetic calcium silicate minerals (Renforth and Manning, 2011), and is particularly significant because the carbonation of natural calcium silicate minerals through 'enhanced weathering' within soils could, by virtue of their widespread natural occurrence, be much more significant (Schuiling and Krijgsman, 2006; Hartmann and Kempe, 2008; Hartmann et al., 2013; Köhler et al., 2010; Renforth, 2012).

2. Rock dust-compost experimental plots

In 2003, Mineral Solutions Ltd (www.mineralsolutions.co.uk), with support from the Minerals Industry Research Organisation (MIRO; www.miro.co.uk), investigated the development of artificial soils for land restoration purposes. The investigation focused on the use of quarry fines (generally <0.5 mm), which arise as a normal by-product of crushing of hard rocks mined for construction aggregates. Mineral Solutions Ltd. carried out pot trials, lysimeter trails and field trials, reporting in the public domain through MIRO and the company's website (Mineral Solutions Ltd., 2004).

At Barrasford Quarry (Lafarge Tarmac Ltd., Tyne Valley, England; Ordnance Survey grid reference NY914745), five trial plots were prepared with two replicates of each treatment and a single control (Fig. 1). These involved use of two quarry fines (Kelso sub-suite basalt from Craighouse quarry, Lafarge Tarmac Ltd., Melrose, Scotland; NT 600 362; dolerite from Barrasford quarry), and two composts (commercially produced composted food industry [FI] waste and material from an anaerobic digester that had subsequently been composted [AD]). Compositional and textural information for the quarry fines and compost is summarized in Tables 1–3.

The purpose of the field trial at Barrasford was to investigate, on a pilot basis, the suitability of blends of composts and quarry fines as an artificial growing medium suitable for land restoration and other purposes. Carbon capture was not part of the design. However, work carried out on the plots since their establishment in the winter of 2003 has shown, unexpectedly, that they have gained and accumulated soil carbonate minerals. This paper takes the opportunity to describe and evaluate the carbon-capture benefits of the Barrasford plots, so that the experience thus gained can be used in future work expressly intended to investigate carbonation of basic rocks as a carbon dioxide removal mechanism.
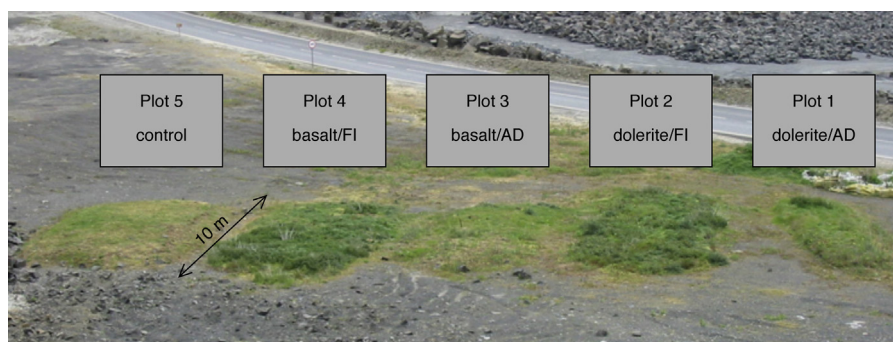
Fig. 1. Photograph (2007) of trial plots established in December 2003 at Barrasford Quarry, looking south.

3. Characterisation and investigation of the trial plots and their soils

When constructed in 2003, the five Barrasford plots were prepared on an area of quarry floor consisting of a freely draining, slightly inclined, compacted coarse crushed aggregate. The quarry fines were spread in 10 m × 3 m plots to a depth of 0.25 m, a 0.25 m layer of compost was added, and the two materials were blended using a rotivator. The masses of materials used were recorded. The control plot was prepared by mixing 0.6 m thickness of dolerite fines with 0.3 m thickness of topsoil, both materials sourced from Barrasford quarry. The south half of each plot, including the control, was then seeded (350 kg ha^{-1}) with a rye grass (*Lolium perenne*)-based reclamation mix.

By 2008, plot 1 had been covered by quarry spoil and was no longer accessible. The other plots had compacted to a depth of approximately 0.3 m, and the original grass mix had been replaced by a diverse, completely different, plant community (Table 4). The new community was predominantly (but not exclusively) plants that use the C3 metabolic pathway.

In the absence of explicit analytical data determined at the time the plots were established, their initial carbon contents have been estimated as follows. Assuming that the composts contain 40% carbon (within dry matter) and have a dry matter content of 20% (anaerobic digestate compost; AD) and 40% (food industry compost; FI), it is estimated that the initial organic carbon contents of the composts is 8% (AD) and 16% (FI). Using the weights of material used to construct the plots, the original carbon contents were estimated and are summarized in Table 5. Plot 5, the control, was prepared from dolerite fines with no added compost; a local topsoil

with a TOC content of 3.19% was added to the plot, giving a bulk initial TOC content of 1.09%.

After completion of the original project in December 2003, the plots were ignored until 2007, when initial investigation of their potential to form pedogenic carbonate minerals was carried out (March and May 2007; sampling round 1). This provided sufficient positive results to justify further work, with repeated sampling in October 2007 (sampling round 2) and October 2008 (sampling

Table 1

Major element composition (X-ray fluorescence analysis; fused bead method, University of Leicester, UK) of fines from Craighouse and Barrasford quarries, and for dolerite from Barrasford quarry (Randall, 1989). The Barrasford fines composition corresponds to a mixture of dolerite with approximately 8% limestone.

Wt% oxide	Craighouse fines	Barrasford fines	Barrasford dolerite
Rock type	Basalt	Dolerite–limestone mix	Dolerite
SiO_2	44.88	45.53	49.50
TiO_2	3.30	1.85	2.36
Al_2O_3	13.05	12.79	14.43
Fe_2O_3	14.97	11.39	3.82
FeO	nd	nd	8.51
MnO	0.18	0.15	0.19
MgO	7.13	4.54	6.12
CaO	7.70	13.24	9.36
Na_2O	3.34	3.10	2.42
K_2O	1.42	0.91	0.95
P_2O_5	1.10	0.40	0.29
SO_3	0.10	0.43	0.00
LOI	2.54	4.90	1.33
Total	99.71	99.24	99.28

nd denotes not determined.

Table 2

Summary of compositional information for composts used in the trials. All concentrations expressed on a dry weight (oven at 110 °C) basis.

Parameter	Units	Food industry waste compost (FI)	Anaerobic digestor compost (AD)
Salmonella		Negative	Negative
E. coli	cfu/g	167	12,556
Dry matter	%	36.0	20.2
pH	pH units	5.89	9.01
Electrical conductivity	μS/cm	1262	607
Organic matter	%, w/w	70.3	88.1
Total C	%, w/w	38.7	41
Total N	%, w/w	4.63	1.74
C:N Ratio		8:1	24:1
Chloride	mg/kg	235	871
Nitrate-N	mg/kg	2731	<0.01
Ammonical-N	mg/kg	3670	3404
Total			
P	%, w/w	0.29	0.45
K	%, w/w	0.59	1.07
Mg	%, w/w	0.18	0.26
Cu	mg/kg	35.7	26.9
Cd	mg/kg	0.154	0.191
Cr	mg/kg	13.6	8.52
Pb	mg/kg	260	38.3
Hg	mg/kg	0.050	<0.05
Ni	mg/kg	5.03	5.68
S	%, w/w	0.44	0.27
Zn	mg/kg	108	131
Available			
P	mg/kg	216	193
K	mg/kg	544	658
Plastic >2 mm	%, w/w	0.09	0.00
Metal >2 mm	%, w/w	<0.01	0.00
Glass >2 mm	%, w/w	0.00	0.00
Stones >2 mm	%, w/w	1.00	0.00

Table 3

Particle size data for Craighouse and Barrasford fines.

	Craighouse fines (wt%)	Barrasford fines (wt%)
3.4–2.0 mm	10	0
2.0–0.063 mm	81	8
0.063–0.002 mm	7	82
<0.002 mm	12	10

Table 4
Summary of vegetation established in Barrasford trial plots by 2007.

Latin Name	Common Name	Plot 2	Plot 3	Plot 4	Plot 5
Anthoxanthum odoratum	Sweet vernal grass				y
Brassica sp.	Mustard sp.	y		y	
Cerastium fontanum	Common mouse ear	y	y		y
Chamaenerion angustifolium	Rosebay willowherb	y			
Cirsium eriophorum	Wooly Thistle	y			
Cirsium vulgare	Spear thistle	y	y	y	
Deschampsia sp.	Hair grass	y	y		
Echinops ritro	Globe thistle	y			
Festuca sp.	Fescue sp.	y	y		
Galium aparine	Cleavers	y			
Holcus lanatus	Yorkshire fog	y			
Myosotis sp.	Forget me not sp.	y	y	y	
Pilosella officinarum	Mouse ear hawkweed		y		y
Poa trivialis	Rough meadow-grass			y	
Rumex obtusifolius	Broad leaved dock	y		y	
Senecio jacobaea	Ragwort		y	y	y
Senecio vulgaris	Groundsel	y	y	y	
Taraxacum officinale	Common dandelion	y	y	y	y
Trifolium repens	White clover	y	y		
Urtica dioica	Common nettle	y	y	y	
Veronica chamaedrys	Germander speedwell				y

round 3). The purpose of repeated sampling was to investigate possible changes in the carbon distribution between different pools: organic (labile, recalcitrant and refractory; Lopez-Capel et al., 2005) and inorganic.

Samples were collected throughout the depth of the soil profiles, which by 2007 was of the order of 0.3 m; the base of the plots was clearly defined by the contact with the coarse crushed rock aggregate of the quarry floor. After air drying, the samples were sieved to <5 mm. For this fraction, calcium carbonate content was determined using an Eikelkamp calcimeter (BS7755-3.10:1995; reproducibility better than ±0.6%), and TOC using a LECO carbon analyzer. TOC pools were separated for a subset of samples using the density fractionation scheme set out by Sohi et al. (2001).

Carbon and oxygen isotopic abundances were determined for carbonate, and carbon isotope abundances for organic carbon, through the commercial service provided by IsoAnalytical Ltd. (Crewe, UK; www.iso-analytical.co.uk), using a Europa Scientific 20:20 instrument (www.iso-analytical.co.uk). After loading into clean Exetainer™ tubes and drying, the samples were flushed with 99.995% helium. 0.5 mL of pure phosphoric acid (Coplen et al., 1983) was injected, mixed and the vials left to stand for 24 h at room temperature. The vials then were heated to 65 °C for 2 h to ensure conversion of all available carbonate to carbon dioxide, which was then analysed by Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS) using a Europa Scientific 20–20 IRMS. Replication had a standard deviation better than ±0.1‰ and values for reference materials were within two standard deviations of the expected result. The results were recorded relative to the Vienna Peedee Belemnite standard (v-PDB).

Thermal analysis was carried out to determine the relative proportions of different C components according to the method of Lopez-Capel et al. (2005), extended by determination of evolved gases (cf. Fernandez et al., 2012). A Netzsch STA 449C Jupiter

TG-DSC system connected by a heated capillary (200 °C) to a Netzsch Aeolos quadrupole mass spectrometer system was used to determine the following parameters: (1) mass change, (2) energy gained or lost from the sample, (3) composition of evolved gases (m/z range 10–300). Individual powder samples (typically 10 mg) were placed within an alumina crucible, using an identical empty reference crucible, and were heated from ambient temperature to 990 °C under flowing He_{80}–O_{20}. Intensities for m/z 44 ($CO_2 + N_2O$) were recorded; no correction was made for evolved N_2O, which was assumed to be negligible compared with CO_2 given failure to detect measurable m/z 30 (NO). Evolved gas evolution curves were interpreted using GRAMS/AI peak fitting software (www.AdeptScience.co.uk) that permits investigation of the contribution of several individual peaks to an overall trace. By defining initial conditions (including a presumed gaussian peak shape), the range of potential values for each peak centre (275–375 °C, 375–475 °C and 475–575 °C, respectively), and the number of iterations to perform (in this case 50), the software fits individual labile, recalcitrant and refractory carbon peaks (Lopez-Capel et al., 2005) such that their combined shapes and areas are the best possible fit for the overall CO_2 trace.

4. Accumulation of inorganic carbon as a proportion of the total C stock

Overall, the organic carbon content of the plots is similar for the three sampling rounds (Fig. 2A). With the exception of a single outlier, all TOC data lie within the range 0.5–4.3% C, and there appear to be no differences between plots or between sampling events. In general, the plots with compost lost TOC compared with the estimated starting composition (3.4–6.3 wt% TOC), and the control plot gained TOC (initially 1.1 wt% TOC).

Compared with total organic carbon, the measured calcium carbonate contents (Fig. 2B) are very variable. The plots produced by blending compost with quarry fines generally contain measurable calcium carbonate contents from near zero to 14%, with a mean of 3.74%. In contrast, Plot 5 (the control), consistently has low calcium carbonate contents, with a mean of 0.10 wt% and a maximum value of 0.27 wt%.

An estimate of the partitioning of carbon between organic and inorganic pools based on the bulk compositional data presented in Fig. 2 (i.e. the measured TOC and TIC contents) is presented in

Table 5
Estimated original TOC contents for the Barrasford plots.

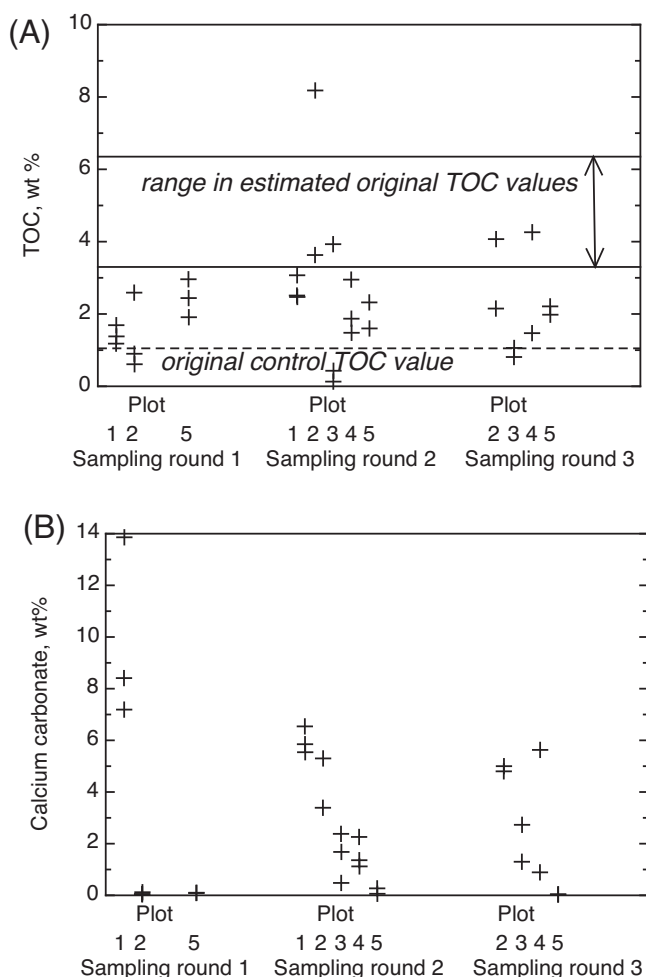|	TOC (wt%)
Plot 1	3.43
Plot 2	6.29
Plot 3	2.26
Plot 4	4.24
Plot 5	1.09

Fig. 2. Observed TOC (A) and calcium carbonate contents (B) for the <5 mm whole soil fraction, Barrasford plots, sampled in May 2007 (round 1), October 2007 (round 2) and October 2008 (round 3).

Table 6
Carbon and oxygen isotope data for calcite within the Barrasford plots, and for two limestone samples taken from the quarry. Values in centimeters are depths below soil surface.

Sample	$\delta^{13}C$ v-PDB (‰)	$\delta^{18}O$ v-PDB (‰)	%Pedogenic C
Collected March 2007			
Plot 1 0–10 cm	−1.62	−12.49	24.5
Plot 1 10–20 cm	−1.59	−12.32	23.4
Plot 1 20–30 cm	0.09	−11.29	9.1
Plot 5 0–10 cm	−0.69	−11.42	16.1
Collected October 2007			
Plot 1 0–10 cm	−1.49	−11.90	23.4
Plot 1 10–20 cm	−1.61	−12.00	24.5
Plot 1 20–30 cm	−2.49	−12.46	32.4
Plot 2 0–10 cm	−3.44	−12.35	41.0
Plot 2 10–20 cm	−3.50	−12.27	41.5
Plot 2 20–30 cm	−2.55	−11.90	32.9
Plot 3 0–10 cm	−2.64	−12.26	33.7
Plot 4 0–10 cm	−1.51	−12.11	23.5
Limestone 1	0.60	−11.06	Not applicable
Limestone 2	1.61	−10.60	Not applicable

relative proportion of carbonate carbon, and this doubled between October 2007 and October 2008 (Fig. 3). Importantly, Fig. 3 reinforces the observation that the control plot (Plot 5) has accumulated extremely low amounts of carbonate.

5. Origin of carbonate carbon

Carbon isotope data determined for samples collected in March and October 2007 (sampling rounds 1 and 2) from the Barrasford plots are shown in Table 6. In principle, using the v-PDB reference, the $\delta^{13}C$ value for marine carbonates (including limestones, which occur at Barrasford quarry above and below the dolerite) is near zero or slightly positive (Andrews, 2006). Photosynthesis results in negative $\delta^{13}C$ values within plant tissue and composts, as low as −14 ‰ for C4 plants and −24 ‰ for C3 plants (Cerling, 1984). Pedogenic carbonates produced from organic carbon from soils in which C3 plants are growing typically have $\delta^{13}C$ values of around −10 ‰. It is assumed that the carbonate mineral in the plots is calcite, from the temperature of the decarbonation endotherm observed using thermal analysis, and the carbon isotope data for the Barrasford trial plots give negative values (Table 6).

Fig. 4 shows a plot of $\delta^{13}C$ vs $\delta^{18}O$ for carbonates from the Barrasford plots. The limited available data show clearly that there is a linear array for samples from the plots, and that this intercepts two

Fig. 3. This assumes that the proportion of inorganic carbon in the plots was zero initially. Although true for plots 3, 4 and 5, plots 1 and 2 used a dolerite with 8% limestone (Table 1), corresponding to <1% inorganic C in that component of the plot after mixing with compost. The available data show clearly an increase in the
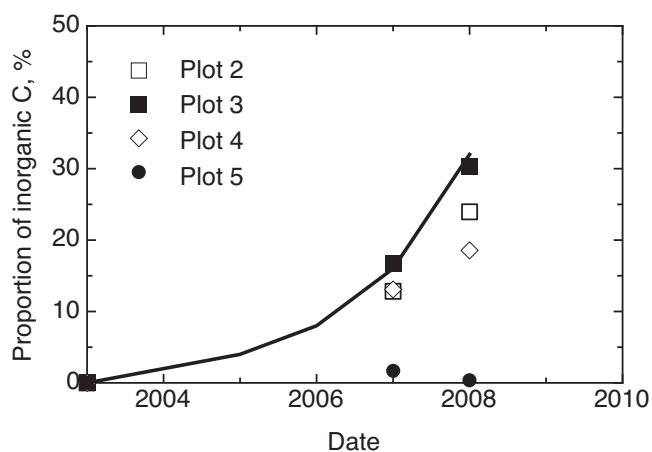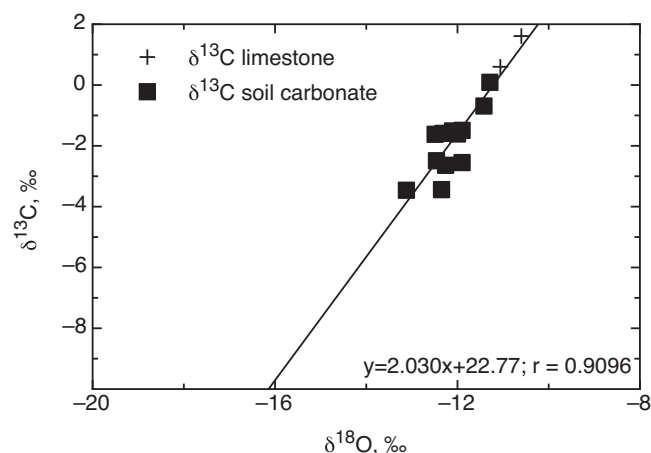

Fig. 3. Proportion of carbonate carbon within the total carbon budget for the Barrasford trial plots, sampling rounds 2 (October 2007) and 3 (October 2008); the line shows a modeled trajectory for Plot 3, assuming doubling each year.

Fig. 4. Plot of $\delta^{13}C$ vs $\delta^{18}O$ for carbonate from the Barrasford plots.

data points for limestone from the quarry. Thus the observed carbonate can be considered to be a mixture of carbonate derived from the limestone (which we know is present in fines for the dolerite, but not the basalt; Table 1) and pedogenic carbonate.

Using the mixing model suggested by Fig. 4, the proportions of pedogenic carbonate have been estimated, and are given in Table 6. It is assumed that the pedogenic calcium carbonate δ^{13}C end-member value is −10 ‰, consistent with fractionation reported by Cerling (1984). All plots show the presence of differing proportions of pedogenic carbonate, reaching 40% of the carbonate-carbon budget.

6. Changes in quality of organic carbon

One of the purposes of the repeated sampling of the plots was to determine whether or not there had been any observable change in the proportions of different organic carbon pools. Two approaches have been taken to characterize the relative proportions of labile, recalcitrant and refractory pools: (1) by weight loss over specific temperature intervals (Lopez-Capel et al., 2005; Dell'Abate et al., 2003), and (2) through interpretation of evolved CO_2, using GRAMS/AI to optimize peak fitting.

Using the terminology developed by Dell'Abate et al. (2003) and Lopez-Capel et al. (2005) in the context of thermal analysis, relative proportions of labile, recalcitrant and refractory organic matter can be recognized from the relative proportions of the weight losses observed in the intervals 200–375 °C (Exo 1), 375–500 °C (Exo 2) and 500–600 °C (Exo 3). Correspondingly, using GRAMS/AI evolved CO_2 peaks were sought in the ranges 275–375 °C, 375–475 °C and 475–575 °C, and generally occurred within the ranges 320–350 °C, 430–470 °C and 500–550 °C.

Fig. 5 shows the relative proportions of the three organic matter pools for individual whole soil samples, determined (a) from evolved gas analysis and (b) from weight loss measurements.

There is considerable scatter in the determination of relative proportions of organic matter using evolved gas data, and data from weight loss determination similarly are varied. But in both cases, it appears that with time the data become more focused, and there is a general trend for the proportions of the soil organic matter pools to become relatively enriched in the Exo 1 component, which is the most labile.

The free light fraction (Sohi et al., 2001) was only extracted for sampling round 3. Separation of this fraction concentrates the soil organic matter substantially (but the residual mass (i.e. the residue after hearing to >900 °C) remains high, at about 40 wt% or more compared with 90 wt% for the whole soil, indicating that the free light fraction is far from pure organic matter). Fig. 6 shows the relative proportions of the soil organic matter pools for whole soil and free light fractions from the third sampling round, determined from observed weight losses. Both are very similar; the figure suggests that dilution by components of the soil removed by density separation does not affect the relative proportions of the three soil organic matter components. In Fig. 6, the plots formed by blending compost and quarry fines show a cluster of points; the outlying point displaced towards the Exo 2 corner corresponds to the control plot.

The data obtained for the organic matter pools are very variable, and it is not possible to identify with confidence any trends that might relate to the evolution of the plots during the period since they were established. However, it is apparent that the importance of the more labile organic matter pool increases in proportion with time. Rather than reflecting evolution of the original compost, it is more likely that these observations reflect the characteristics of the organic matter pool that has developed in the plots since they were established, with inputs from present day vegetation
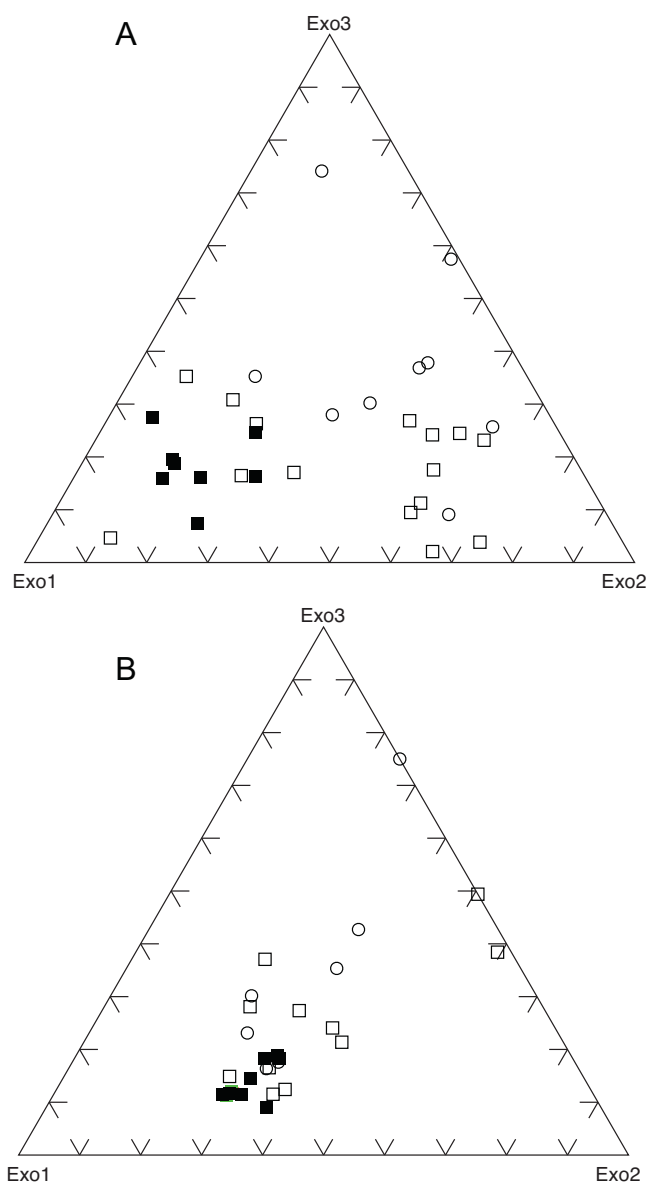

Fig. 5. Relative proportions of organic matter pools (Exo 1, Exo 2 and Exo 3) determined by (a) evolved gas analysis and (b) weight loss measurements. Open circles: sampling round 1; open squares: sampling round 2; filled squares: sampling round 3.

(which is dominated by grasses and flowering plants; Table 4) and soil microbial communities. Given the rates at which composts and labile organic matter turn over within soils (e.g. Triberti et al., 2008), it is unlikely that the organic matter recovered from samples taken in 2007 and 2008 reflects the nature of the compost used to construct the plots in 2003, instead reflecting the developing vegetation population and associated soil microbial community (Breulmann et al., 2012).

7. Implications for carbon sequestration

The Barrasford plots suggest, from mass balance and stable isotope data, that 20–40% of carbon from a biological source (the compost and the plants growing on the plots) has been fixed as calcium carbonate. This has been achieved as a consequence of mineralization of organic matter to give CO_2, a proportion of which
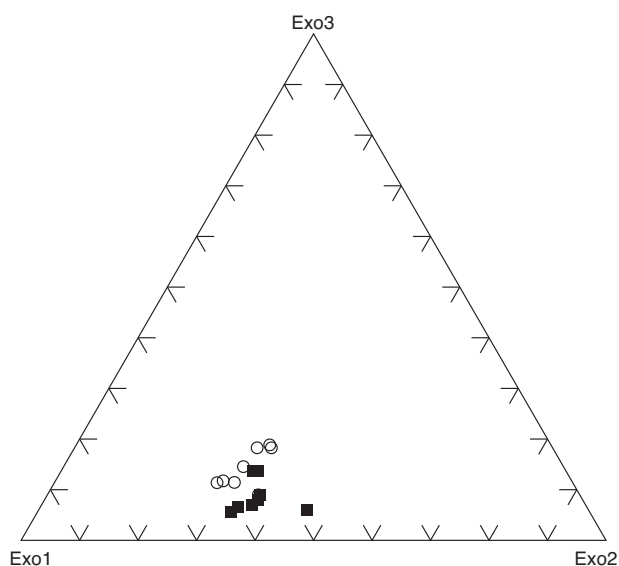
Fig. 6. Relative proportions of soil organic matter pools (based on weight loss measurements), sampling round 3, for whole soil (open circles) and free light fraction (filled squares).

occurs within the soil solution (at an appropriate pH) as a consequence of reaction (1):

$$H_2O + CO_2 = H^+ + HCO_3^- \qquad (1)$$

The geological component of the plots consists of two basic igneous rocks: dolerite and basalt. In both of these the calcium silicate minerals plagioclase ($CaAl_2Si_2O_8$–$NaAlSi_3O_8$) and pyroxene ($Ca(Mg,Fe)Si_2O_6$) are dominant mineral components (Macdonald, 1975; Randall, 1989). Weathering of these releases Ca ions, enabling the calcite precipitation reaction to occur:

$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+ \qquad (2)$$

There are many ways in which reaction (2) can be expressed. As written, it involves generation of a proton. In a complex soil system, pH effectively is buffered (for example, by reactions involving organic acid anions associated with organic matter decomposition), and provided that the soil solution is saturated with respect to calcite this mineral will precipitate over a wide range of pH values (cf. precipitation of calcite within sanitary landfill; Manning, 2001; Van Gulck et al., 2003).

The rates of weathering under field conditions of calcium silicate minerals are notoriously difficult to determine (Blum and Stillings, 1995). In general, the rate of dissolution measured under laboratory conditions is one or two orders of magnitude smaller than that measured in the field.

Similarly, the rate of production of inorganic carbon in solution as a consequence of plant growth is very difficult to determine. Moulton et al. (2000) investigated DIC within water draining from natural wooded slopes in Skorradalur, Iceland (no scope for geological C inputs), and demonstrated that production of carbon in solution exceeded values determined for plant root exudate production (Ryan et al., 2001) by, again, one or two orders of magnitude. Climate conditions at Skorradalur and Barrasford are similar. The mean annual temperature at Skorradalur is 4.6 °C, and annual precipitation is 1000–1500 mm (Moulton and Berner, 1998), compared with 6.5–7.5 °C and 900–1200 mm at Barrasford (http://www.metoffice.gov.uk).

Irrespective of the detailed chemical controls on mineral weathering and the production in solution of inorganic carbon from an organic source, the results of the investigation of the Barrasford plots clearly show that calcium carbonate has accumulated,

although there is also evidence of its removal, and the plots are clearly heterogeneous and act individually as an open system. Notwithstanding these limitations, the net rate of accumulation as inorganic carbonates for plots that used carbonate-free crushed rock (plots 3 and 4) is estimated to be of the order of $0.8\,g\,C\,kg^{-1}$ soil annually. This corresponds to accumulation at the present site of $4.8\,t\,C\,ha^{-1}$ annually to a depth of 30 cm, equivalent to a monthly rate of $1.5\,t\,CO_2\,ha^{-1}$.

The rate at which natural silicate minerals dissolve in the soil is one of the fundamental uncertainties in the feasibility assessment of enhanced weathering (Renforth, 2012). The surface area of the rock fines was not included in the initial characterization of the material. However, assuming a surface area $>1\,m^2\,g^{-1}$ which is typical for silicates crushed to $<63\,\mu m$ (appropriate for 92% of the dolerite fines; see O'Connor et al., 2005), a density of $2\,t\,m^{-3}$, a log weathering rate of $-16.3\,mol\,cm^{-2}\,s$ is determined. This value may be an underestimate given that it only accounts for the weathered calcium captured in carbonate minerals and does not include the weathered material that is lost from the plots in run-off solutions. It may also be an over-estimate given that a relatively small surface area was assumed. However each variable is unlikely to change the weathering rate by more than 2–3 orders of magnitude. Thus the value is similar to that reported for silicate weathering in natural soils (White and Brantley, 2003).

The observations from the Barrasford plots are consistent with those made on urban soils, where we have observed accumulation after 10 years of $300\,t\,C\,ha^{-1}$ to a depth of 3 m (Renforth et al., 2009), equivalent to $10\,t\,C\,ha^{-1}$ annually in 1 m depth of soil, or $3\,t\,C\,ha^{-1}$ to a depth of 30 cm. A much higher annual rate ($325\,t\,C\,ha^{-1}$) has been estimated for the urban soils at Science Central, Newcastle (Washbourne et al., 2012), reflecting differences in mineralogy: the Science Central soils contain calcium silicates and calcium hydroxide derived from cement products. Given that there were no artificial inputs following construction of the Barrasford plots, the development of soil carbonates can be regarded as a passive carbon sequestration process or carbon dioxide removal mechanism (Royal Society, 2009), and is analogous to the use of wetlands to remove pollutants from contaminated waters.

A key difference between the work reported here and work on urban soils (Renforth et al., 2009; Washbourne et al., 2012) relates to the overall carbon cost of the two processes. In urban soils, carbonation involves reaction with artificial minerals derived from Portland cement (calcium silicates and calcium hydroxide), and this partly explains why much greater rates of reaction are observed. However, these artificial minerals have been manufactured by calcining limestone, and so carry a high embedded carbon value that corresponds to the loss of CO_2 driven off during calcining as well as combustion of fuel used in their manufacture. Carbon capture by reaction of these minerals in urban soils can at best only compensate for CO_2 lost by calcining. In contrast, the process observed in the Barrasford plots involves no equivalent embodied carbon value associated with firing during manufacture; the carbon cost in processing relates simply to mining, crushing and transport (all of which also apply to the manufacture of cement). Nevertheless, the estimated embodied carbon content for crushed rock aggregates is estimated to be $3.76\,kg\,CO_2\,t^{-1}$ (Thomas et al., 2009), corresponding to approximately $1.7\,t\,C\,ha^{-1}$. Thus the Barrasford plots appear to have removed 3 times as much C as was used to manufacture the aggregate. A second important point is that the processes observed in the Barrasford plots provide a mechanism for the stabilization of carbon within composts derived from putrescible organic waste streams. This provides an alternative destination for such materials, that are no longer permitted to go to landfill.

When originally designed, the experiment reported here was not intended to address carbon capture, and so many uncertainties remain. Neither the turnover of organic carbon nor the durability of

calcite precipitates within the artificial soils has been determined, and the plots are no longer accessible. Natural pedogenic carbonates are believed to grow at rates of up to 1 mm in 1000 years, and to persist for thousands of years (Pustovoytov, 2003), far longer than the persistence of compost-derived carbon (Triberti et al., 2008). Clearly, further work needs to be done using the approach taken here, but with experiments carefully designed to investigate the fate of carbon in soils prepared from crushed rock and organic matter.

8. Conclusions

The combination of composted waste materials with calcium silicate-rich rocks derived from quarrying permits the formation of an artificial blended soil that has the capacity to produce pedogenic carbonate minerals, representing a long-lived sink for atmospheric CO_2. In the Barrasford plots, up to 40% of the carbonate carbon appears to be derived from photosynthesis carried out by plants growing on the soil. Although the plots were not designed originally to investigate carbon capture, our investigations have shown that carbon has accumulated as carbonate minerals at a rate equivalent to $4.8\,t\,C\,ha^{-1}$ annually to a depth of 0.3 m, similar to rates observed for carbonation of artificial silicates in urban soils.

The bulk composition of organic matter (as determined using thermal analysis) within the Barrasford plots is highly variable, reflecting the rapid and early turnover of the compost and the subsequent establishment of new plant communities. Despite the limitations of the work presented here, it demonstrates that there is scope for the blending of quarry fines (derived from basic igneous rocks) with composts to produce soils that have a specific carbon capture function.

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