Biological enhancement of soil carbonate precipitation: passive removal of atmospheric CO$_2$

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ABSTRACT

Soils are the dominant terrestrial sink for carbon, containing three times as much C as above-ground plant biomass, and acting as a host for both organic and inorganic C, as soil organic matter and pedogenic carbonates, respectively. This article reviews evidence for the generation within the soil solution of dissolved C derived from plants and recognition of its precipitation as carbonates. It then considers the potential value of this process for artificially-mediated CO$_2$ sequestration within soils. The ability of crops such as wheat to produce organic acid anions as root exudates is substantial, generating 70 mol/(y kg) of exuded C, equivalent to the plant's own 'body weight'. This is still an order of magnitude less than measured C production from Icelandic woodlands (Moulton *et al*., 2000), which have no other possible source of C. Thus, there is apparently no shortage of available dissolved C, as bicarbonate in solution, and so the formation of pedogenic carbonates will be controlled by the availability of Ca. This is derived from mineral weathering, primarily of silicate minerals (natural plagioclase feldspars and pyroxenes; artificial cement and slag minerals). Within the UK, existing industrial arisings of calcium silicate minerals from quarrying, demolition and steel manufacture that are fine-grained and suitable for incorporation into soils are sufficient to account for 3 MT CO$_2$ per year, compensating for half of the emissions from UK cement manufacture. Pursuing these arguments, it is shown that soils have a role to play as passive agents in the removal of atmospheric CO$_2$, analogous to the use of reed beds to clean contaminated waters.

Introduction

OVER the last 20−30 years, increasing concern about the possible impact of human activities on atmospheric carbon dioxide and methane contents has led to the development of models designed to understand the flux of carbon-bearing gases from soils and the ocean to the atmosphere (e.g. IPCC, 2007, for an overview; Manning *et al*., 2005). In summary (Smith, 2004), the oceans dominate as reservoirs for C, containing ~38,000 Pg (1 Pg = 10^{15}g or 1 Gt) compared with atmospheric C (730 Pg) and soil organic C (1500 Pg; upper 100 cm). Carbonate carbon in soils is a further

720 Pg C (Batjes, 1996) or more (750−950 Pg; Schlesinger, 1995), and land-plant biomass contains ~500 Pg C (Smith, 2004), mostly below ground within root systems. Thus, soil is the largest terrestrial carbon reservoir within the biosphere. Compared with ocean-atmosphere exchange (90 Pg C per year), there are greater fluxes of C between the atmosphere and the combined terrestrial plant-soil system (120 Pg C per year; Smith, 2004); as a result soil is a major player in controlling the atmospheric carbon cycle. Unlike the ocean, it is a component of the carbon cycle that human activity can influence readily, through management of landuse. In the context of the theme of this set of papers, 'Minerals in Biological Systems', soils represent the interface between minerals and biological systems on continental surfaces, and are the

product of interaction between plants, animals and microbes with mineral materials, water and soil gases.

In order to fully understand and quantify the carbon cycle that links soils and the atmosphere, many studies have focused on the role of soil organic matter, which is known to be a dynamic carbon pool. Recent work has shown that in general the organic carbon content of UK soils may be decreasing with time (Jones *et al.*, 2005; Knorr *et al.*, 2005), adding concern that weathering and erosion are removing soil carbon increasingly in response to climate change. In contrast, rather little is known about the dynamic contribution of pedogenic (i.e. formed within soil) carbonates to the carbon cycle, although ancient pedogenic carbonates are commonly used to identify past arid-semiarid climate conditions in the geological record. Importantly, these demonstrate that pedogenic carbonates are stable for extremely long periods of time, and hence act as a geologically permanent sink for carbon.

Given the weight of current attention that is paid to reducing artificial perturbation of atmospheric CO_2, and the associated work on reducing atmospheric CO_2 levels by sequestration processes of various kinds, this paper addresses the possible role of pedogenic carbonates as a sink for atmospheric CO_2. Importantly, soils offer scope for development in a manner analogous to the use of reed-beds for the passive treatment of polluted waters. If ways can be found to increase the formation of pedogenic carbonates in soils through appropriate land management, then these may be worth exploiting as a low-cost, low energy input process for the removal of atmospheric CO_2. What is needed is a thorough understanding of the ways in which plants interact with soils, and recognition of the circumstances that enable pedogenic carbonates to form. This paper introduces the concept of soils as a sink for inorganic C within the context of present concerns, and is intended to act as a foundation for future work. It reviews: (1) the occurrence of pedogenic carbonates in nature; (2) the origin of carbonate in solution in soil systems; and (3) plant root exudation. It then explores the implications of combining information from these three areas of work to promote carbonate precipitation artificially through the addition of calcium silicates derived from industrial sources, and hence the potential for carbon sequestration.

Soil carbonate occurrence

Perhaps the most authoritative observational work on the occurrence of soil carbonates, in terms of its pedigree, is based on mapping soils in the United States early in the 20th century. Marbut (1935) divided US soils into pedocals (those with pedogenic carbonates; mean annual rainfall <30" (750 mm)) and pedalfers (those that produced ferric oxy-hydroxide mineral precipitates; rainfall >30"; Fig. 1).
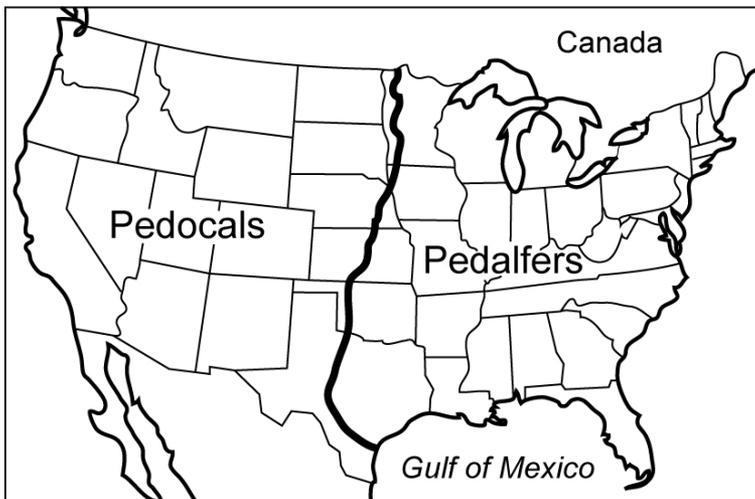

FIG. 1. Distribution of soils with pedogenic carbonates (pedocals) and Fe-Al oxide rich soils in mainland USA (after Marbut, 1935).

In general, the depth of occurrence of pedogenic carbonate within soil systematically increases with rainfall (Fig. 2; Jenny, 1980), and is >1 m once mean annual rainfall is >800 mm. More recent work in Kansas (ideal for the investigation of relationships between rainfall and pedogenic carbonate formation in soils derived from loess parent material) confirms this general trend (Gunal and Ransom, 2006). Thus, the spatial distribution of soil carbonates in the context of precipitation and the depth of the wetting front (i.e. the depth to which draining rainfall penetrates) has long been known. In contrast, the origin of the calcium carbonate (usually calcite, but rarely specified) is less clear. Accumulations of transported calcium carbonate derived from preexisting soils or rocks need to be distinguished from carbonates that have precipi-tated *in situ*, require careful description of soil profiles combined with petrography (micromor-phology) coupled with appropriate chemical and isotopic analysis (e.g. Salomons *et al*., 1978; Salomons and Mook, 1976). As an example of the

complications that can be encountered, an investigation of the occurrence of calcite in termite mounds (Liu *et al*., 2007) showed that termites are responsible for transporting calcite of geological origin from depths of up to 1 m within a soil upwards to form part of the structure of their mounds.

In terms of relationships with soil parent materials, it is often assumed that the formation of pedogenic carbonates requires remobilization of carbonate rock regolith, either *in situ* or present as transported particles within the soil. However, pedogenic carbonates are described from soils with no carbonate rock as a parent material. For example, Durand *et al*. (2007) describe carbonates formed in present-day soils in India developed on Precambrian silicate rocks, and show that their formation relates to the presence and distribution of calcium silicate-rich parent rocks, especially amphibolites, with up to 20% CaO. Similarly, Khalaf *et al*. (2000) report pedogenic carbonate formation on basalts in Syria, and Kalin *et al*. (1997) describes ancient pedogenic carbonates from interbasaltic soils in Northern Ireland. Thus, the calcium required for pedogenic carbonate formation can, in appropriate circumstances, be derived from silicate parent rocks, from the weathering of plagioclase feldspars and calcic ferromagnesian silicates.
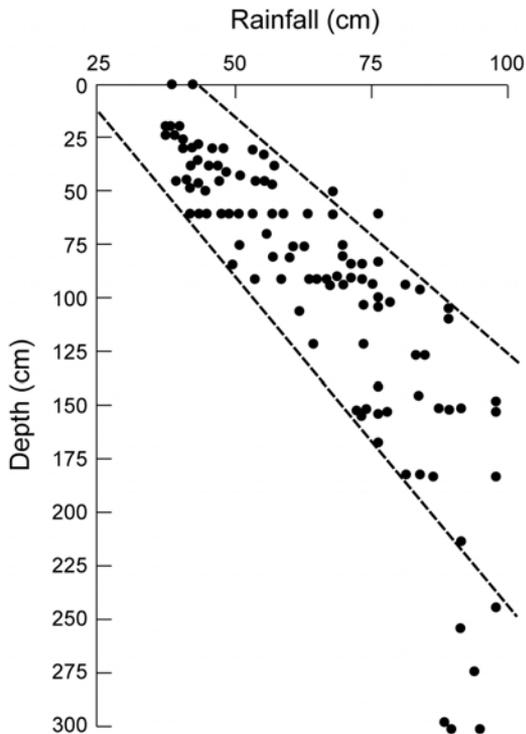
Origin of soil carbonate carbon

Early work by Salomons and Mook (1976) and Salomons *et al*. (1978) distinguished biogenic soil carbonates from those of geological origin for pedogenic carbonates from a range of locations, including the Netherlands, France and Italy as well as more arid locations. Subsequently Cerling (1984) demonstrated in detail the use of carbon stable isotope ratios to demonstrate that pedo-genic carbonates incorporate carbon derived from the plant community growing on those soil systems. He showed that there is a relationship between the carbon isotope ratio in the pedogenic carbonates and the proportion of C_4 biomass in the soil, taking advantage of the differences in carbon isotope fractionation in C_3 and C_4 plants. Typically, C_4 plants have biomass with a $\delta^{13}C$ value of −12 to −13‰ PDB, and C_3 plants have $\delta^{13}C$ values of around −27‰ PDB. Depending on the soil respiration rate and CO_2 concentration, Cerling (1984) estimates that soil CO_2 $\delta^{13}C$ values typically vary between −8.5‰ PDB (C_4 biomass) and −22.2‰ PDB (C_3 biomass). Once

FIG. 2. Depth distribution of carbonate minerals in soils as a function of rainfall, central Great Plains, USA (after Jenny, 1980).

fractionation between carbon dioxide and calcium carbonate is taken into account, soil carbonate minerals precipitated in equilibrium with the soil atmosphere will have $\delta^{13}C$ values of $-2.9‰$ PDB (C_4 origin) and $-7.2‰$ PDB (C_3 origin; Cerling, 1984). These can be distinguished from carbonates of geological origin, which typically have heavier $\delta^{13}C$ values (marine carbonate minerals have $\delta^{13}C$ values typically close to zero).

Pedogenic carbonate formation in Saskatchewan soils has been investigated by Landi et al. (2003). The origin of the carbonate carbon was clearly attributed to C_3 and C_4 plant inputs, with carbonate $\delta^{13}C$ values varying between -4 and $-9‰$ PDB. The rates of accumulation of pedogenic C were estimated to exceed those of organic C when considered in terms of net primary productivity (0.65% compared to 0.46%), with absolute pedogenic carbonate accumulation rates of $0.99-1.37$ $g/m^2/y$ (as C; this is equivalent to $10-14$ kg C/ha/y). With rainfall between 200 and 700 mm/year, the rate of pedogenic carbonate formation increased. Similarly, Stevenson et al. (2005) demonstrated that the $\delta^{13}C$ values in a C_3 dominated system for pedogenic carbonates (-4 to $-11‰$ PDB) across a climate gradient ($200-1000$ mm mean annual precipitation) correlate with precipitation, above-ground productivity and total soil carbon content.

The use of carbon isotopes has clearly shown that the primary productivity (i.e. the type of plants growing on a soil) relates closely to the formation of pedogenic carbonates. Taking this into account, Kuzyakov and Domanski (2000) estimate that cereal production can store 1500 kg C per hectare annually in soils, 90% as organic matter, 10% as carbonate. Andrews and Schlesinger (2001) suggest accumulation of $170-215$ kg carbonate C/ha for forest soils.

Plant root exudation

Primary productivity transfers carbon from the atmosphere to the plant system, and then to the soil. In addition to reactions involving the decomposition of plant tissue when it is part of or enters the soil directly as solid organic matter (plant debris, microbial biomass, fungal tissue etc), plant roots also exude organic acid anions, providing a flux of low molecular weight dissolved organic C to the soil system. Plant root exudates include low molecular weight organic acid anions (e.g. acetate, malate, oxalate and citrate; Ryan et al., 2001). These organic

acids increase the bioavailability of nutrients (e.g. P; Hinsinger, 2001) and reduce the bioavailability of potentially toxic soil solution components (e.g. Al; Hoezenga et al., 2006). Organic acid anions are known to have a major effect on the decomposition of silicate minerals, enhancing dissolution rates significantly (Manning et al., 1992; van Hees et al., 2002) and accelerating weathering (Drever, 1994). Although important in terms of their impact on soil minerals, organic acid anions are unstable and decompose rapidly, ultimately forming a combination of carbon dioxide and dissolved bicarbonate, at isotopic equilibrium (Cerling, 1984).

The decomposition of exuded organic acid anions is largely controlled by microbiological activity within the soil (Jones et al., 2003). In detail, intermediates in the decomposition of citrate and malate will include other low-molecular-weight organic acids including acetate, and a number of possible degradation pathways may exist (analogous to those that occur in anaerobic systems; Manning, 1997). Overall, however, it can be assumed that the decarboxylation of citrate and malate ultimately leads to the formation of bicarbonate in solution (bicarbonate is the dominant solution species for carbonate between pH 6 and pH 9; Drever, 1997), which is then coupled to soil-gas carbon dioxide contents by the pH-dependent equilibrium:

$$HCO_3^- + H^+ = CO_2 + H_2O \qquad (1)$$
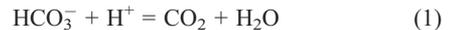
It can be assumed that the amount of bicarbonate produced is equivalent to the number of carboxyl groups in the decomposing organic acid. Additional bicarbonate may be produced by the oxidation of the alcohol OH group in malate and citrate. In addition, root respiration introduces CO_2 into the soil gas-water system, supplementing exudate inputs (e.g. van Hees et al., 2005; Bowling et al., 2008).

Examples of the productivity of malate and citrate for specific plants are given in Table 1 (Ryan et al., 2001). The original data were reported in nanomoles of the organic acid per gram fresh weight per hour, and are for plants subject to stress (P deficiency or Al excess). In Table 1, these figures have been recalculated as the milliequivalents of carboxylate per gram fresh weight per hour, considering that citrate has three carboxyl groups and malate two. Assuming direct correspondence between carboxyl and bicarbonate, the productivity of carboxylate expressed as milliequivalents is numerically equal to the

TABLE 1. Estimates of root exudates production (Ryan *et al.*, 2001) expressed as potential yields of inorganic carbon per gram fresh weight per week.

		nmol/(h gFW)	mEeq carboxylate/(week gFW)	mg inorganic C/(week gFW)
Wheat	malate	4000	1.34	16.1
Brassica napus	citrate	70	0.10	1.2
	malate	200		
Lupin	citrate	570	0.46	5.5
	malate	510		

productivity of bicarbonate. Thus, Table 1 estimates the potential production of bicarbonate expressed as grams inorganic carbon.

The figures given in Table 1 are quite remarkable. They suggest that under certain conditions wheat, for example, can produce its own 'body weight' in inorganic C, if all its root exudate production ultimately becomes bicarbonate, in 11 weeks, which is approximately equivalent to the plant's life (it is uncertain how root exudates productivity varies with plant age). However, little is known about the true rate of organic acid production and persistence in soil systems. Jones *et al.* (2003) point out that there are many difficulties inherent in measuring organic acid anions in soil solution, partly because of their rapid consumption by soil microorganisms, and suggest that steady-state concentrations may be of the order of $1-50$ µm. Van Hees *et al.* (2003) suggest that soil solution citrate contents in forests may reach 70 µm; this corresponds to 0.21 mEq of carboxylate, or ~2.5 mg/l dissolved inorganic carbon if the carboxyl groups are completely mineralized.

On a catchment scale, the ability of plants to generate dissolved bicarbonate has been demonstrated very elegantly by Moulton *et al.* (2000). These authors determined the flux of carbon and other elements through forested systems in Iceland in basaltic soils for which there was no possible input from limestone or dissolution of other mineral carbonates. They measured the bicarbonate content of stream and groundwater for bare and wooded areas, and showed (Table 2) that up to 12 kg C per hectare was produced annually as bicarbonate (60 kg bicarbonate; 1000 moles/y/ha), exported via through-drainage. Moulton *et al.* (2000) also show that the inorganic solutes Ca and Mg are significantly greater for vegetated soils, demonstrating the ability of plant growth to accelerate the weathering of soil silicate minerals (in this case olivine, pyroxenes and plagioclase). Considering the mass balance for carbon within the coupled woodland-soil system (but neglecting soil carbonate precipitation as a sink), Moulton *et al.* (2000) estimated that the birch and conifer woodlands retained 74% and 82%, respectively, of the assimilated C, losing

TABLE 2. Carbon and calcium fluxes through vegetated and non-vegetated ground, SE Iceland (Moulton *et al.*, 2000), with corresponding estimated carbon fluxes from organic acid exudates (Ryan *et al.*, 2001).

	Weathering fluxes mol/(y ha)			Weathering flux/kg biomass mol/(y kg)		
	HCO$_3^-$	Ca	Mg	HCO$_3^-$	Ca	Mg
Bare, soil	353	127	49			
Bare, no soil	362	96	39			
S birch	911	290	162	543	173	96
N birch	985	252	167	580	148	98
Conifer	999	277	164	381	106	63
Wheat				70		
Brassica napus				5.3		
Lupin				24		

26% and 18%, respectively, to the soil-water system as bicarbonate.

In Table 2, the weathering fluxes estimated by Moulton *et al.* (2000) are compared with the corresponding productivity of root acids, expressed as their ultimate degradation product bicarbonate, estimated using data from Ryan *et al.* (2001). Estimates from the geochemical approach, using a large scale woodland experiment, give values 10−100 times greater than those estimated in the laboratory for stressed crop plants, even when normalized to take into account differing amounts of biomass. Obviously, uncertainties affect both approaches. Moulton *et al.* (2000) do not take into account possible precipitation of carbonates within the soil (but the soil solution compositions are undersaturated with respect to calcite, hence precipitation may not have occurred), and so their values may be underestimates of plant-derived carbon fluxes. Determination of plant root exudates is very difficult practically (Jones *et al.*, 2003), and values reported for specific organic acid anions may be an incomplete assessment of exuded C..

Exploitation of these phenomena: engineering pedogenic carbonate formation

From the literature reviewed above, it is apparent that the formation of pedogenic carbonates should be expected as a normal consequence of the weathering processes associated with plant growth on a soil that contains calcium silicates or is derived from a calcium silicate-rich regolith. For precipitation to occur, the solution needs to be saturated with respect to calcite (or other carbonate minerals if appropriate). Mechanistically, calcite precipitation removes the carbonate ion from solution:

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \qquad (2)$$

As soil pH decreases to <9, the proportion of carbonate in solution diminishes. Calcite precipitation thus consumes bicarbonate and generates protons:

$$HCO_3^- = CO_3^{2-} + H^+ \qquad (3)$$

This is equivalent to writing the precipitation reaction as:

$$Ca^{2+} + 2HCO_3^- = CaCO_3 + H_2O + CO_2 \qquad (4)$$

because at a near-neutral pH water and CO_2 will equilibrate as bicarbonate. Although protons are generated by calcite precipitation, the effect on soil pH is likely to be negligible, simply because the organic acid anions (and carboxylated higher-molecular-weight organic acids) are very effective pH buffers (see Manning *et al.*, 1992). Thus the driving force at constant (buffered) pH that promotes calcite precipitation, with a constant flux of bicarbonate derived from plants, will be the availability of calcium:

$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+ \qquad (5)$$

This process is summarized in carbon form in Fig. 3.

Although pH is clearly a variable that controls calcite stability in soils, it has been shown that the precipitation of calcite within landfill leachates takes place over a pH range 5.9−8.0 (Manning and Robinson, 1999; Manning, 2001). Landfill leachates are compositionally similar to the soil solution in that they contain organic acid anions and have elevated pCO_2. In modelling work reported by Manning and Robinson (1999), it was shown that the calcium content of the leachate is a key factor that influences calcite saturation, over a range of pH values likely to be encountered in soils (Hinsinger *et al.*, 2003).

Within any soil system, the availability of calcium for calcite precipitation is either from preexisting carbonate minerals that may dissolve and reprecipitate, or from the weathering of
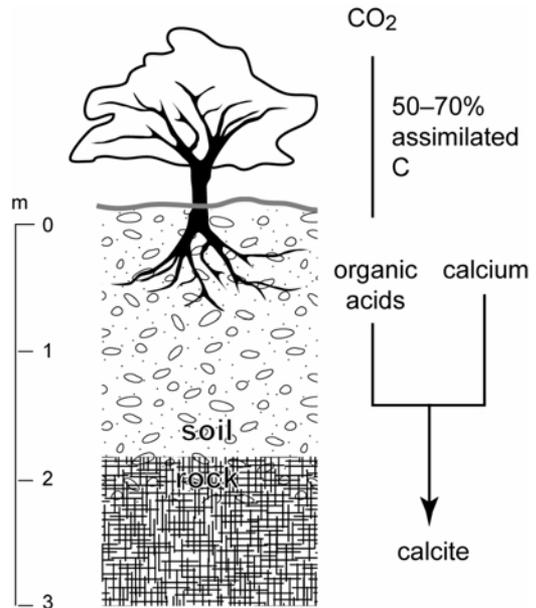

FIG. 3. Schematic diagram showing pathway for formation of calcite within soils.

calcium silicate minerals, especially feldspars. Carbonate mineral dissolution and reprecipitation is a 'carbon-neutral' phenomenon, and so carbon sequestration benefits will only be expected in situations where calcium silicates are present. These occur in natural soils developed on basic igneous rocks, but in the UK (for example) most outcrops of these are in the north of the country, overlain by tills and other drift deposits. Nevertheless, soils developed on tills that include material derived from basic igneous rocks have been reported to contain carbonates (Ragg et al., 1959), but as yet there is no evidence concerning a biological control on calcite formation in these circumstances. Similarly, the depth of precipitation needs to be determined, as (in accordance with Fig. 2) it may take place well below the root zone.

Although basic igneous rocks at outcrop are unlikely within the UK to act as significant sinks for C through associated pedogenic carbonate formation, there is scope for exploiting products quarried from basalt and dolerite. Because of their engineering properties, basic igneous rocks are an important source of crushed rock aggregate. The crushing process inherently generates a fine fraction (typically <5 mm), which may not be interesting or valuable as a commercial product. Additionally, aggregates are produced from demolition of concrete structures, similarly giving rise to a fine fraction, in this case dominated by artificial calcium silicates (the hydrated cement minerals) and portlandite (Ca(OH)$_2$). Finally, slags derived from steel production are crushed to produce aggregates for a variety of uses, again generating fines that may accumulate pending attractive commercial uses. In all cases, the crushing process may generate typically 25−30% fines, depending on the geotechnical properties of the material and the design of the crushing plant.

The possible contributions of different calcium silicate materials to carbon sequestration are considered below, and are summarized in Table 3:

(1) Cement-based materials: 12.5 MT of cement is produced annually in the UK, representing use of 15 MT of quarried limestone and 55−60 MT of shale raw materials; these lose 6 MT of CO$_2$ on firing. Although strength is achieved through hydration reactions, natural aging of cement products involves carbonation (N.B. in historical lime mortars, bonding is achieved through carbonation of portlandite, Ca(OH)$_2$).

Using statistics for the production of secondary aggregates (40 MT; ODPM, 2003; Lawson et al., 2001), the amounts of concrete and mortar that arise in the UK annually from demolition as a fine fraction (<6 mm) is estimated to be as much as 12 MT per year (Woods et al., 2004). According to Stolaroff et al. (2005), 1 T of demolition waste absorbs 0.06 T CO$_2$, giving a sequestration potential of 0.72 MT as CO$_2$. However, the CaO content of the fines fraction (i.e. correcting for dilution by a proportion of the aggregate) may be as much as 20 wt.%, giving a sequestration potential of 1.9 MT CO$_2$.

(2) Basic slags from steel making: incorporating limestone and dolomite (2.5 MT quarried for this purpose per year), 3 MT of blast furnace and 1 MT of steel (basic oxygen furnace) slag are produced annually in England and Wales (ODPM, 2002). Much of this is directed to aggregate uses. Stolaroff et al. (2005) explored the possibility of using a washing process in which dissolved calcium hydroxides derived from basic slag removes atmospheric CO$_2$ by reaction in water,

TABLE 3. Estimated arisings of crushed rock fines from UK aggregate production (Woods et al., 2004), with carbon capture potential assuming that all CaO within the fine fraction reacts to form CaCO$_3$.

'Rock' type	Annual production (MT)	Typical % fines	Estimated fines production (MT)	CaO content (wt.%)	CO$_2$ capture potential (MT)
Igneous rock	45	30	12; 6 basic igneous rock	9	0.4
Concrete demolition waste	40	30	12	20	1.9
Slag	4	30	1.2	49	0.5
Total CO$_2$ sequestration potential					2.8

and suggest a hypothetical uptake of 0.27 T CO_2 per tonne of slag at a cost of US\$8/per tonne CO_2 of which US\$1 per tonne is attributable to energy costs (excluding transport and vehicle fuel on site). The approach is deemed feasible, but requires a purpose-built plant and significant energy inputs. In England and Wales, this would correspond to 1 MT CO_2 per year if all arisings of basic slags are used. If only the fines that arise incidentally from crushing slags are used, the sequestration potential is of the order of 0.4 MT CO_2 per year.

(3) Calcium-rich aggregates: production of crushed igneous rock aggregates (45 MT/y) involves the generation of significant quantities (estimated 9 MT/y) of 'fines' (material that is produced in crushing and is below the minimum size of the graded aggregate product; Woods *et al.*, 2004). A significant proportion of this consists of basic rocks containing typically 9% CaO (dolerite). Using the arguments proposed by Stolaroff *et al.* (2005), a hypothetical 0.1 T CO_2 could be fixed by reaction with 1 T of dolerite. For the UK production of dolerite, perhaps as much as 0.4 MT CO_2 could be fixed by complete reaction with quarry fines.

Combined, these three materials offer the possibility of removing as much as 3 MT per year of atmospheric CO_2 (which corresponds to just less than 1 MT C; UK annual emissions from all sources are around 550 MT CO_2; www.naei.org.uk). This figure needs to be compared with the current UK target under the Renewables Obligation (16 MT CO_2 through reductions of emissions associated with electric power generation), suggesting that widespread use of fines to remove CO_2 by passive sequestration in soils is equivalent to current major renewable energy initiatives. In any case, the removal of 3 MT per year of CO_2 corresponds to half of the emissions that are produced in cement manufacture in the UK.

In addition to contributing to the removal of atmospheric CO_2, the possibility of using calcium silicates within soil systems potentially reduces the need to quarry primary raw materials for agricultural liming (~1.6 MT per year of limestone and related materials annually; www.bgs.ac.uk). Liming typically involves applications of 1−3 T/ha of CaO equivalent. If this is added as a material that can take up CO_2, the equivalent amount of CO_2 is of the order of 0.8−2.4 T/ha, or 0.2−0.6 T/ha C, similar to sequestration values for organic carbon (0.3−0.8 T/ha C) suggested for

soils by Smith (2004; note that on average for the UK, the total carbon stock in agricultural soils is 84 T/ha C; Smith *et al.*, 2005).

Practical obstacles to the use of fines for CO_2 sequestration are significant. Within the UK, calcium silicate-rich fines arise from rural dolerite and basalt quarries (mostly in northern England/ southern Scotland), from urban demolition and steel production sites. In all cases transport to locations where fines could be applied to soil needs to be minimized. In addition, it is not clear that present regulatory systems would accept application of fines to land (although quarry fines can be used as a fertilizer by organic farmers); applications to soil of basic slag (once widespread as a lime and phosphorus source) are now permitted (subject to a risk assessment) in England and Wales, after a period in which their use was forbidden.

If, however, there were no obstacles to the transport and application of calcium silicate fines to land, what would be the best option for rapid progress, using the UK as an example? This review has highlighted the potential of wheat to generate malate as a root exudate, and has suggested that wheat can pass its own weight in carbon through its root system as organic acid anions within a single growing season. Root exudates data are also available for *Brassica napus*, and can be used as an estimate of the exudate production for oilseed rape. Typical yields for production of these two crops are given in Table 4.

Table 4 uses data from Table 1 to estimate the weekly exudation of C through the root systems of the two crops, and then estimates the amount of dolerite or basaltic fines (assuming 9% CaO) needed to supply calcium for the complete consumption of exuded C by precipitation of calcite. At present it is not possible to estimate the production of root exudates throughout the life cycle of the crops concerned (values quoted in Table 1 are for plants of differing maturity) but the equivalent of 5−10 times the weekly demand figure given in Table 4 would be appropriate for a first estimate of demand for the full growth cycle. Given that applications of typically 10 but up to 20 T/ha are usual for agricultural lime, the amounts of dolerite or basalt fines needed for passive carbon sequestration are similar in order of magnitude, and so are not unreasonable in terms of the logistics of their application. Extrapolating further, in England, 2.5 million ha are devoted to cereal production (http://farmstats.defra.gov.uk),

TABLE 4. UK crop yields for wheat and oilseed rape, with estimates of weekly exuded C and equivalent demand for crushed dolerite fines.

UK production 2006	Yield (T/ha)	Tonnage (MT)	Weekly Exuded C (T/ha)	Weekly fines demand T/ha
Wheat	8	14.7	0.129	6.69
Oilseed rape	3.3	1.87	0.004	0.21

giving a total (organic + inorganic) sequestration potential of >3 million tons C per year (removing 14 million tons of atmospheric CO$_2$ annually (total *English* emissions of 400 million tonnes; Salway *et al*., 2001). As a passive system, with no additional energy inputs, soil sequestration of CO$_2$ as soil carbonates is in addition to benefits otherwise obtained from planned soil use.

Conclusions and outstanding questions

This review has shown that available information for the production of plant root exudates demonstrates that very substantial amounts of assimilated carbon pass through the plant and into the soil system. For common crop plants such as wheat, 16 mg of readily mineralized C are exuded weekly per gram of fresh weight. Observations from catchment-scale studies in Iceland demonstrate greater yields of plant-derived bicarbonate within water draining from woodlands, with mass balance calculations suggesting that $18-26\%$ of assimilated C passes through the roots into the soil-water system. There can be little doubt that plants are a significant source of carbon within the soil solution, and stable isotope evidence demonstrates clearly that a proportion of that carbon is captured by the precipitation of pedogenic carbonates, especially calcite.

The key question that arises concerns whether or not it is possible to manipulate crop production, both for food and bioenergy crops, to maximize carbon capture as pedogenic carbonates. Application of calcium-silicate rich fines, from aggregate production, provides an opportunity to exploit the ability of plant root exudates such as malate and citrate to accelerate mineral dissolution, releasing calcium and so promoting the precipitation of calcite. Although this process occurs naturally in soils developed on calcium silicate regoliths, it needs to be demonstrated that it also occurs when calcium silicate fines are applied to a soil.

In order to assess the significance of carbon capture by amendment of soils with calcium silicates, much more information is needed concerning the production and decomposition of root exudates with time during the life cycle of the plant, and how that relates to the dissolution kinetics of calcium silicate minerals. Clearly, a focused programme of experimental work is needed that couples the different disciplines from which this review has drawn.

Acknowledgements

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