Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide

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Abstract

Turnover of C in soils is the dominant flux in the global C cycle and is responsible for transporting 20 times the quantity of anthropogenic emissions each year. This paper investigates the potential for soils to be modified with Ca-rich materials (e.g. demolition waste or basic slag) to capture some of the transferred C as geologically stable $CaCO_3$. To test this principal, artificial soil known to contain Ca-rich minerals (Ca silicates and portlandite) was analysed from two sites across NE England, UK. The results demonstrate an average C content of 30±15.3 Kg C m^{-2} stored as $CaCO_3$, which is 3 times the expected organic C content and that it has accumulated at a rate of 25 ± 12.8 t C ha^{-1} a^{-1} since 1996. Isotopic analysis of the carbonates gave values between -6.4 and -27.5‰ for $\delta^{13}C$ and -3.92 and -20.89‰ for $\delta^{18}O$ respectively (against V-PDB), which suggests that a combination of carbonate formation mechanisms are operating including the hydroxylation of gaseous CO_2 in solution, and the sequestration of degraded organic C with minor remobilisation/precipitation of lithogenic carbonates. This study implies that construction/development sites may be designed with a C capture function to sequester atmospheric C into the soil matrix with a maximum global potential of 290 Mt C a^{-1}.

1. Introduction

The global C cycle transports approximately 210 Gt of C per year between a multitude of pools including the biosphere, geological sediment, the ocean and the atmosphere. During this cycle, 60% of all the C flux passes between the atmosphere and the terrestrial system (120 Gt C a^{-1}; Dupre et al., 2003). Thus within the context of the possible use of geoengineering procedures to compensate for artificial CO_2 emissions (e.g. Lal, 2003), it is highly appropriate to consider the role of the coupled plant-soil system in C capture, and to develop ways of enhancing natural processes artificially.

In temperate climates, the role of soils as C sinks is often associated with the accumulation of soil organic C (SOC) in agricultural soils (Smith, 2004). Documentation of soil inorganic C (SIC) is usually confined to soils formed in arid climates, where unbroken 'calcrete' structures can cover an area of several km^2. Schlesinger (1985) suggests that soils of this type may contain between 24.5 and 33 kg C m^{-2}.

Recent work has demonstrated substantial variability of organic C content in urban soils which can be as high as 28.5 kg C m^{-2}, although the average C content is expected to be between 8 and 10 kg C m^{-2} (Pouyat et al., 2002, Pouyat et al., 2006, Banaitis et al., 2007). Pouyat et al. (2002) have demonstrated the influence of landuse on SOC and suggest that soils beneath impervious surfaces or in clean engineered fill material will return the lowest values for organic C. Moreover, the turnover of C in urban soils and the characterisation of the C pool (labile to refractory) have yet to be determined.

By investigating the formation of inorganic C (SIC) as carbonate minerals, the aim of this study is to enhance the understanding of the C cycle in urban soils.

Soils at two brownfield sites in NE England, UK were investigated for the accumulation of SIC as geologically stable $CaCO_3$. Brownfield sites are commonly but not exclusively characterised by the presence of waste material arising from the historical use of the site, a proportion of which becomes part of the soil matrix. Some of this is derived from construction materials, including Ca-rich components (artificial mortars, plaster, concrete, natural basic rock aggregates, slag (e.g. Fredericci et al., 2000). It is hypothesised that weathering of Ca-rich minerals (silicates, hydroxides, sulphates) within these materials will result in precipitation of $CaCO_3$ within soils through equation (1) by reaction with C cycled through plant roots (Manning, 2008).

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2 \quad (1)$$

The availability of Ca depends on the stability of the Ca minerals in the soil system. The rate at which these materials weather and release Ca is dependant on various factors including mineralogy, physical grain properties (including surface area), solution pH, the presence of organic complexes and flow rate, but is estimated to vary between 10^{-15} and 10^{-6} mol cm^{-2} s^{-1} (Blum and Stillings, 1995, Berg and Banwart, 2000, van Hees et al., 2002).

Carbon is transferred into the soil through dissolution in rainwater or through biological processes. During growth, plants exude large quantities of C through their roots as organic compounds which ultimately degrade to CO_2 and return to the atmosphere (Kuzyakov and Domanski, 2000, Ryan et al., 2001). This is the dominant conveyor in the global C cycle, and transports approximately 120 Gt Ca^{-1} compared to 6 Gt C a^{-1} produced by anthropogenic sources (Lal, 2003). The rate at which plants turnover C is difficult to measure, but Manning (2008) suggests between 1.2 and 16.1 mg C g^{-1} of fresh weight per year is exuded from plant roots based on in-vitro experiments (Ryan et al., 2001). However, Moulton et al. (2000) have monitored the carbonate concentration of waters issuing from a groundwater system in Iceland, showing that plant-derived HCO_3^- concentrations of waters draining forested areas were between 911 and 999 mol ha^{-1} a^{-1}, or approximately 500 mol kg^{-1} a^{-1} when normalised against biomass per ha (Manning, 2008). This is an order of magnitude larger than the exudation rates calculated from the laboratory experiments.

Carbon dating of pedogenic (soil formed) carbonates indicates long residence times in soils (>30 ka; Kalin et al., (1997) and field studies of carbonates in ancient soils similarly support the refractory nature of carbonates (up to 2.6 Ga; e.g. Watanabe et al., 2004). Furthermore, Kuzyakov et al. (2006) demonstrated, in controlled conditions, the dissolution and reprecipitation of carbonate minerals under the influence of plant roots. They concluded that a 100% turnover of the carbonate can take between 0.4 and 2 ka. Both the field and laboratory scale investigations have demonstrated the stable nature of pedogenic carbonates on human time scales.

The aim of the research reported here is to investigate the extent to which soils modified by the artificial introduction of Ca minerals can capture C exuded from plants to give a semi-permanent sink, and the significance of this process as compensation for artificial C emissions.

2. Study Sites

An urban brownfield site was chosen in Newcastle upon Tyne approximately 2.5 km east of the city centre (GB National Grid: NZ275649 – see insert of Fig. 1) which was previously occupied by a concrete office complex that was demolished in 1996. The site has remained unused since then, apart from storage of a soil heap excavated from an adjacent development site (approximate location shown in Fig. 1). A contaminated land report completed by Newcastle City Council in 1998 presented soil profiles that show the presence of demolition waste throughout the site to 2-3 m in depth. Furthermore, the study found pH levels of up to 11.8 and a SO_4 content of up to 20313 mg kg^{-1} towards the north of the site indicating portlandite ($Ca(OH)_2$) and gypsum ($CaSO_4.2H_2O$) dissolution respectively. Vegetation on the site comprised of C_3 grasses (including species typical of a restoration seed mix) and C_4 ornamental garden escapes. The bedrock geology of the area is dominated by Carboniferous sandstone which is superficially overlain by glacial till. The site has been heavily modified by industrial activity and a substantial thickness (>3m) of made ground is present.

A second site was selected adjacent to a former steel works in Consett (GB National Grid: NZ094492), County Durham, England which was closed in the 1980s creating 290 ha of derelict land. In a review of the contamination problems typically associated with iron and steel making, Harber and Forth (2001) describe remodelling of the ground profile at the Consett site with the emplacement of 'clean slag'. At the site, slags of different types have accumulated as steeling making processes evolved since the early 1800s. The basic slag used for the cover is a lime-rich calcium silicate glass, containing calcium silicate minerals (such as merwinite, melilite and larnite; Fredericci et al, 2000), calcium oxide as calcium ferrite and portlandite as well as iron oxides (Harber and Forth 2001). The final stage in restoration involves emplacement of top soil, from which the samples were taken. Subsequent analysis of the area (Mayes et al., 2006) has discovered pH levels of 12.5 within leachate draining the site which was attributed to the weathering of portlandite and Ca silicate

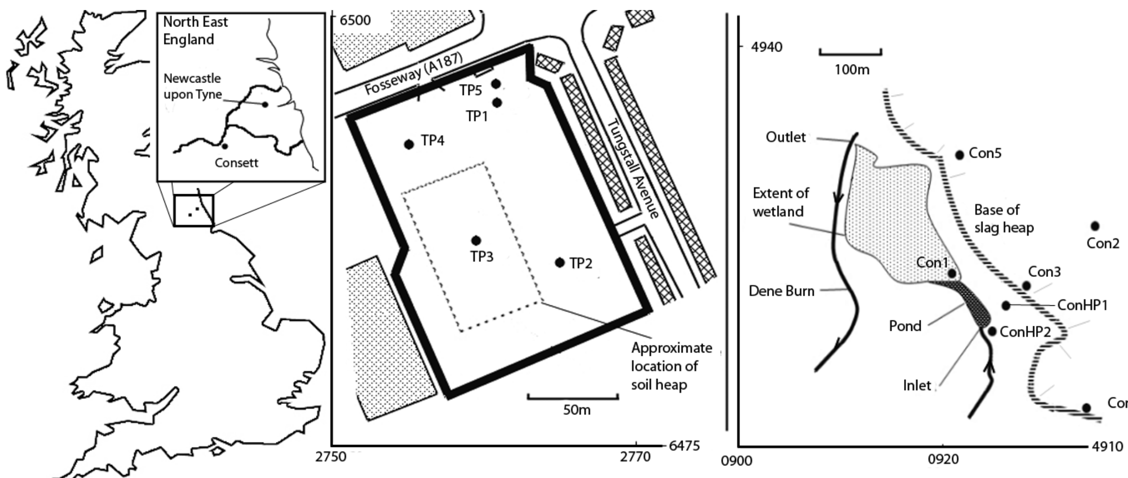

Fig 1. Sampling locations (●) at an urban brownfield site in Newcastle upon Tyne (centre) and a former steelworks in Consett (right) (Grid based on the Ordinance Survey National Grid of Great Britain - tile NZ)

minerals. The waters were supersaturated with respect to calcite and showed a relationship between precipitation and biological activity, coupled with attenuation of pH through a pond and calcareous wetland which has developed on a watercourse draining the former steel works area. A calcareous hardpan has formed at the surface adjacent to the pond and covers an area of approximately 400 m^2. The bedrock geology of the area is dominated by the Carboniferous mudstones of the Lower Coal Measures, but the landscape has been considerably altered by industrial activity.

3. Methodology

At the brownfield site in Newcastle upon Tyne, Ian Farmer Associates (www.ianfarmerassociates.co.uk) were contracted to excavate 5 trial pits to 3.5 m. At the former steelworks at Consett, soil samples were collected with a hand auger to depths up to 20 cm prior to contact with large fragments of slag. Furthermore, sediment was collected from the bottom of the high pH pond (locations are shown in Fig. 1). Samples were collected through the soil profile at both sites, air-dried and sieved to <2 mm. Calcium carbonate content was determined using an Eijkelkamp calcimeter to BS 7755-3.10:1995 (reproducibility better than ±0.6%), the residue was collected, washed, filtered and oven dried at 80°C and used for the determination of organic C isotope ratios. Soil pH was analysed according to ISO 10390 1994, using a Jenway 3020 pH meter.

Isotope ratio mass spectrometry was conducted using a Europa Scientific 20-20 IRMS (Iso-Analytical, Cheshire UK) for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ for $CaCO_3$ and $^{13}C/^{12}C$ for organic C collected from the calcimeter residues. IA-R022, NBS-18, NBS-19 were used twice as reference materials for carbonate (C and O) isotope analysis and IA-R001, IA-R005 and IA-R006 were used for organic carbon isotope analysis. Replication had a standard deviation better than ±0.1‰ and all but one of the 6 reference materials were within two standard deviations of the expected results (<0.2‰ difference from NBS-18; two separate analysis batches). The results were recorded relative to the Vienna Peedee Belemnite scale (V-PDB).

4. Results

4.1. Urban Brownfield, Newcastle upon Tyne

In some trial pits, visible precipitates of $CaCO_3$ occurred as coatings and concretions on

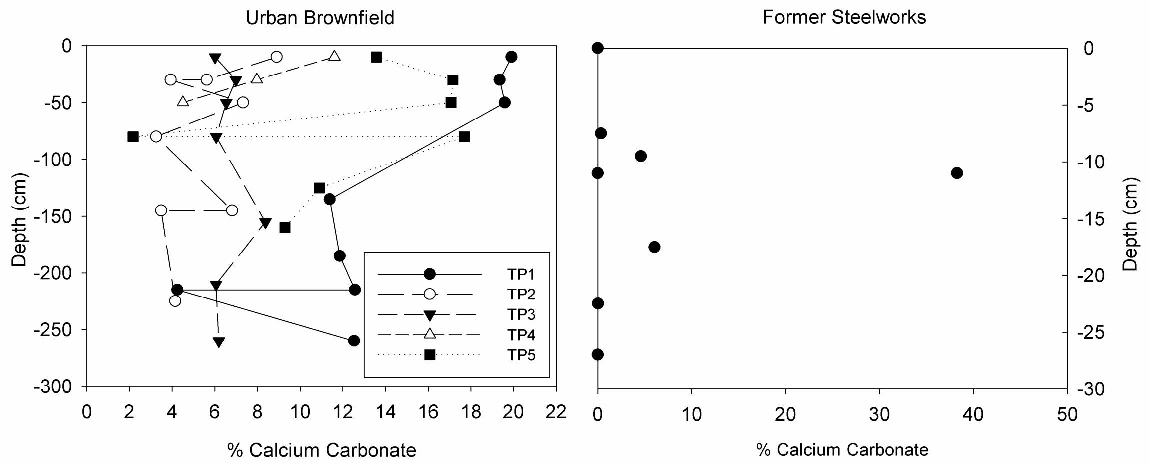

Fig 2. Carbonate concentrations with depth at both sites

demolition rubble. Chemical analysis determined $CaCO_3$ quantities within the soil to be between 2.2 and 19.9 wt % ($\overline{X}$ = 9.5% s = 5.1). Trial pits TP1, TP4 and TP5 showed negative correlation of $CaCO_3$ with depth (r^2=0.78, 0.99 and 0.50, respectively, after removal of outliers from the basal clay in TP1, for which a carbonate content of 4.3% was measured compared with values between 11% and 20% returned for other samples from the same trial pit, and unconsolidated sand in TP5, which had a similar lower value than the other samples from the same pit). There was no variation in carbonate content with depth in TP2 and TP3 (see Fig. 2 – note error bars are within the data point symbols).

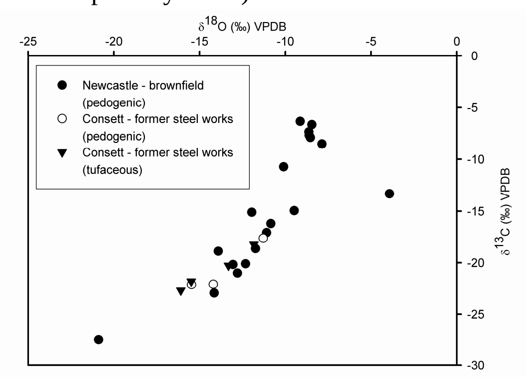

Fig 3. Isotopic ratios from carbonates formed in an urban brownfield soil (●) and within the drainage regime of the former steelworks (○).

Carbon and O isotope analysis of the carbonates gave $\delta^{13}C$ values between -6.3‰ and -27.5‰ and $\delta^{18}O$ between -3.9‰ and -20.9‰ (Fig. 3). The most negative carbon isotope values (between -13.3‰ and -27.5‰) were detected in precipitates on demolition rubble. There is a positive correlation between inorganic O and C isotope values (r^2 = 0.66 or 0.86 after the removal of outliers). Analysis of the organic C isotope ratios gave values between -19.0‰ and -24.0‰ $\delta^{13}C$ (all but one value lies within 1 standard deviation of the mean of 22.9‰).

Sample No	Sample depth (cm)	$\delta^{13}C$	$\delta^{18}O$
Urban Brownfield (NZ275649)			
A2TP1 1	0-20	-7.7	-8.6
A2TP1 2	40-60	-20.2	-13.1
A2TP1 3	200-230	-18.6	-11.7
A2TP2 1	0-20	-15.1	-12.0
A2TP2 2	40-60	-10.7	-10.1
A2TP2 3	200-250	-7.9	-8.5
A2TP3 1	0-20	-6.7	-8.5
A2TP3 2	40-60	-6.4	-9.1
A2TP3 3	190-230	-7.4	-8.6
A2TP4 1	0-20	-8.5	-7.9
A2TP4 2	40-60	-15.0	-9.5
A2TP5 1	0-20	-16.2	-10.8
A2TP5 2	40-60	-20.1	-12.3
A2TP5 3	150-170	-17.1	-11.1
A2TP1 RS 1	100-170	-27.5	-20.9
A2TP1 RS 2	170-200	-23.0	-14.2
A2TP2 RS 1	200-250	-21.0	-12.8
A2TP2 RS 2	100-190	-13.3	-3.9
A2TP5 RS 1	40-60	-18.9	-13.9
Former Steelworks (NZ094492)			
CON 01 1	0-35	-22.1	-14.2
CON 01 2	Surface	-22.7	-16.1
CON 04 1	0-19	-17.6	-11.3
CON HP1 1	0-8	-22.1	-15.5
CON HP1 2	8-15	-18.2	-11.8
CON HP2 1	>15	-20.3	-13.3
CON HP2 2	0-15	-21.8	-15.5

Table 1 Isotopic values and sample depth for pedogenic carbonates at both sites

Comparison of pH values recorded in this study with those presented in the contaminated land report suggest a decline in soil pH over time (from 12 to 7 at the present day). However, a comparison is speculative due to variation in sampling sites.

4.2. Former Steelworks, Consett

Calcium carbonate occurred in both the soil (pedogenic carbonate) and within the drainage system of the site (tufaceous carbonate). Quantities of $CaCO_3$ ranged between 0% and 93.4% ($\overline{X}$ = 29.6% s = 36.6) over both systems. The largest concentration of $CaCO_3$ was recorded in the sediment of the pond (>90%) and the hardpan (48-87%). The concentration of pedogenic carbonate was extremely variable (between 0% and 38.3% -$\overline{X}$ = 7.0% s=14.0) and there appears to be no relationship between concentration and depth (see Fig. 2). Carbonate isotope ratios were between -17.6‰ and -22. 7‰ for $\delta^{13}C$ and -11.3‰ and -16.1‰ for $\delta^{18}O$ (see Table 1 and Fig. 3)

5. Discussion

5.1 $\delta^{13}C$ and $\delta^{18}O$ Stable Isotopes of Carbon

Stable isotope analysis has been used to study carbonates since the 1950s (Craig, 1953) primarily to investigate diagenesis conditions in limestone and the influence of organic C during the remobilisation of $CaCO_3$ in soils (Hudson, 1977). Early work by Solomans and Mook (1976) and Cerling (1984) demonstrate the incorporation of organic C in pedogenic carbonates which characteristically have isotopic values between -2‰ and -10‰ for $\delta^{13}C$ and 0‰ and -5‰ for $\delta^{18}O$, respectively. Similar values have been found in more recent studies from a range of environments. It is clear that carbonate isotope values are controlled by precipitation conditions, including climate, rainfall, temperature, underlying geology and continentality (Andrews, 2006). The data obtained for the artificial soils investigated here are compared with published data from both natural and artificial soil in Figures 4 and 5.

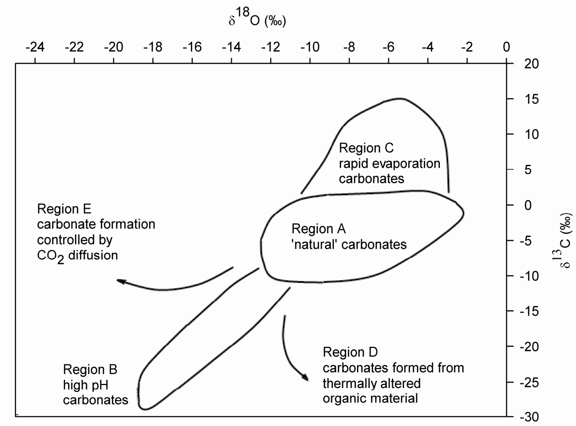

Fig 5. $\delta^{13}C$ and $\delta^{18}O$ isotope values returned from carbonates formed in a range of environments. Region A depicts carbonates formed in 'natural' conditions (Salomons and Mook, 1976, Cerling, 1984, Liu et al., 1996, Zanchetta et al., 2000, Knauth et al., 2003, Piovano et al., 2004, Bajnoczi et al., 2005, Boguckyj et al., 2006, Kovda et al., 2006, Sinha et al., 2006, Singh et al., 2007, Wang and Greenberg, 2007, Sikes and Ashley, 2007, Łącka et al., 2008, Yanes et al., 2008). Region B depicts the range of values returned from carbonates in high pH environments (Macleod et al., 1991, Andrews et al., 1997, Krishnamurthy et al., 2003, Boguckyj et al., 2006, and Fléhoc et al., 2006). Region C depicts values returned from evaporation dominated environments (Achyuthan et al., 2007, Knauth et al., 2003). Region D includes values from carbonates which have been formed under the influence of thermally modified organic carbon (Ohlsson, 2000, and Fourcade et al., 2007). Region E depicts carbonates formed under closed/semi closed systems where the diffusion of CO_2 becomes rate limiting (Van Strydonck et al., 1989, and Kosednar-Legenstein et al., 2008).

In Figure 4, Region A represents the precipitation of carbonates in 'natural' sedimentary environments. In Figure 5, the expected range of $\delta^{13}C$ values is shown for carbonates formed under the influence of C3 vegetation. Measurements from several studies fall within this range (Salomons and Mook, 1976, Cerling, 1984, Zanchetta et al., 2000, Bajnoczi et al., 2005, Kovda et al., 2006, Boguckyj et al., 2006, Wang and Greenberg, 2007, Singh et al., 2007, and Łącka et al., 2008). According to Andrews (2006) there is a general decrease in $\delta^{18}O$ with increasing continentality (from $\delta^{18}O$=-4‰ to -14‰). Many authors (Boguckyj et al., 2006; Singh et al., 2007; Wang and Greenberg, 2007; Łącka et al., 2008) record the occurrence of rhizoliths, which are carbonates formed in close proximity to plant roots and are dominated by organic .

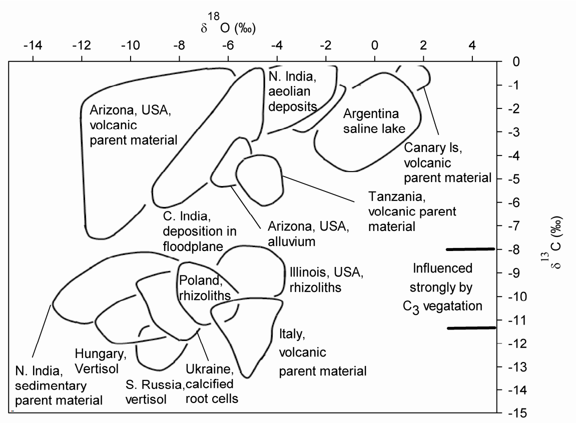

Fig 6. Detailed breakdown of isotope values in Region A.

The provenance of C within pedogenic carbonates is usually a combination of that which is derived from organic C, and remobilisation of lithogenic carbonates. Pedogenic carbonates formed under these influences will return an isotopic signature which is between the organically-dominated region and the lithogenically-dominated region contiguous with $\delta^{13}C$= 0‰ (Hudson, 1977). However, the use of isotope ratio data to determine host geology is potentially ambiguous, as demonstrated by Zanchetta et al. (2000), Sikes and Ashley (2007) and Yanes et al. (2008), who have independently found differing values for carbonates formed in soils on igneous parent rocks.

Several studies have published isotopic data for carbonates formed in anthropogenic environments (Region B in Fig. 4). van Strydonck et al. (1989), Macleod et al. (1991), Dietzel et al. (1992), Krishnamuthy et al. (2003) and Kosendnar-Legnstein et al. have investigated the formation of carbonates in alkaline environments associated with concrete and attribute the observed negative isotopic signatures to kinetic fractionation when CO_2 gas is dissolved in solution, which rapidly reacts with OH^- ions (from portlandite dissolution) to form carbonate through equation 2.

$$OH^- + CO_2 \leftrightarrow CO_3^- + H^+ \tag{2}$$

The rate of this is governed by equation 3 (Dietzel et al., 1992):

$$r = C_o \cdot (D \cdot k \cdot [OH^-])^{0.5} \tag{3}$$

where k is the rate constant (cm³ mol^{-1} s^{-1}) for hydroxylation, D is the diffusion coefficient of CO_2 through the liquid (cm² s^{-1}) and C_o the CO_2 concentration in solution (mol cm^{-3}). Assuming typical values for k and D of $10^{-4.83}$ cm² s^{-1} and $10^{6.41}$ cm³ mol^{-1} s^{-1}, respectively, it can be seen that the primary rate controlling step is the reaction between hydroxide and dissolved CO_2 gas. Dietzel et al. (1992) have associated this phenomenon with an isotope fractionation of -18.8‰ for $\delta^{13}C$, and a similar fractionation is experienced by O isotopes. Further to this, Andrews et al. (1997), Boguckyi et al. (2006) and Flehoc et al. (2006) have published data which conform to this model. Collectively, the isotopic signatures observed in this study fall within a tight regression (r^2 = 91.8%) against the line $\delta^{13}C = 1.6\ \delta^{18}O + 2.8$, which corresponds to carbonates formed in a combination of natural and high pH conditions. Indeed, the position on this line in comparison to the two approximate end members ($\delta^{18}O$ = -6.75‰, $\delta^{13}C$ = -8‰) for organically derived C (Cerling, 1984) and ($\delta^{18}O$ = -17.6‰, $\delta^{13}C$ = -25.3‰) for high pH carbonate (Dietzel et al., 1992), can be used to estimate the proportion of

C derived organically and that which has been sequestered through hydroxylation.

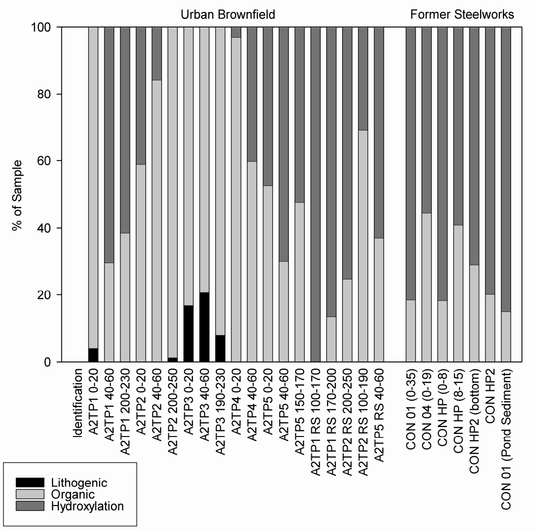

Fig 7. Proportions of carbonate precipitation mechanisms

Results from the isotopic analysis carried out in this study suggest that 3 mechanisms of carbonate formation (lithogenic remobilisation, hydroxylation of gaseous CO_2 and organic C sequestration) were operating in the urban brownfield site and two (hydroxylation and organic C sequestration) were operating at the former steelworks. The relative proportions of each process can be deduced from proximity to each end member, as described previously, and is summarised in Figure 6. The recorded isotope values at both sites comply with the trend observed for other published data, and there is no statistical difference between slopes ($p<0.05$). Remobilisation of lithogenic carbonate was assumed to be negligible in high pH waters.

5.1. Carbonate precipitation in soil modified with demolition rubble

The analysis of the urban brownfield site suggests that an average of 56.8% of the carbonate C is of organic origin, 40.5% is derived from hydroxylation and 2.7% from lithogenic carbonate. Extending these figures spatially for 10% average carbonate accumulation to 2.5m depth and assuming 1 t m^{-3} density of crushed concrete (Dhir et al., 1999), it can be theorised that this particular urban brownfield site has a SIC content of 30 ± 15.3 kg C m^{-2}, 97.3% of which has been sequestered ultimately from the atmosphere. The SIC content is 3 times greater than the value reported for the average organic C content in urban areas (Pouyat et al., 2006). Extrapolating these figures through the life of the brownfield site, it can be estimated that the soil has accumulated C at a rate of approximately 25 ± 12.8 t C ha^{-1} a^{-1}. It can be speculated that the accumulation of carbonate is accordingly matched by a decrease in soil pH. Indeed, the pH levels recorded in both this study and the contaminated land report completed in 1998 were not sufficiently high to cause hydroxylation. Therefore, it can be hypothesised that the accumulation of hydroxylated carbonate was rapid (within 2 a) and the subsequent carbonate accumulation is the result of Ca silicate weathering and organic C sequestration. However, the clast-supported nature of the soil suggests that the site drains freely; therefore, it is possible that the micro-environment around individual soil grains experience high pH levels.

5.2. Carbonate precipitation in soil modified with basic slag

Similar analysis of the carbonate C formed within soil modified with basic slag suggests that 31.4% of the carbonate C is derived from organic C and 68.6% is the product of hydroxylation of soil CO_2. Carbonate concentration is heterogeneous throughout the site and is clearly dependent on the drainage regime, with high concentrations at the pond/wetland and lower concentration at the brow of the slope. High pH levels are still present within the drainage waters on site almost 30 a after the steelworks were closed, which suggests sustained weathering of portlandite.

The rate of carbonate formation within the aqueous regime at the former steelworks was calculated by Mayes et al (2006) using the Dreybrodt limestone tablet method. They found that precipitation rates decrease across the flow path of the wetland between 0.6 t C ha^{-1} a^{-1} and 1.8 t C ha^{-1} a^{-1} over an area of 1500 m^2. The high variability of soil carbonate concentration means that it is not possible to carry out spatial accumulation calculations.

5.3. Implications for carbon capture and geoengineering

Brownfield sites are ubiquitous in the UK as a consequence of the country's industrial heritage, and cover approximately 42,000 ha of land (see Table 2 for details). Extrapolating 30 kg C m^{-2} for carbonate concentration found in this study, it can be estimated that the UK stores approximately 12.5 Mt C as carbonate in brownfield soil. It is interesting to speculate the C capture potential of urban soils if they were designed for that purpose. For example, the 625 ha occupied by London Olympics 2012 by the authors' calculations could sequester 180,000 t C. The formation of $CaCO_3$ within soils by reaction with construction materials is one way to compensate for the production of CO_2 during cement manufacture. Given the importance of concrete in construction (an industry which contributes 8% of the UK economy; DBERR, 2008), a full understanding of the possible value of concrete as a C sink at the end of its life allows the full life cycle impact of C emissions associated with construction to be understood in the context of sustainably mitigating climate change.

The maximum capacity of inorganic C capture technology is limited by the availability of Ca-rich minerals. DCLG (2007b) suggests approximately 88.6Mt of construction and demolition waste is produced annually in the UK and 46.5Mt of this is currently landfilled or spread on demolition sites. Assuming a CaO content of 20%, the maximum potential of carbonate capture is estimated to be 2 Mt C a^{-1}. These figures can be extrapolated to the global 'geoengineering' scale, under the assumption of a global production to waste ratio for concrete similar to the UK, and suggest that the upper limit for C capture using this technology is approximately 290 Mt C a^{-1} which is equivalent to 90% of the emissions associated with cement manufacture (Hendriks et al., 2004).

6. Conclusions

It is believed that this is the first reported case that demonstrates how artificial soils (i.e. made ground) can act as C sinks by accumulating $CaCO_3$. Precipitation of $CaCO_3$ was found to be associated with the weathering of portlandite at both sites, but it is unknown to what extent other Ca-rich minerals (Ca silicates, gypsum) are responsible for the formation of $CaCO_3$.

Brownfield land and Concrete Production in the UK and Globally		
UK Figures		
Urban settlement area	1,286,000 ha*	(General Register Office for Scotland, 2000, The Northern Ireland Statistics and Research Agency (NISRA), 2001, DCLG, 2008)
Brownfield/vacant land	42,200 ha†	(Scottish Executive - Statistical Bulletin, 2002, DCLG, 2007a)
Carbon currently stored in brownfield sites	**12.7MtC**	
Cement production	15.7Mt	(British Cement Association, 2009) – 2007 figures
Estimated concrete production	110Mt‡	
Concrete waste production (not recycled)	46.5Mt	(DCLG, 2007b)
Maximum capture potential	**2MtCy^{-1}**	
Global Figures		
urban settlement coverage	44,237,400 ha	(Demographia, 2008)
brownfield/vacant land	1,451,000 ha**	
Estimated current storage	**435.3MtC**	
Cement production	2,310Mt	(USGS, 2004)
Estimated concrete production	16,200Mt‡	
Estimated concrete waste production	6,800Mt+	
Maximum capture potential	**290MtCy^{-1}**	

Fig 7. Proportions of carbonate precipitation mechanisms active at both study sites.
*Statistics for England and Wales amended with data for Glasgow, Edinburgh, Dundee, Motherwell and Belfast.
†Brownfield contribution estimated based on relative proportions of urban area to brownfield in England, Wales and Scotland.
‡Based on a concrete mix of 1:2:4 w/w of cement, sand and aggregate.
** Calculated by extrapolating the ratio of brownfield to urban land in Scotland, England and Wales for the total global urban area.
+Estimated using the UK concrete production to waste ratio.

The capacity for the OH^- ion to buffer pH in soil at the urban brownfield site has diminished over time as a result of hydroxylation of gaseous CO_2, biological activity and site hydrology, which facilitated a decrease in soil pH. It is possible that a similar pH regime is progressing at the former steelworks site but a larger initial concentration of portlandite has sustained the process. With this in mind, the prevalence of hydroxylation on site will be replaced by the incorporation of biologically influenced carbonates as the weathered cations from silicates exert greater influence on the precipitation of $CaCO_3$. To that extent, further research should be undertaken to investigate the weathering and contribution of silicate minerals on carbonate formation. It is also important to note that the study area at the former steelworks is only a small fraction of the original site and it is impossible to gauge the efficiency of C capture without additional work to quantify the extent of the Ca-rich material using extensive groundwater/hydrological analysis and soil profile analysis.

Brownfield soils are extremely heterogeneous and additional studies are required to investigate how other artificial soils accumulate C. The results of this study suggest that demolition waste recycled into the soil will sequester C at a rate of 25 ± 12.8 t C ha^{-1} a^{-1}. However, additional work is required to investigate carbonate dynamics and stability over time. Furthermore, investigations are needed to ascertain the C capture potential of soils specifically engineered for that purpose.

Decoupling economic development with the production of greenhouse gases is the most important step in sustainably mitigating climate change. Economically developed countries support a strong construction sector which is a direct physical manifestation of development.

One of the primary materials of construction is cementious products (i.e. concrete), which is produced by calcining $CaCO_3$ and is responsible for 8% of the world's CO_2 emissions (Wilson, 1993) and steel which is responsible for approximately 5% (von Scheele, 2006). Reforming $CaCO_3$ in soils would partially close the loop on the C footprint from steel and cement production and decouple a substantial part of the construction industry from greenhouse gas emission.

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