



Investigating carbonate formation in urban soils as a method for capture and storage of atmospheric carbon

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ARTICLE INFO

Article history:

Received 12 March 2012

Received in revised form 8 May 2012

Accepted 13 May 2012

Available online 7 June 2012

Keywords:

Urban soil

Inorganic carbon

Carbon dioxide removal

Carbonate precipitation

Stable isotope

Carbon sequestration

ABSTRACT

This paper investigates the potential for engineered urban soils to capture and store atmospheric carbon (C). Calcium (Ca) and magnesium (Mg) bearing waste silicate minerals within the soil environment can capture and store atmospheric C through the process of weathering and secondary carbonate mineral precipitation. Anthropogenic soils, known to contain substantial quantities of Ca and Mg-rich minerals derived from demolition activity (particularly cement and concrete), were systematically sampled at the surface across a 10 ha brownfield site, Science Central, located in the urban centre of Newcastle upon Tyne, U.K. Subsequent analysis yielded average carbonate contents of $21.8 \pm 4.7\%$ wt CaCO_3 . Isotopic analysis demonstrated $\delta^{18}\text{O}$ values between -9.4% and -13.3% and $\delta^{13}\text{C}$ values between -7.4% and -13.6% (relative to Pee Dee Belemnite), suggesting that up to $39.4 \pm 8.8\%$ of the carbonate C has been captured from the atmosphere through hydroxylation of dissolved CO_2 in high pH solutions. The remaining carbonate C is derived from lithogenic sources. 37.4 kg of atmospheric CO_2 has already been captured and stored as carbonate per Mg of soil across the site, representing a carbon dioxide (CO_2) removal rate of $12.5 \text{ kgCO}_2 \text{ Mg}^{-1} \text{ yr}^{-1}$. There is the potential for capture and storage of a further $27.3 \text{ kgCO}_2 \text{ Mg}^{-1}$ in residual reactive materials, which may be exploited through increased residence time (additional in situ weathering). Overall, the Science Central site has the potential to capture and store a total of 64,800 Mg CO_2 as carbonate minerals. This study illustrates the potential for managing urban soils as tools of C capture and storage, an important ecosystem service, and demonstrates the importance of studying C storage in engineering urban anthropogenic soils.

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1. Introduction

Carbon capture and storage as a consequence of soil processes is a form of carbon sequestration, removing CO_2 from the atmosphere and storing it as organic (soil organic matter) and inorganic (pedogenic carbonates) forms of carbon (C). During silicate weathering, calcium (Ca) and magnesium (Mg) silicate minerals naturally react with dissolved carbon dioxide (CO_2) to form carbonates (Berner et al., 1983), effectively capturing and fixing atmospheric C. Weathering involves leaching and transport of Ca^{2+} and Mg^{2+} in solution, some of which reacts with carbonate anions (depending on pH, as H_2CO_3 , HCO_3^- and CO_3^{2-}) formed by CO_2 dissolution in soil pore waters, or in the surface ocean, to precipitate pedogenic (soil-formed) and marine carbonates. This process contributes to the stabilisation of

atmospheric CO_2 concentrations over geological timescales (Berner et al., 1983; Berner and Lasaga, 1989) and forms pedogenic carbonates in both natural (Nettleton, 1991) and artificial soils (Renforth and Manning, 2011). A simplified version of the carbonation reaction for artificial calcium silicates is given in Reaction 1.



By this reaction, C is captured and stored. It has been proposed that through addition of Ca and Mg-rich silicates to soils it may be possible to promote the accelerated draw-down and storage of CO_2 from the atmosphere as relatively stable carbonate minerals (Schuiling and Krijgsman, 2006; Manning, 2008). Recent research has found that this process occurs in urban brownfield soils where Ca-rich demolition waste derived from cement mortar is mixed into the soil profile (Renforth et al., 2009). Isotopic analysis of carbonate C and oxygen (O) shows that pedogenic carbonates in urban soils have similar isotopic compositions to carbonates from natural soils in which photosynthesis contributed to their formation (Cerling, 1984), and confirms that a significant proportion of the C has been captured from the atmosphere (Wilson et al., 2009; Renforth et al., 2009). This may be a characteristic phenomenon of urban brownfield

Abbreviations: C&D, Construction and Demolition; CCS, Carbon Capture and Storage; IRMS, Isotope Ratio Mass Spectrometry; SOC, Soil Organic Carbon; SIC, Soil Inorganic Carbon; TC, Total Carbon; TG DSC QMS, Thermogravimetry-Differential Scanning Calorimetry Coupled with Quadrupole Mass Spectrometry; TOC, Total Organic Carbon; TIC, Total Inorganic Carbon; XRD, X-ray Diffraction; XRF, X-ray Fluorescence.

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sites and other anthropogenic soils, as construction activities in urban soils usually involve addition of Ca/Mg-rich substrates. If added to such soils, construction and demolition (C&D) waste, fly ashes, iron and steel slag etc. may enhance C capture and storage in the urban environment (Renforth et al., 2009, 2011a, 2011b; Morales-Flórez et al., 2011), thus the value of materials which may otherwise be regarded as 'wastes' is increased. In principle, carbonation of these materials could be used to offset the C emissions associated with their production. There is potential for C capture and storage to become a routine design consideration in the engineering of anthropogenic soils, with minimal additional energy input, little change in current management practise and minimal translocation of materials.

1.1. Mineral carbonation for carbon capture and storage

The use of Ca/Mg-rich wastes for C sequestration (especially capture) has been extensively considered (e.g. Huijgen et al., 2005; Rawlins et al., 2008; Huntzinger et al., 2009; Gunning et al., 2010). This work has largely focused on carbonation in batch reactors, where elevated pressure and/or temperature is applied to accelerate dissolution/corrosion of a Ca/Mg silicate or oxide, leading to carbonate precipitation (Lackner et al., 1995; Huijgen and Comans, 2006). This may also involve pre-treatment of the material (grinding, heat treatment etc.) to accelerate dissolution. The efficacy of the carbonation reaction has been demonstrated (Huijgen et al., 2007), but pilot scale studies have yet to be implemented. Acceleration of capture and storage by wastes in passive in situ settings, soils and open-air stockpiles, is an alternative low energy process (Renforth et al., 2009; Wilson et al., 2009). At present there is insufficient available information concerning material fluxes to permit comprehensive quantitative assessment of global C capture and storage potential. An estimate of slag, construction and demolition waste, pulverised fuel ash and quarry fines production since the 18th century is provided in Renforth et al. (2011b); overall these materials have the potential to collectively capture 190–332 Tg C yr⁻¹. Globally 7–17 Pg of waste silicates suitable for this purpose are produced each year, and so there appears to be a considerable incentive to develop and assess procedures that harness this potential. Further understanding of the settings in which the natural carbonation reaction is promoted must be developed through an understanding of soil C storage processes.

1.2. Carbon storage in soils

The potential of soils to store C has long been recognised (IPCC, 1996; Lal, 2004), however, the magnitude and significance of this store have only recently been quantitatively estimated (Smith et al., 1997; Smith, 2004). In a global context, soils are now recognised as an important potential tool for mitigation of rising atmospheric CO₂ concentrations. The 1997 Kyoto Protocol highlighted soils as a 'major carbon store' and recognised that processes underlying soil function should be considered in CO₂ emissions accounting. In the UK, DEFRA's *Soil Strategy documents* (2009) highlighted a pressing need to 'develop a better understanding of steps that can be taken to protect or enhance levels of soil carbon'.

Total carbon content in soil is a combination of organic compounds and inorganic carbonate minerals, which are consumed, produced and mobilised by biotic and abiotic processes. While total carbon content usually refers to that contained in solid matter, there is a substantial proportion that is turned over rapidly through the soil solution (organic acids, dissolved carbonate species) ultimately becoming CO₂ in the gaseous phase (Manning, 2008). Organic carbon in soils is functionally differentiated into labile (rapid turnover) and recalcitrant (slow turnover) pools, with differing chemical reactivity and residence times, ultimately derived from photosynthesis (Sohi et al., 2001). Inorganic carbon storage in soils is dominated by Ca- and (to a lesser extent) Mg-carbonates (Schlesinger, 1982).

There is a wide acceptance that the preservation of soil organic matter (SOM) is critical in maintaining soil carbon stores, which may be increased through effective management (Kyoto Protocol 1997; EU Soil Framework Directive 2006), especially in agricultural soils, many of which are net C sources to the atmosphere. Research on the potential impact of preserving or increasing the inorganic C pool has been limited by the scarcity of data relating to the formation of soil carbonate in temperate climates (Rawlins et al., 2011). The significance of soil inorganic C storage may have been historically underestimated due to the belief that pedogenic carbonates, formed by mineral carbonation, were not widespread phenomena, tending to be a feature of arid soils (Jenny, 1980). However, recent work has identified pedogenic carbonates in temperate regions (Boguckij et al., 2006; Łacka et al., 2008). In both natural and anthropogenic soil, carbonates appear to form readily in the presence of Ca/Mg source materials.

1.3. The importance of urban soils

Extensive urban areas are now a global phenomenon, with the world's urban population projected to increase by 1.76%yr⁻¹ between 2009 and 2025 (UN, 2009), reaching 6.3 billion people by 2050, and then representing ~69% of the world's population. As urban areas grow in magnitude and complexity, an understanding of the environment which supports them becomes critical to ensuring sustainable growth and maintenance of ecosystem services, benefits provided by the natural environment. Urban soils are the basal component of built and green infrastructure within cities and are a critical element of the urban ecosystem. As noted by Lehmann and Stahr (2007), they can be seen as a fundamental ecological asset for land-use planning and are critical in urban landscaping. Physical and chemical development of urban soils often differs from their rural counterparts and may include extensive excavation, emplacement, compaction or translocation (Rosenbaum et al., 2003). It may also include the addition of anthropogenic or technogenic materials, some of which may be considered contaminants or pollutants (Lorenz and Lal, 2009). Urban soils, however, are also subject to the same pedogenic influences as 'natural' soils (e.g. climatic, hydrological). Soil forming processes in urban soils may occur at different rates and be mediated by agents within the urban environment which are not present in natural settings, e.g. translocation by pedestrian footfall rather than excavation by natural fauna (Effland and Pouyat, 1997). Soil scientists generally accept that these complex formation histories create 'manipulated' soils which function differently from soils in the 'natural' landscape (Craul, 1992). Although they are frequently grouped with natural soils (Lehmann and Stahr, 2007), agricultural soils can also be regarded as a class of non-urban anthropogenic soils, with complex histories of human intervention where organic C content is considered a particularly significant managed factor.

Urban soils provide an opportunity for in situ manipulation and monitoring of properties over well constrained, easily observable geographic areas. Much research on urban and anthropogenic soils has been 'comparative', focussing upon disparities in physical properties and the respective enhancement or depletion of nutrient cycling when compared to 'natural' counterparts (Yaalon and Yaron, 1966). The preparation and management of urban soils can have a detrimental effect on nutrient availability and organic C content (Scharenbroch et al., 2005). Pouyat et al. (2006) demonstrated the potential for soil organic carbon (SOC) to be significantly depleted through soil degradation in temperate urban settings, though it is proposed that urban soils under effective management regimes (with water and nutrient supplies) may actually act as effective C stores, possessing higher SOC than natural analogues (Kaye et al., 2005). Few studies have focussed on the potential for inorganic C capture and storage by mineral carbonation in urban settings (Manning, 2008; Renforth et al., 2009).

Lal et al. (2007) argued that there is a need to conduct a combined approach to urban soil management, taking into account all potential C sinks, and constraining the manner in which these interact. Renforth et al. (2011a) have proposed a novel C systems approach to be utilised in urban soil management, involving the development of a holistic understanding of soil C pools to increase their C storage capacity. This approach would aim to integrate both SOC management, using labile and recalcitrant organic materials, and SIC management, via the weathering of Ca/Mg source materials to form carbonates.

1.4. Scope of the study

Data relating to C storage in urban and artificial soils is currently limited to large scale assessment of organic C concentration (Pouyat et al., 2006; Lorenz and Lal, 2009) and small scale opportunistic determination of inorganic C (Renforth et al., 2009). Large-scale spatial investigation of inorganic C storage has not previously been undertaken. This manuscript presents a field-scale investigation of inorganic C storage in an urban soil at a large UK urban redevelopment site, with specific reference to the ability of silicate minerals derived from demolition to form stable carbonates under the influence of short-term weathering. This study aims to quantitatively assess C storage in pedogenic carbonates in temperate anthropogenic urban soils, whilst incorporating an assessment of other soil parameters including organic carbon content. It includes:

- I. High-resolution field-scale coverage of a 10 ha site: to address spatial significance of carbonate formation processes and to address heterogeneity

- II. Broad spectrum geochemical analysis (acid digestion, thermal analysis, stable isotope analysis, X-ray fluorescence, X-ray diffraction) of materials: to determine the linkages between soil geochemistry and carbonate formation and to investigate the active geochemical processes
- III. Quantification of the potential for inorganic C storage at a 'typical' urban redevelopment site: to investigate the significance of carbonate formation and allow the potential of other similar sites to be estimated.

This study is timely in light of increasing interest in urban soils (Renforth et al., 2011a and references therein; Rawlins, 2008) and will inform current and future investigations of urban soil chemistry and sustainable management. The findings contribute strongly towards the contemporary urban planning concept of city as a force for good (Beck et al., 2010), highlighting the capacity for engineering to restore and maintain ecosystem services in the urban setting while providing wider environmental benefits. Urban soil engineering is an important ongoing focus for contemporary regeneration and development, with the potential to be coupled with aspects of green infrastructure in long-term projects, or even short term, temporary uses of vacant urban land (Taylor, 2008).

2. Study site

The study site, "Science Central", is a 10 ha development located in the central business area of Newcastle upon Tyne (UK; National Grid Reference: NZ 2401 6404 Fig. 1). The site was most recently occupied by structures owned and operated by Scottish and Newcastle Breweries plc, which were demolished in 2007. A large proportion of material

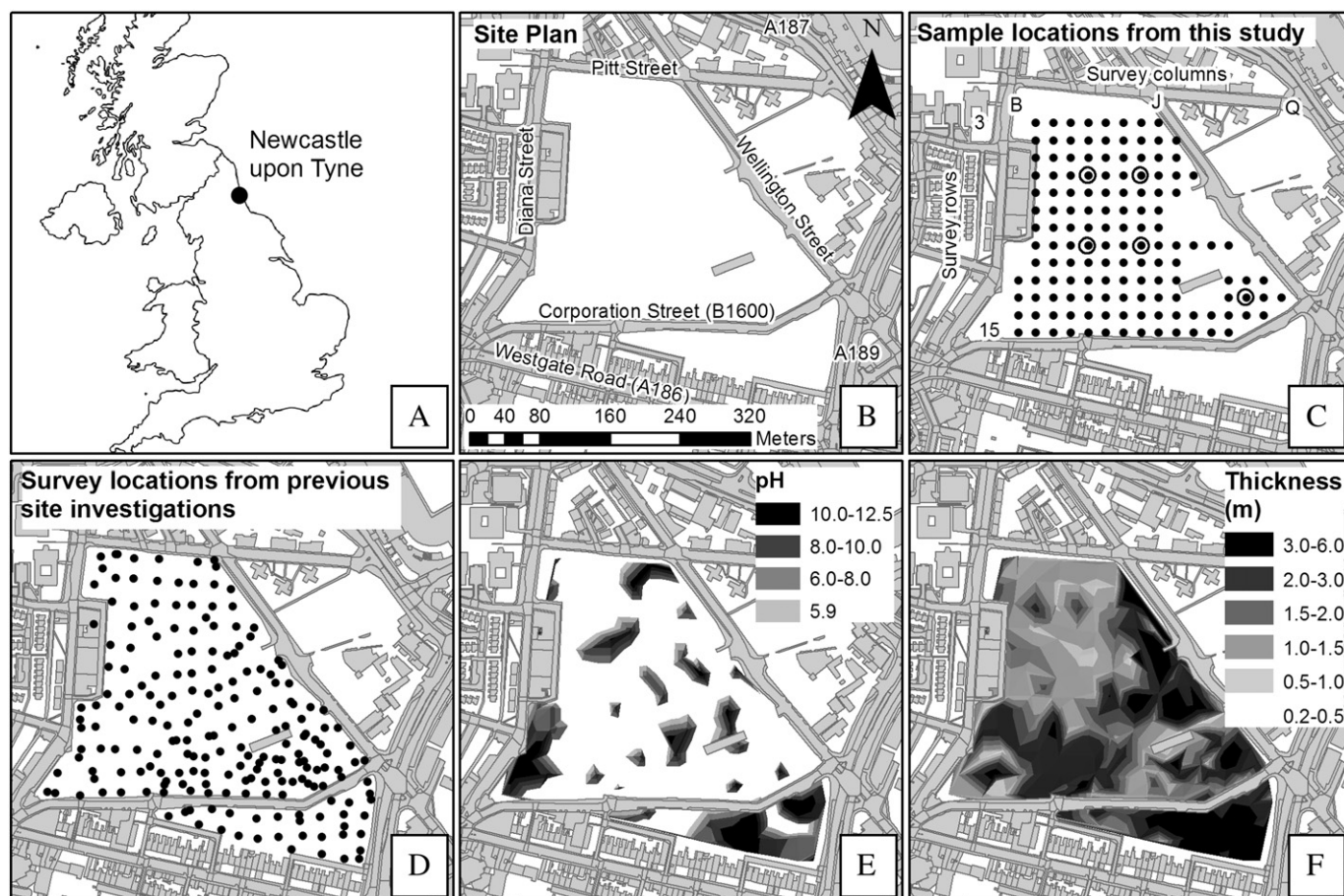


Fig. 1. A) Location of study site, B) site layout C) survey points used in this study, D) survey points from previous site investigations, E) soil pH findings from previous investigation (white shading implies no data) and F) thickness of made ground across the site.

derived from demolition was crushed and spread on the site as a layer of 'made ground' from 0.2 to 6.0 m in thickness. Surface elevation and depth profile information from intrusive ground investigations (Fig. 1d) carried out by an engineering consultancy (October 2005) was used to estimate that approximately 1 Tg of demolition-derived material is present at the site. During its long urban history (earliest development is likely to have been in the late 18th and early 19th centuries), the site hosted numerous heavy and light industrial works (including iron and steel works, food manufacturers, the North Elswick Colliery (1805–1940's) and finally the Scottish and Newcastle Brewery, which closed in 2005). A commercial contaminated land report (July 2009) presented a suite of soil analyses, identifying areas with elevated soil pH (up to pH 11.7) (Fig. 1e) and was used to determine the possible presence of contaminants. Although generally below trigger values (low risk contamination) (DEFRA/EA, 2002a, 2002b; Environment Agency, 2011), the presence of arsenic (sporadic), polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbon species were noted at concentrations normal for urban soils.

Geologically, the site is underlain by Devensian Till, overlying Carboniferous bedrock (High Main Post Member and Pennine Middle Coal Measures Formation) which was historically mined for coal. The hydrogeology of the site is complex; although the emplaced material is free-draining, it overlies infilled basement construction within natural clays which reduce the permeability of the site to rain water and locally strongly influence groundwater behaviour. Water table varies from 2.4 to 12.0 m below ground level, with the presence of perched water tables noted across the site. The site slopes significantly to the south east, with a gradient of 5%, providing a potential preferential drainage path.

The site has not been significantly modified since the end of the demolition programme in 2007. Some material has been remobilised and surfaces have been compacted by vehicle movements, but it can be assumed that the chemical properties of the C&D waste are as they were at the time of deposition. The point of demolition is taken as 'time zero' for carbonate formation, with all newly-formed material assumed to have developed between this point and the time of sampling (the validity of this assumption will be discussed later). Prior to demolition, carbonation would have been limited by the quantitative exposed surface area of reactive materials and their potential for exposure to the external environment. Demolition and processing of resultant material are expected to have significantly increased both parameters prior to eventual deposition.

3. Methodology

A systematic sampling survey divided the site in to 72 accessible sampling points (Fig. 1c) located using Leica GPS equipment (Leica GS15 with a CS16 controller with a Smartnet RTK correction 25 mm accuracy). 1–2 kg of material was collected between 0 and 100 mm depth using hand tools and wet sieved to <2 mm onsite. 2 trial pits were dug to ~1 m depth using a mechanical excavator with back-actor; samples were collected at 10 cm depth intervals. All samples were air dried and analysed for bulk carbonate using an Eijkelkamp calcimeter (in accordance with BS 7755-3.10:1995), and organic and inorganic C using a Leco CS-244 Carbon/Sulphur Determinator. 5 kg of material was taken at 5 points indicated on Fig. 1c (circled points, grid refs) (I6, I10, E6, E10, O13). These samples were air dried and particle size distribution (PSD) analysis carried out to BS 1377-2:1990.

47 samples were analysed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ by Iso-Analytical Ltd (Cheshire UK), using a Europa Scientific 20–20 continuous-flow isotope ratio mass spectrometer (IRMS); IA-R022 was used 9 times, NBS-18 used 4 times and NBS-19 used 3 times as reference materials for analysis. Replication had a standard deviation better than 0.12‰ and all of the 16 reference material analyses were within two

standard deviations of the expected results. The results were recorded relative to the Vienna Pee Dee Belemnite scale (V-PDB).

XRF analysis was conducted by the University of Leicester, Department of Geology using a PANalytical Axios Advanced XRF spectrometer. 38 powdered samples were mixed with 1:5 ratio of flux (80% lithium metaborate, 20% lithium tetraborate). The samples and flux were ignited at 1100 °C and cast into fused beads. The machine was calibrated using a range of certified standards, including British Chemical Standards (BCS) BCS375 (sodium feldspar), BCS376 (potassium feldspar) and BCS372/1 (hydrated cement).

Thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC QMS) was conducted at Newcastle University. 3 samples were ground to <63 μm and analysed using a Netzsch Jupiter STA449C TG-DSC system connected to a Netzsch Aeolos 403C QMS for the mass spectral analysis of evolved gas. Samples were heated from 30 °C to 1000 °C at a rate of 10 °C min^{-1} in an atmosphere of 80% He + 20% O₂ (purge gas, flow rate 30 ml min^{-1}). QMS was operated in full scan mode over the range m/z 10–300, and mass spectrometric data were acquired and processed using Quadstar 422 IPI software.

XRD analysis was carried out on 2 samples (with 2 replicates) using a PANalytical X'Pert Pro Multipurpose Diffractometer fitted with an X'Celerator and a secondary monochromator, operating with a Cu anode at 40 kV and 40 mA. Spectra were acquired for Cu K α ($\lambda = 1.54180 \text{ \AA}$) or Cu K α_1 ($\lambda = 1.54060 \text{ \AA}$) radiation over 2–70°2 θ with a nominal step size of 0.0167°2 θ and time per step of 100 or 150 s. All scans were carried out in continuous mode using the X'Celerator RTMS detector.

4. Results

4.1. Soil description

All materials encountered onsite were classified as 'made ground' or anthropogenic soils (BS EN ISO 14688:2). Most samples were recorded as grey-brown (10YR 6.5 2 Munsell soil colour chart), although soil samples taken from column B of the sampling grid (Fig. 1c) were yellowish (2.5YR 7 2 Munsell soil colour chart) and with visible carbonate formation. Following PSD analysis of the soil onsite all samples were classified by BS 1377-2:1990 as gravelly sandy soils (Fig. 2). It should be noted that this classification was achieved by wet sieving and does not take into account the presence of aggregated particles or fines adhering to the material surface which may contribute significantly to bulk geochemical behaviour. Average moisture content $15.6 \pm 3.4\%$ was measured by mass difference

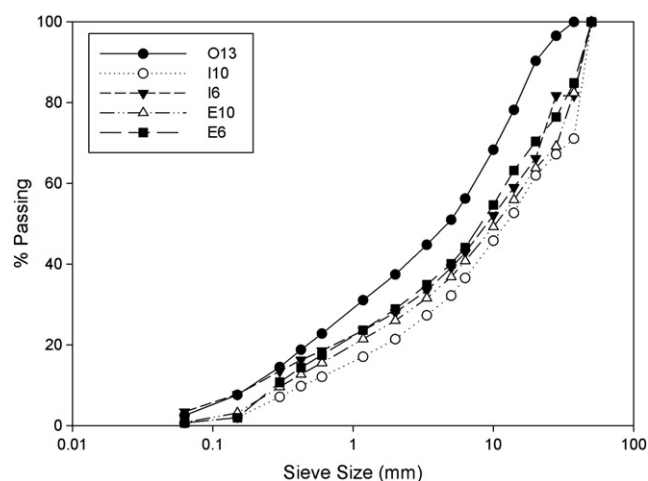


Fig. 2. Particle size distribution (PSD) curves for soils at Science Central.

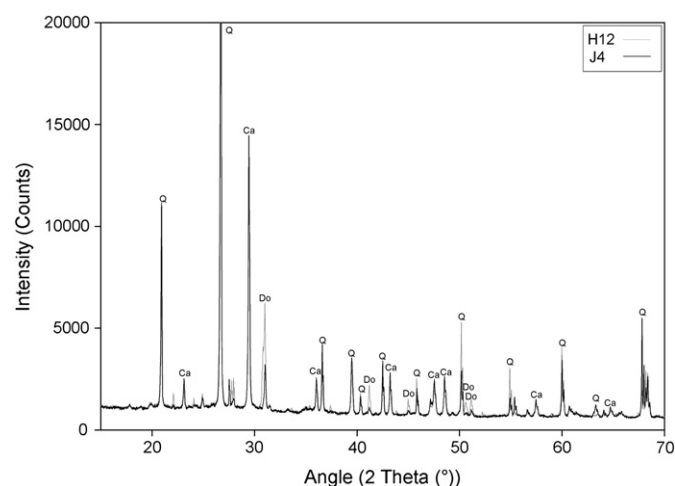


Fig. 3. XRD diffractogram of samples from Science Central indicating characteristic peaks (Q—quartz, Ca—calcite, Do—dolomite).

before and after overnight incubation and is consistent with data from previous commercial site reports (October 2005).

4.2. Mineralogical and elemental analysis

Mineralogical analysis by X-Ray Diffraction (XRD) demonstrated the presence of calcium silicate and hydroxide minerals. Quartz, dolomite and calcite dominate the diffractogram due to their greater crystallinity (Fig. 3).

TG-DSC-QMS investigation of the materials has shown that all samples exhibit similar thermo-gravimetric profiles. Peaks characteristic of hydroxyl water-loss and decarbonation reactions occur at 300–400 °C and approximately 750 °C respectively (Fig. 4) indicating the presence of hydrated minerals such as portlandite ($\text{Ca}(\text{OH})_2$) in the first instance and carbonate in the second. QMS data (Fig. 4) show emissions of CO_2 at approximately 750 °C, confirming the presence of carbonates.

SiO_2 , CaO and MgO concentrations are between 38.9 wt.% to 65.1 wt.%, 8.0 wt.% to 22.0 wt.% and 0.9 wt.% to 6.2 wt.% respectively (Table 1). CaO is more abundant than MgO , but there is much greater variation in CaO concentration. A strong negative correlation between CaO and SiO_2 content was noted ($r^2 = 0.85$; Fig. 5) suggesting presence of calcium carbonate, as opposed to silicate, minerals. The CaO intercept with the $\% \text{SiO}_2 = 0$ axis suggests that the carbonate phase is not purely calcite and may include ~35% dolomite ($\text{CaMg}(\text{CO}_3)_2$).

Loss on Ignition (LOI) data are consistent with the total C content (organic and inorganic) of the samples, forming a 1:1 gradient when plotted as $\% \text{LOI}$ vs $\% \text{CO}_2$ (not shown).

4.3. Inorganic and organic carbon analyses

The average organic C content of the samples is $1.8 \pm 0.6\%$ wt, ranging from 0.3% to 5.7%. Inorganic C contents were $2.7 \pm 0.7\%$ wt (min. 0.6% max. 6.0%), corresponding to carbonate concentrations $22.5 \pm 6.0\%$ wt (min. 5.3% max. 50.2%). For comparison Eijkelpamp calcimeter analysis reported bulk carbonate (inorganic C) contents $21.8 \pm 4.7\%$ wt (min. 2.1% max. 44.4%), which correspond well within experimental error margins. High organic C values of 3.3–5.7% are mainly located around the site periphery, where the lowest inorganic C values of 0.6–2.4% are also found. The highest values for inorganic C are found in the south west of the site where a change in substrate colour suggests a variation in material, decreasing to a minimum of 2.1% in the south east of the site. Otherwise, minimum and maximum values for both organic and inorganic C are homogeneously distributed across the site, with little discernible spatial pattern.

The carbonate depth profile from a similar previous site investigation in Newcastle (Renforth et al., 2009) found no strong correlation between sample depth (down to 2.7 m) and carbonate concentration. The Science Central data are similar to those found by Renforth et al. (2009), bearing in mind that they are limited to a depth of 0.8 m (Fig. 6). There is no systematic variation with depth at Science Central, which is as expected given the heterogeneous nature of the ground within the top metre.

4.4. Isotopic analysis

Isotopic analysis yielded $\delta^{18}\text{O}$ values between -9.40% and -13.30% and $\delta^{13}\text{C}$ values between -7.42% and -13.55% . $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show a linear correlation ($r^2 = 0.6$), gradient 1.9, intercept 10.3 (Fig. 7). These data allow estimation of the formation routes of soil carbonates in the following section. Isotopic values for C and O maxima and minima have a similar spatial distribution across the site.

4.5. Spatial distribution

Fig. 8 summarises the results presented in Sections 4.1–4.3, demonstrating the spatial distribution of values across the Science Central site. Inorganic C, organic C, CaO , MgO , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are shown.

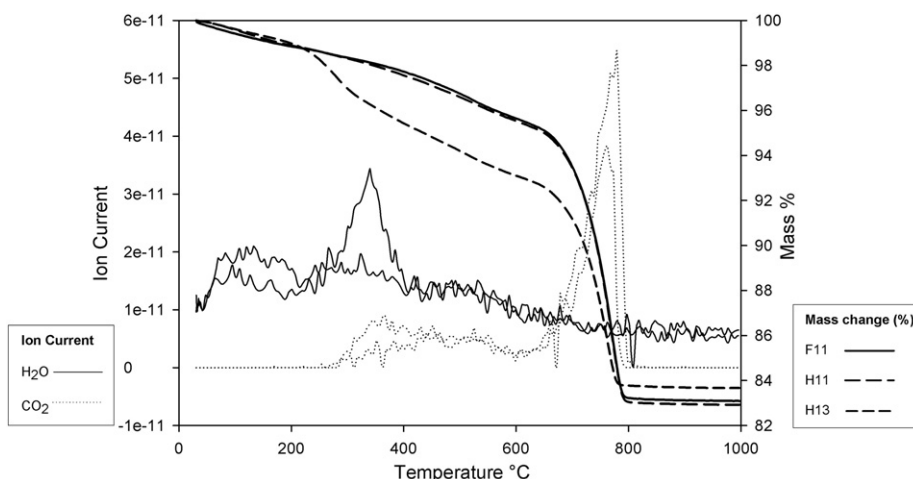


Fig. 4. Combined thermogravimetric curve and QMS trace, evolved gas (H_2O and CO_2).

Table 1
XRF data summary.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Total
Av. %	56.74	0.42	6.75	3.85	0.08	1.85	13.68	0.43	1.17	0.09	0.28	14.61	99.95
St dev	5.36	0.06	0.95	0.27	0.01	1.01	2.84	0.05	0.14	0.01	0.07	2.81	0.26

5. Discussion

The data from Science Central strongly support the proposition that carbonate formation is not restricted to arid soils, or unique to wholly natural soils, but can be a significant process within temperate urban and engineered soils. Considering the mean value $21.8 \pm 4.7\%$ wt carbonate, it can be seen that a significant quantity of soil carbonate is present in this environment. Overall carbonate values of 2.1–44.4% wt are highly variable, and illustrate the inherent heterogeneity of the substrate material at Science Central. This may be explained in part by the structural nature of the soil, with coarse gravels and sands providing surface area-limited environments for silicate dissolution and mineral formation, or construction and demolition waste materials (brick, cement) presenting high levels of adhered fines and complex internal porosity. Anthropogenic soils of this type are immature, texturally poorly mixed and composed of a number of different source materials, making the overall composition highly variable. This in turn strongly dictates the distribution and extent of soil carbonate formation. The small reported standard deviation of $\pm 4.7\%$ wt carbonate for the dataset, however, illustrates that the carbonate values in this study are more closely constrained than other similar datasets (Renforth et al., 2009), indicating the value of a high-resolution sampling approach in addressing and managing heterogeneity of this type. Determination of calcium carbonate concentration with depth suggests that there may be localised carbonate-rich horizons; trial pit TP1 illustrates a carbonate content of 97.3% wt (almost pure carbonate) occurring at 60 cm below ground level. As compositional data with depth are limited, however, it is difficult to confirm whether this is simply due to variation in constituents of the source material throughout the profile, indicative of a more complex formation process including transport or weathering of parent material, or linked to the depth limit of permeation of CO₂ into the soil profile. There is also the potential for inclusion of lithogenic carbonate materials (derived from construction aggregates, e.g. limestone and dolomite) in sites of this type, which may lead to unusually high values that are not indicative of materials formed in situ by C capture and storage. A means of elucidating this relationship in field samples is discussed further in the following section.

When examining soils of this type with varying pH (6.1–11.7), it is important to remember two points. First, carbonate mineral precipitation depends on the bulk soil solution chemistry, not just pH. If

the activities of both Ca²⁺ and dissolved carbonate species are sufficiently high, calcite will precipitate at pH values as low as 5.1 (as in landfills; Manning and Robinson, 1999), and in laboratory experiments; Renforth and Manning (2011) report calcite precipitation at pH 5. Secondly, there is substantial local variation in pH in soils, reflecting their heterogeneity. The solution that wets a calcium silicate surface might be buffered at very high values if mortar (containing Ca(OH)₂) is present, while the pore water within an adjacent saturated piece of rotten timber might have a pH close to 4.

SOC values vary across Science Central and spatially appear to be inversely related to the SIC values. High SOC values of 3.3–5.7% are located around the site periphery, where the lowest SIC values of 0.6–2.4% are found. It must be noted that significantly more vegetation cover exists around the site periphery, and this would be expected to contribute to the elevated values of SOC in this region. The low values of SIC in high SOC regions may be an artefact of the drainage regime of the site, leading to the leaching of carbonate from the material washing from the sloped portion in the south east and its emplacement outside the site boundaries or at a greater depth than that sampled in this exercise. Considering the environmental variations noted in the available data it is not possible to conclusively determine whether the presence of high SOC or SIC are mutually incompatible phenomena, or whether one inherently limits the other.

5.1. Quantifying mineral carbon capture in urban soils

Inorganic C capture and storage in soils in this context is limited ultimately by the cation (Ca²⁺, Mg²⁺) content of the silicate material and limited temporally by the reactivity and weathering rate of the host phase as illustrated in Table 2. Calcium silicate minerals have a wide range of weathering rates, however, many artificial silicates weather more rapidly than natural silicates, allowing greater potential for carbon capture and storage through pedogenic carbonate formation on short timescales (years-decades). Capture and storage may also be limited to some extent by the rate of supply of CO₂ in to the system.

It is assumed that inorganic C concentrations should be intrinsically spatially correlated to the presence of Ca and Mg at Science Central. As illustrated in Fig. 8c and d, Ca and Mg (expressed as CaO and MgO respectively) concentrations vary spatially across the site surface, generally correlated with one another: the lowest values, between 8.0 and 9.6% CaO and 0.9 and 1.5% MgO respectively, occur around the margins of the site, especially the south east corner. CaO exhibits three spatial regions of very high concentration (20.5–22.0%) falling on a diagonal transect between the south east and north west of the site. MgO exhibits two smaller regions of high concentration (5.0–5.6%) in the centre of the site and to the south.

From XRF analysis it could be assumed that the locations with highest contemporary CaO–MgO concentrations correlate with high inorganic C values if pedogenic carbonates are being formed in situ from high Ca parent materials (Fig. 7a, c). The largest values of CaO–MgO and carbonate appear to be spatially coincident. Inorganic C content does show close spatial agreement with CaO–MgO content, with concentration peaks of 5.4–6.0% in a roughly diagonal transect from south east to north west. Variation in these values demonstrates the heterogeneity of the material, indicated by the presence of regions of high CaO–MgO concentration, and may also be influenced

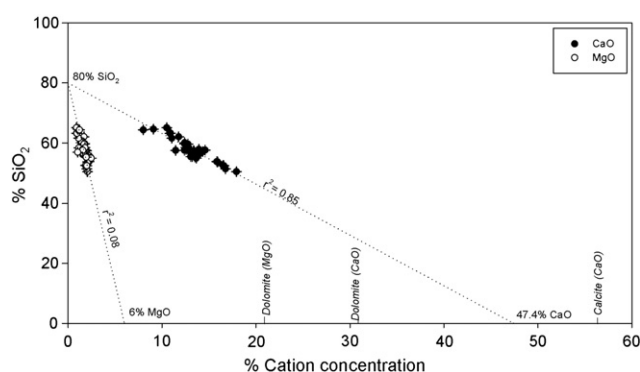


Fig. 5. CaO and MgO versus SiO₂ content of samples from Science Central, illustrating likely mineral phases present.

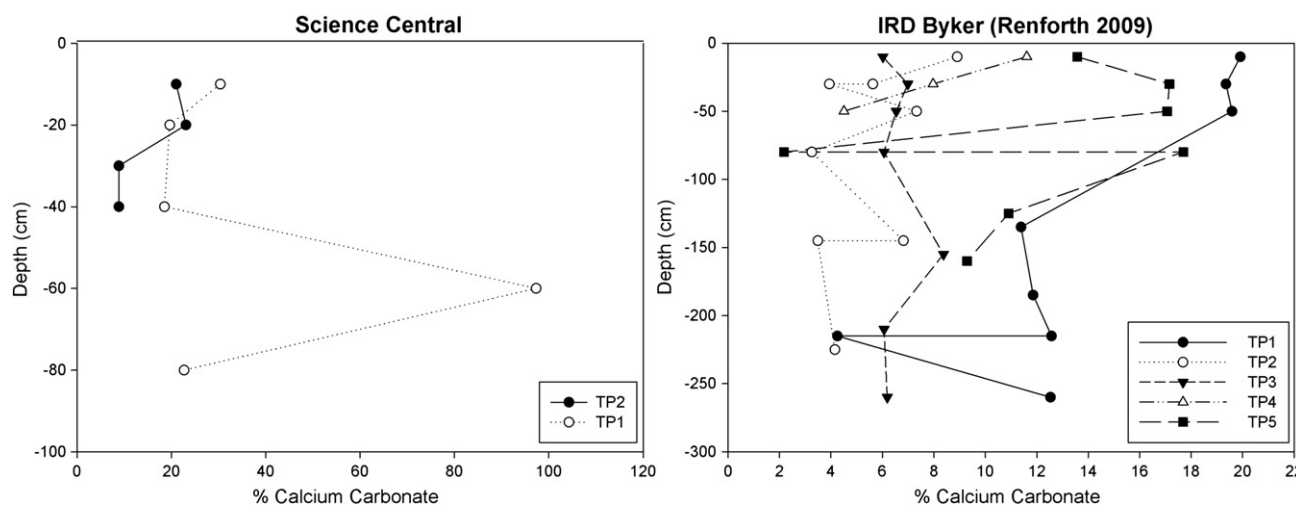


Fig. 6. Variation in calcium carbonate content with depth at Science Central and other comparative urban soils (Renforth et al., 2009).

by site-specific properties leading to variation in weathering rate or translocation of materials.

Recent research has estimated the extent of pedogenic carbonate formation by using stable isotopes to investigate the provenance of C and O contained in carbonates. The C and O stable isotope values presented in this study agree closely with those determined in similar studies of carbonate formation on demolition waste (Renforth et al., 2009), and concrete structures (Krishnamurthy et al., 2003; Macleod et al., 1991; Dietzel et al., 1992), which show an apparent linear relationship between high-pH carbonates (more depleted in ^{13}C and ^{18}O by kinetic fractionation) formed in pedogenic settings, and lithogenic carbonate (contiguous with $\delta^{13}\text{C}=0\text{‰}$). A diagrammatic summary of these findings is shown in Fig. 9, where lithogenic samples (such as limestone construction aggregate) plot close to the origin and other data follows a theoretical diagonal 'mixing line'. 'End member' analysis can be used to estimate the likely contribution of different carbonate formation routes.

The observed $\delta^{18}\text{O}$ values (-9.4‰ to -13.3‰) and $\delta^{13}\text{C}$ values (-7.4‰ to -13.6‰) are close to those observed for natural pedogenic carbonates (Cerling, 1984), where photosynthesis has contributed to their formation. However, there is very little vegetation present on the study site so this may be a coincidence. The linear array could, alternatively, be interpreted as a mixing line between a

lithogenic source and carbonate formed through a high pH process (c.f. Renforth et al., 2009). The latter interpretation has been utilised during further analysis of the data. It must be noted that quantitative conclusions drawn from this interpretation are conservative; they report lower atmospheric C contributions to carbonates than if a large photosynthetic component were assumed, due to the proximity of the photosynthetic end member to the average data value. The majority of samples collected at the site are shown to be significantly depleted with respect to both ^{18}O and ^{13}C , plotting between the hydroxylation (high pH) and lithogenic end members presented in Fig. 9. The most negative (isotopically light) values for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, indicative of high pH carbonates, predominate in the areas where inorganic C and CaO concentrations are lowest. Less negative values, indicating a larger lithogenic contribution to carbonate formation, predominate in central and western areas of the site. This may be due to the pattern in which materials were emplaced onsite, an artefact of overprinting by the drainage regime onsite, or due to a more complex interaction between minerals in the parent material and the environment. The observed values are not as depleted in ^{13}C as those from previous studies (Renforth et al., 2009; Dietzel et al., 1992), indicating a higher contribution by lithogenic sources of C to the carbonates. Tendency towards less-negative values than expected from other studies may, in some areas, be due to the inclusion of lithogenic carbonates. This confirms a mixed source of carbonate in the samples analysed, of pedogenic carbonate from atmospheric sources with a reasonable lithogenic contribution. End member analysis suggests that $39.4 \pm 8.8\%$ of the carbonate C has been derived from the atmosphere using the following end-member figures, lithogenic end member: $\delta^{18}\text{O} = -0.0\text{‰}$, $\delta^{13}\text{C} = -0.0\text{‰}$ (Andrews, 2006; Renforth et al., 2009), hydroxylation (high pH) end member: $\delta^{18}\text{O} = -20.5\text{‰}$ (Dietzel et al., 1992; Usdowski and Hoefs, 1986); assuming meteoric water $\delta^{18}\text{O} = -7.8\text{‰}$ vs SMOW (Darling et al., 2003), $\delta^{13}\text{C} = -25.3\text{‰}$.

From this information, the C capture and storage potential of the site, with respect to the presence of divalent cations (Ca^{2+} , Mg^{2+}), can be calculated. Fig. 9b illustrates that on average 60.6% wt C appears to have a lithogenic source, with 39.4% wt formed through a high-pH hydroxylation route. The amount of pedogenic carbonate which has formed to date can be estimated and the residual C capture and storage potential of the site can also be determined.

5.2. Significance

Table 3 summarises the current storage of inorganic C as carbonate on the Science Central site, by presenting carbonation figures

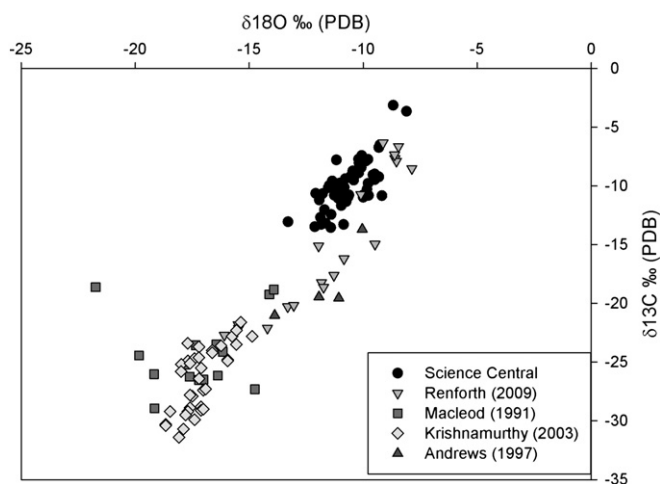


Fig. 7. IRMS data of samples from Science Central: $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ (repeatability error bars are within point), in comparison with IRMS values from other sites (Renforth et al., 2009; Macleod et al., 1991; Krishnamurthy et al., 2003; Andrews et al., 1997).

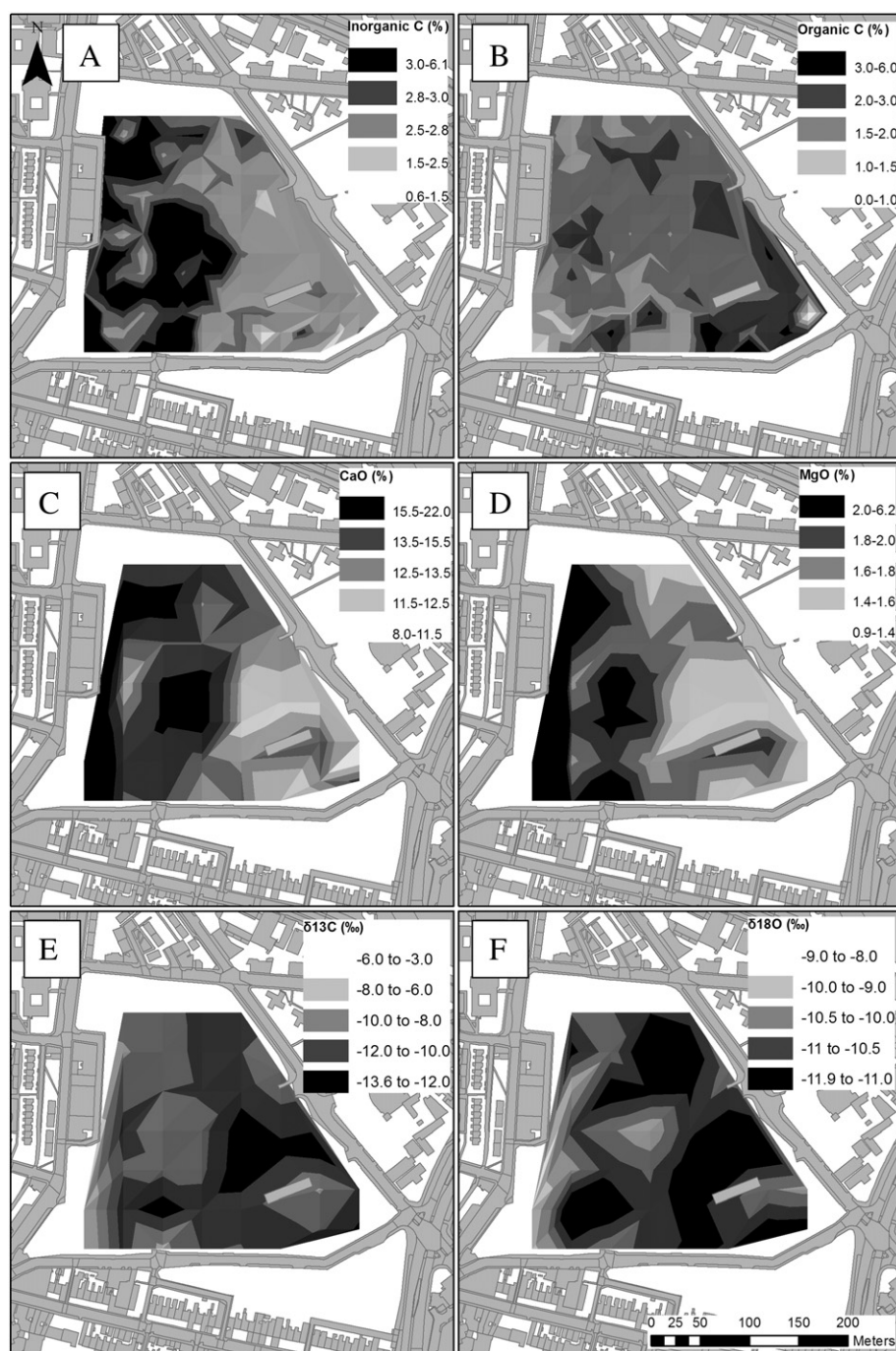


Fig. 8. Spatial variation in collated soil analysis data across the Science Central site: A) inorganic carbon B) organic carbon C) CaO % D) MgO % E) $\delta^{13}\text{C}$ IRMS values F) $\delta^{18}\text{O}$ IRMS values.

based upon the measured contemporary divalent cation (from CaO–MgO) contents and known carbonate contents. Both datasets were converted to molar notation then end member analysis was used to estimate the molar proportions of Ca–Mg in lithogenic and pedogenic carbonate respectively. Any residual mass of divalent cations not incorporated in carbonates was, therefore, assumed to be representative of the divalent cations contained within cement or other Ca/Mg silicates that is available for future carbonation, and is expressed here as the residual C capture and storage potential of the site.

Science Central is covered by approximately 1 million tonnes of demolition material (commercial site report, October 2005). Based on XRF and stable carbonate isotopes, it is likely that the initial material onsite possessed an overall C capture and storage potential of 64,804 Mg CO_2 . The current concentration of divalent cations at the

Table 2

Hypothetical dissolution time for the weathering of a 1 mm diameter particle for calcium bearing minerals (Lasaga, 1995) and a calcium silicate gel (Renforth and Manning, 2011).

Mineral	Dissolution time (years)
Albite ($\text{NaAlSi}_3\text{O}_8$)	575,000
Andesine ($(\text{Ca},\text{Na})(\text{Al},\text{Si})_4\text{O}_8$)	80,000
Diopside ($\text{MgCaSi}_2\text{O}_6$)	6800
Forsterite (Mg_2SiO_4)	2300
Calcite (CaCO_3)	0.1
Calcium silicate hydrate gel ($\text{Ca}_x\text{Si}_y\text{O}_z(\text{OH})_\alpha$) ^a	0.01 ^b

^a Typical composition ($\text{CaO} = 25\%$, $\text{SiO}_2 = 55\%$, hydration $\text{H}_2\text{O} = 7\%$).

^b Derived by applying a shrinking core model to the rates in Renforth and Manning (2011).

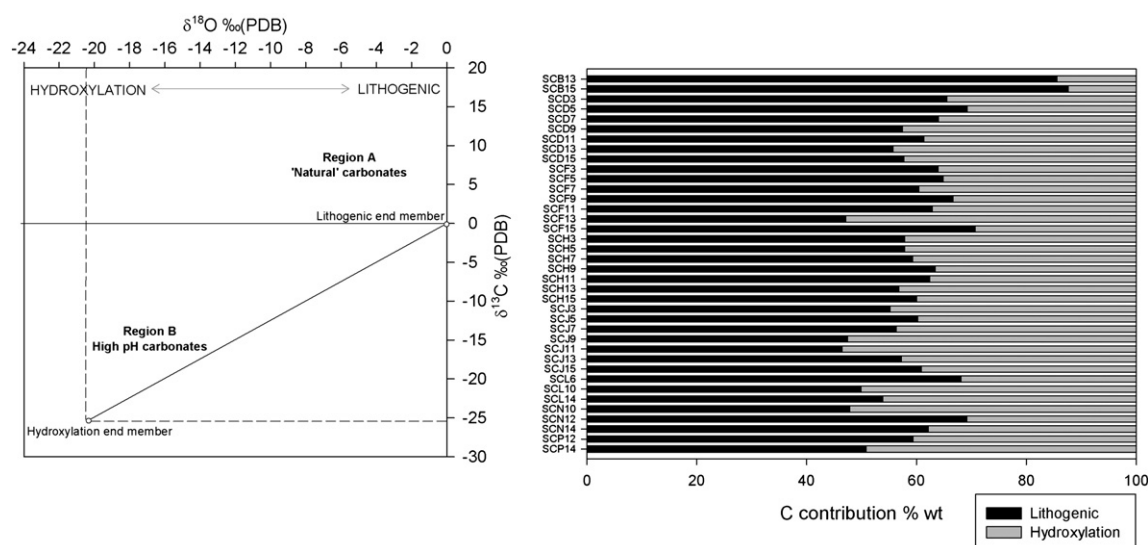


Fig. 9. Illustration of 'mixing line' method by which proportional contribution of different carbonate formation pathways is calculated from IRMS data, and relative partitioning of C indicating formation by lithogenic or hydroxylation processes.

site not currently bound in carbonates suggest that approximately 58.4% of this potential has already been exploited, capturing 37,463 Mg CO₂, leaving a remaining capture potential of 27,341 Mg CO₂. This quantity is significant within the scope of a development project of this type, as it presents a potential for offsetting C produced during production of the original construction materials and can be considered as an ongoing offset by the site developers if the capture and storage reaction is promoted in areas of exposed soil or managed vegetation.

The C capture and storage potential of any site of this type depend upon the quantity of material present, the quantity of material which is composed of Ca/Mg-silicate minerals and the depth to which carbonation reactions are able to occur. The rate at which carbonation occurs is determined by the supply of cations from weathering and by CO₂ supply that forms carbonate in solution. One of the major challenges is constraining the depth to which carbonation naturally occurs. Sampling depth was restricted by the presence of concealed structures during trial pit operations, therefore the calculations in Table 3 present an idealised C capture and storage potential, assuming complete carbonation of materials throughout their full depth profile.

Table 3
Summary of site data to estimate carbon capture potential.

Description	% of material	Mol kg ⁻¹	kgCO ₂ t ^{-1a}
1 Total inorganic carbon—from acid digestion	2.74 ± 0.85	2.28	
2 Carbonate-C derived from lithogenic sources (old)—from isotopic end-member analysis	60.61 ± 8.83	1.43	
3 Carbonate-C derived from high pH solution (new)—from isotopic end-member analysis	39.39 ± 8.83	0.85	
4 Total calcium (CaO)	13.68 ± 2.84	2.44	
5 Total magnesium (MgO)	1.85 ± 1.01	0.46	
6 Total cations (4 + 5)		2.91	
7 Total carbon capture potential (6–2)		1.47	64.8
8 Residual carbon capture potential (7–3)		0.62	27.3
		(41.6%)	
9 Already exploited carbon capture potential (7–8) or (3)		0.85	37.4
		(58.4%)	

^a Assumes 1 million tonnes of material.

The value of urban soils as C capture and storage devices depends heavily upon the level of intervention and management required to optimise their function (which is assumed in this case to be minimal), and the inherent 'value' of the C they remove from the atmosphere. Mineral carbonation techniques have not yet been granted status as a valid C mitigation technology by the European Union Emissions Trading Markets (EU ETS) Directive 2003/87/EC. Theoretically assuming that this occurs, with the current CO₂ trading cost of £8–£12/tCO₂, the current value of CO₂ capture and storage at the Science Central site is £518,432–£777,647 or £51,843–£77,765 ha⁻¹. In this context in situ mineral capture and storage has the economic benefit, in comparison to engineered mineral carbonation processes, of requiring minimal mechanical intervention or management.

6. Conclusions

This study adds to a growing body of evidence for the formation of carbonate minerals in urban soil settings where Ca/Mg-rich silicate minerals occur. It also adds weight to the idea that engineered soils could be effectively utilised for C capture and storage.

This paper illustrates the potential for urban soils to provide C capture and storage as an ecosystem service. It also demonstrates the potential C capture and storage value of materials considered to be anthropogenic 'wastes' in helping to develop and support the urban ecosystem, providing an important route for re-use. Including a C capture and storage function in urban soil design can add environmental value with little additional energy input. Ultimately if soil carbonates are included in emissions offsetting schemes, alongside management of soil organic C, this technology has potential to provide a C capture and storage capability to an urban development.

Further research is needed to demonstrate optimised C capture and storage processes in soils specifically designed for this purpose and to determine the potential for accelerating passive C capture and storage by urban soils in a synergistic system of urban planning and green infrastructure development. It is necessary to focus on a long term (5–10 years) investigation of C dynamics in artificial soils at field scale. Additional research is also required to establish appropriate practises for promoting C accumulation in soils, both organic and inorganic, and a life cycle analysis is needed to evaluate the long term suitability and value of these materials as a C capture and storage technology.

Acknowledgements

We thank NERC (Natural Environment Research Council) for research studentships to P.R. and C.-L.W. and EPSRC Impact Award 2011, and 1NG, ARUP and Newcastle University for granting access to the Science Central Site. We also thank Maggie White (Newcastle University) for carrying out XRD analysis. Bernard Bowler (Newcastle University) for TG DSC QMS analysis, Isoanalytical for IRMS analysis and Nick Marsh (Leicester University) for XRF analysis.

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