

# Technologies for increasing carbon storage in soil to mitigate climate change

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## Abstract

Means to enhance storage of carbon in soil or avoid its loss from soil are discussed and examined from the viewpoint of policy. In particular, technologies that have until now received little attention are assessed. The main means by which soil carbon might be increased are first listed. These are: (i) increasing the rate of input of organic matter; (ii) decreasing the rate of its decomposition by biological or chemical means; (iii) increasing the rate of its stabilisation by physico-chemical protection within aggregates and organo-mineral complexes; and (iv) increasing the depth or more correctly the total soil volume sequestering carbon at maximum rate.

Immediate gains in carbon storage might be made by switching to more perennial crops, especially grasses that as a result of breeding put more carbon into soil. In the longer term, targets for research such as understanding the role of enzymes in carbon turnover and the exploitation of the capacity in subsoils are suggested. Increased fixation of CO<sub>2</sub> as inorganic carbonate in soils by application of silicate wastes may have some role.

## Introduction

The UK Department for Environment, Food and Rural Affairs (Defra) sets soils policy for the England and Wales and since the Millennium Assessment (2001), has adopted an Ecosystem Services approach which is exemplified by the UK National Ecosystem Assessment (Anon, 2011) and has fed into policy through the Natural Environment White Paper (Anon, 2011). Safeguarding Our Soils, A Strategy for England (Defra, 2009) stresses the role that storage of carbon in soil can play in helping to combat climate change and meeting the UK Government's emission reduction targets and carbon budgets in England, introduced by the Climate Change Act 2008. Of particular importance is the ability of soils to regulate carbon in the environment through storage or other means in the soil and the wider value of soil organic carbon (SOC) on soil quality and the role it plays in the provision of habitat for biodiversity. Safeguarding our soils also points out, however, the need that policy-makers have for a robust evidence base with which to inform policy. Although there have been several recent reviews of existing science and methodologies for increasing levels of carbon in soil, here we

consider less tried and tested technologies for their potential to retain carbon that would otherwise increase atmospheric CO<sub>2</sub>. Despite the use of UK data, many of the conclusions reached here are relevant to policy-makers world-wide who are grappling with issues surrounding soil carbon and most issues discussed are relevant to policy-makers in NW Europe.

There are two major components to the global carbon cycle: (i) a geological cycle which acts over epochs but cycles very large amounts of carbon because of the time and spatial scales involved, and (ii) a biological cycle that operates over much shorter periods of time. Humanity's current problems and confusion with carbon stem from exploitation of the geological carbon and attempts to fix this by manipulating the biological cycle. Because the two operate at different timescales there are huge amounts of carbon to exploit from geological reserves but little capacity to fix this within the biology. Nevertheless, the biological cycle does have some capacity and it is also worth noting that the two cycles are not entirely distinct: the *soil* carbon cycle and chemical cycles sit somewhat in between since soil C is derived from the annual biological cycling of plants on the one hand but is capable of long-term physico-chemical preservation in soil for thousands of years in some instances.

Although there is some interest in means to stimulate the uptake of inorganic carbon dioxide directly from the atmosphere, most carbon enters the soil through the plant

In this review we consider some novel ways in which policy might be used to steer interventions in these short-term natural cycles in order to weigh the balance in favour of increased net input or storage of carbon in soil. The principal factors that determine C sequestration in the soil are:

1. the rate of input of organic matter;
2. the rate of its decomposition by biological or chemical means;
3. the rate of its stabilisation by physico-chemical protection within aggregates and organo-mineral complexes; and
4. the depth or more correctly the total soil volume sequestering carbon at maximum rate.

In this analysis a distinction has been made between physical methods of reducing decomposition (3) of organic matter which tend to halt turnover, and methods which act on the chemical and biological processes (2) because these latter tend to slow decomposition down rather than stop it altogether. For previous reviews of this topic see Smith *et al.* (2000), Powlson *et al.* (2011) and Stockmann *et al.* (2013).

## **Increasing the rate of input of organic matter to soils**

### *Agroforestry and intercropping*

Forest and woodland ecosystems contain more carbon than pasture or arable (Bolin *et al.*, 2000). Although levels of soil carbon in the soils of the most productive pastoral systems can approach the

levels found in forest soils (Bolin *et al.*, 2000), arable soils usually contain much less C than either forest or pasture (Bolin *et al.*, 2000). Mixed systems, that is to say trees and arable (known as silvoarable or agroforestry systems) or trees and grass (known as silvopastoral systems) have been proposed as a means to extend the benefits of forest to farmed land. Because different species use resources differently, they can be complementary with one another, often yielding more and consuming less than corresponding sole crops. It has been suggested recently that agroforestry and intercropped systems increase the store of carbon in land managed for production (Nair *et al.*, 2009a,b). Nair *et al.* (2009b) report a range of soil C sequestration data with modest values of around 1 Mg C ha<sup>-1</sup>. Gupta *et al.* (2009) found 3 Mg increase in one year and a 6 Mg ha<sup>-1</sup> increase during six years, with little difference in loamy sand and sandy clay soils. Agroforestry and silvopastoral systems contain more carbon in soil than cropland, but almost all the evidence comes from work in tropical and sub-tropical soils with little work in temperate systems (Jose, 2009). Even in these studies, few woodland controls exist so it is not clear if the resource-use complementarity referred to above leads to extra carbon storage relative to sole species. Quinkenstein *et al.*, 2009; and Montagnini & Nair (2004) who reviewed C sequestration in soils under temperate agroforestry systems cite a figure of 63-76 Mg C ha<sup>-1</sup> but the source of these values is unclear. There is a need to assess the potential of temperate agroforestry systems for increasing soil C

Mixed tree and crop systems will stimulate the nitrogen cycle as well as the carbon cycle and a 25% increase in emissions of N<sub>2</sub>O has been found on a loamy soil in China (e.g. Guo *et al.*, 2009). Verchot *et al.* (2008), however, found no increase in N<sub>2</sub>O emitted on a sandy soil in the Amazon, nor was CH<sub>4</sub> oxidation capacity of the soil affected. Results from the UK are lacking. If intercropped systems are to be widely adopted in the UK, for whatever reason, the potential for increased N<sub>2</sub>O emissions needs to be assessed. Leaching of dissolved organic carbon (DOC) can often be high in forest systems (e.g. Kalbitz *et al.*, 2004), but there is no evidence to show a change in DOC production and loss in agroforestry or silvopastoral systems.

Intercropping field crops might improve C storage relative to monoculture controls too. Bolin *et al.* (2000) quote data suggesting that temperate grasslands store 236 C Mg ha<sup>-1</sup> as a global average. Sequestration rates of 65-70 Mg ha<sup>-1</sup> in 100 years have been quoted (Abberton *et al.*, 2007). On the other hand Skinner *et al.*, (2006) found that soil C either remained the same with species mixtures or declined during two years after sowing into a soil that had previously supported winter wheat. The potential for soil carbon storage in intercropped soils does not appear to have been widely investigated.

#### *Perennial in place of annual crops*

The development of perennial crops in place of current annual ones such as wheat through plant breeding may lead to gains in soil C (Royal Society, 2009a). In general, perennial plants store more C than annuals as the annual cycle of cultivation does little to maintain storage. Perennial crops are in

the ground all year long and intercept more of the sun's radiation as a result (e.g. Glover et al., 2010). It follows that a change from arable to perennial grassland is likely to lead to a significant increase in soil C (Guo & Gifford, 2002). By implication therefore, a change from annual to perennial grain crops should also lead to an increase in SOC. Because they live longer, many perennials invest in deep, extensive root systems which are efficient in scavenging for nutrients and water as well as putting carbon in to soil. The amount of C retained by soils is influenced greatly by management practices, with those that lead to reduced soil disturbance and for increased crop persistency having the greatest benefits on C sequestration. Moreover, perennial vegetation may receive fewer passes with machinery, so consuming less energy because perennial systems are more diverse and receive fewer sprays that consume fossil fuels in their manufacture. However to date there are no perennial crop species that produce adequate grain yields. The Royal Society (2009a) estimates that it will be at least 10 years before the development of commercial varieties.

#### *Improved grasses*

The key plant traits likely to influence C sequestration (root depth, structure and architecture; litter composition and amount) are reasonably well established and genetic variation is beginning to be characterized for many of them. Some early progress has been made with regard to mapping of genes in perennial ryegrass for C sequestration, with effective C return in litter (Abberton *et al.*, 2007). Key questions to be resolved are the extent to which investment of photosynthate below ground is at the expense of above-ground productivity, and how much of the additional below-ground carbon can be stored in subsoils for the long term.

#### *Roots, exudation and priming effects*

Although roots obviously put carbon directly belowground, root turnover can be appreciable and the roots of many plants exude large amounts of carbon-containing polymeric compounds into soil over the course of a growing season. Grazing enhances rhizodeposition thus temporarily changing the balance between root and shoot production (Hamillton III et al, 2008). Plants are themselves also subject to grazing by animals whose droppings or carcasses (in the case of wild animals) usually return carbon to soil eventually. Grazing can occur both above and below-ground since many insects have a larval stage in the soil. Clearly, total input to soil depends on the balance between the reduction in photosynthesis due to grazing and the temporary diversion of carbon into soil.

Plants send varying amounts of carbon belowground and a large part of the belowground C is exuded from roots into the rhizosphere. Jones *et al.* (2009) estimate net rhizodeposition at around 11% of the net fixed C or 27% of C allocated to roots. This would correspond to 400–600 kg C ha<sup>-1</sup> during the vegetative period of grasses and cereals. However below-ground C allocation and exudation vary between and within plant species, and with light conditions, soil moisture and nutrient conditions, grazing and other variables. Soil microbes and fungi also release carbon compounds into the

environment. While bacteria are relatively well studied, far less is known about soil fungi (de Boer, 2005). In the vast majority of cases, however, the ultimate source of the carbon that is processed and exuded by the soil microbes is derived originally from plants and photosynthesis.

Some authors suggest that inputs of fresh plant-derived carbon and other root-induced changes in the soil increase the turnover of existing Soil Organic Matter (SOM, Paterson *et al.*, 2009; Kuzyakov, 2010). Such 'priming' effects are not well understood, and they are not allowed for in most current models (Wutzler & Reichstein, 2008; Blagodatsky *et al.*, 2010). However, artefacts may account for many of these observations. Fontaine *et al.* (2007) working with *ex situ* cores found turnover of old SOM in subsoil was stimulated by addition of fresh organic matter but Salome *et al.* (2009), who carefully reproduced subsoil conditions, found no priming in soils from below 30cm. While it is possible that some observed instances of priming are the result of artefacts there is nonetheless considerable interest in this area (Stockmann *et al.*, 2013)

## **Decreasing the rate of decomposition of organic matter in soils**

In this section we review recent advances in the understanding of certain biological and chemical controls on the rate of decomposition of organic matter (OM) in soils, largely drawn from observation in the natural environment. In this respect the research is at a preliminary stage, so it is not yet possible to draw conclusions about practical soil management interventions based on it.

### *SOC turnover*

Studies of decomposition of organic matter in peatlands have shown inhibition of the enzymes responsible by phenolic compounds (Freeman *et al.*, 2001; Zibilske & Bradford, 2006; Toberman *et al.*, 2008; Sinsabaugh, 2010; Benoit & Starkey 1968a,b). These studies point to a particular role of phenolic compounds in the carbon cycle with three key features: (i) few enzymes degrade these abundant materials and those enzymes that do are inhibited almost completely by certain conditions or a combination of conditions found in peat; (ii) phenolic compounds inhibit other enzymes, particularly those that decompose organic matter in soil; and (iii) many phenolic compounds bind other OM especially proteins and enzymes, this in itself has two further effects: (a) it reduces the availability of OM for decomposition and (b) it removes other enzymes such as hydrolases that effect that decomposition.

The surprising conclusion from this review of research is that a key oxidation step in the decomposition of organic matter in soil is susceptible to inhibition by a specific class of phenolic compounds. Carbon accumulation in peat soils may be the result of restricted oxidase and peroxidase activity that remove these phenols, which in turn is the result of a lack of oxygen but does not result from any general impact of the lack of oxygen on the soil microflora as a whole. If so, organic matter decomposition in soil might be reduced by the application of inhibitors or anti-oxidants.

Aerts *et al.* (1999) have exploited the ability of phenol-containing substances to bind proteins by ensuring their presence in the rumen of sheep by adding polyphenol-containing (tannin) forage residues to the animals' diet. Aerts *et al.* (1999) attribute the beneficial effects on the animals to the ability of the tannins to bind both proteins in the feed and the enzymes responsible for degradation under the anaerobic conditions in the rumen. Proteins, especially then survive long enough to reach other parts of the animals' guts where they can be absorbed, so improving the effectiveness of the nutrition. Intriguingly, this raises the possibility that tannin-rich diets might lead to the introduction of tannins to soil via manure and so reduce the turnover of organic carbon in soil.

In separate work, Rimmer (2006) proposed the more general hypothesis that the decomposition of plant residues in soil is effected by free radicals and that anti-oxidants such as quinines which are common in soil, moderate this activity by quenching the free radicals. Thus, observed SOC turnover would be the balance between these components. Phenols and polyphenols are anti-oxidants. Rimmer & Smith (2009) have found anti-oxidants in soil and have related the anti-oxidant capacity of soils to the total soil carbon content but did not find evidence that the anti-oxidant capacity of the soil was derived from plant litter. Additionally they found that anti-oxidant capacity decreased with depth in the soil (Rimmer & Smith, 2009). There has been little further uptake of these ideas in the scientific literature and the key experiments where anti-oxidants are deliberately introduced into soil or removed appear to be lacking. Organic amendments naturally containing large amounts of anti-oxidants were found to decompose more slowly during an initial 7 day period than amendments without anti-oxidants (Rimmer *et al.*, 2013)

## *Biochar*

Biochar – the porous carbonaceous solid produced by thermochemical conversion of organic materials in an oxygen depleted atmosphere has been reviewed recently by Shackley & Sohi (2009) and will not be repeated here. Essentially these authors conclude the residence time of biochar in soil is often in the order of millennia as opposed to a few tens of years for other soil organic carbon. They review benefits to yield and possible mechanisms for this but also the risks associated with adding biochar to soil. These include a liming benefit but also the potential addition of long-lived toxins along with the char.

## *Wetlands*

Grip (drain) blocking in peat soils is hypothesised to reduce carbon losses through reduced decomposition and reduced loss of dissolved organic carbon. Billett *et al.* (2010) suggest that current rates of accumulation of carbon in UK peatlands (56 to 72 g C m<sup>-2</sup> yr<sup>-1</sup>) are at the low end of rates seen during the last 150 years. However, losses of methane may increase and the tradeoff between reduced emissions of CO<sub>2</sub> and adverse effects of emission of CH<sub>4</sub> are currently being assessed for the UK (Defra, 2012). Consequently, it is too early to assess restoration of upland peat as a

technology for reducing overall Green House Gas (GHG) emissions even if it is highly likely to increase stores of carbon.

Managed realignment of coastal defences is also a possible means to increase carbon storage if the deposited sediments contain carbon eroded with soil. Here it appears that a balance must be struck with the emission of N<sub>2</sub>O from denitrification and that the ideal is the establishment of saline rather than non-saline marshes (Andrews *et al.*, 2006)

#### *Tillage*

Powlson *et al.* (2011, 2012) have reviewed the scope for increasing soil carbon by reducing tillage and adding organic materials to soil. In general this work agreed with earlier studies as to the quantities of carbon involved but differed somewhat in interpretation. Direct drilling probably allows soil to increase in SOC by about 0.3 t ha<sup>-1</sup> yr<sup>-1</sup> although the data available for UK conditions is not sufficient to say if this figure is statistically greater than zero. Most soils in the UK that are not ploughed are in some kind of rotational tillage. Here the risk is that even if there is a gain in carbon stored during the non-inversion rotation, on ploughing this gain will be lost (Conant *et al.*, 2007). Powlson *et al.* (2011, 2012) also consider the addition of organic waste materials to soil such as manure or straw. Here the result is less equivocal as regards a change in soil organic carbon status but with regard to climate change Powlson *et al.* (2011) also caution that the original use of a material must be considered before its addition to soil can be considered as carbon sequestration in the service of mitigation of climate change. If the material is simply diverted from one soil to another then this can hardly be interpreted as genuine sequestration

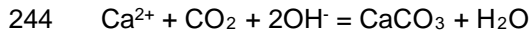
#### **Enhanced mineral weathering in soils to sequester CO<sub>2</sub>**

One of the methods proposed to 'geo-engineer' the global climate is to accelerate the weathering of silicate rocks on land to form carbonate rocks, thereby fixing CO<sub>2</sub> from the atmosphere (Royal Society, 2009b). Conversion of silicates to carbonates is the main natural control on atmospheric CO<sub>2</sub> on Earth on geological timescales. The proposal is to accelerate it by applying finely-divided silicate rocks (e.g. olivine) to soils, with the carbonate so fixed being stored in the soil as mineral carbonate and, ultimately, exported in drainage waters to rivers and the deep ocean. The ecological consequences of this for the land surface and seas are highly uncertain. In addition, the potential for this method and its immediate consequences for soils are unknown.

The literature on this at the planetary or national scale is thin (Schuiling & Krijgsman, 2006; Hartmann & Kempe, 2008). However there is plenty of information on rates of mineral weathering in soils (e.g. Moulton *et al.*, 2000; Andrews & Schlesinger, 2001; and references therein) and the fate of lime (e.g. Kirk *et al.*, 2010 and references therein). The conclusions from this literature review are as follows.

#### *Large-scale application of silicates to sequester carbon*

242 The removal of CO<sub>2</sub> from the atmosphere by precipitation as mineral carbonates (either Ca or Mg or  
243 both) can be summarised with the reaction



245 i.e. the reaction requires sources of (a) CO<sub>2</sub>, (b) Ca<sup>2+</sup> or Mg<sup>2+</sup> cations and (c) base, i.e. Brønsted  
246 base, capable of neutralizing H<sup>+</sup> ions. Soils are a good source of CO<sub>2</sub> for this purpose because CO<sub>2</sub>  
247 fixed from the atmosphere by plants is released into the soil through the decomposition of plant  
248 exudates and residues. As a result the CO<sub>2</sub> pressure in the soil air is typically five to 50 times that in  
249 the bulk atmosphere.

250 The planetary-scale carbon sequestration sought by geo-engineers requires silicate applications in  
251 excess of acidifying processes so that the base in the silicates is transformed to carbonates on land  
252 or ultimately in the deep ocean. Precipitation of carbonates in the soil as a result of large additions of  
253 silicate base might occur, depending on rates of carbonate precipitation versus rates of HCO<sub>3</sub><sup>-</sup>  
254 leaching. But large-scale carbonate precipitation in soils is probably not desirable given its likely  
255 effects on soil conditions and plant growth. So the aim would be to generate increases in the flux of  
256 HCO<sub>3</sub><sup>-</sup> through soils, rivers and into the sea. If the carbonate remains dissolved in the sea, rather than  
257 precipitating, then two moles of CO<sub>2</sub> are stored per mol of Ca silicate weathered, or four moles of  
258 CO<sub>2</sub> in the case of Mg silicates.

259 Transfer of carbonate out of the soil requires that the soil pH be raised to the point where leaching of  
260 the bicarbonate anion HCO<sub>3</sub><sup>-</sup> with metal cations M<sup>+</sup> is significant. Typically this means pHs greater  
261 than neutral. Similar reasoning explains the well-known phenomenon that the neutralizing effect of  
262 lime applied to the soil surface is only transferred to the subsoil when there is an excess of CaCO<sub>3</sub> in  
263 the surface. Russell (1973) reports that soils containing free CaCO<sub>3</sub> in temperate regions may lose  
264 Ca<sup>2+</sup> with HCO<sub>3</sub><sup>-</sup> in leachate at rates of the order of 2.5 kg CaCO<sub>3</sub> ha<sup>-1</sup> y<sup>-1</sup>, based on measurements  
265 in lysimeters. Calcareous soils at Rothamsted lose 300–400 kg CaCO<sub>3</sub> ha<sup>-1</sup> y<sup>-1</sup>. Soils without free  
266 CaCO<sub>3</sub> will also leach Ca<sup>2+</sup> + HCO<sub>3</sub><sup>-</sup>. But the lower the pH and the less the saturation of the soil  
267 exchange complex with Ca<sup>2+</sup>, the lower will be the loss. In arable land with heavy dressings of  
268 ammoniacal fertilizers, loss of Ca<sup>2+</sup> with NO<sub>3</sub><sup>-</sup> will be much greater than its loss with HCO<sub>3</sub><sup>-</sup>.

269 A further issue is how to maximise the rate of dissolution of silicates, favoured by low pH, whilst  
270 maximising the leaching of M<sup>+</sup> + HCO<sub>3</sub><sup>-</sup>, favoured by high pH. Manning and Renforth (2013) give data  
271 on the thermodynamics of dissolution of the most widely distributed Ca and Mg silicates in acid and  
272 neutral solutions, and conclude that rates of dissolution will in general be far slower than rates of CO<sub>2</sub>  
273 generation in plant and soil organic matter turnover. Based on the activation energies given by  
274 Manning and Renforth (50–80 kJ mol<sup>-1</sup>), rates of dissolution are likely to be limited by surface  
275 processes rather than by diffusion away from the dissolving surface (for which activation energies are  
276 typically in the range 15–30 kJ mol<sup>-1</sup> – Glasstone *et al.*, 1941). On the same basis, calcite (CaCO<sub>3</sub>)

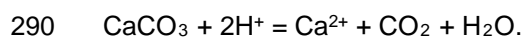
277 dissolution is much faster, and likely to be limited by diffusion and the degree of saturation of the soil  
278 solution (Nye & Ameloko, 1987).

279 Also unknown are the ecological consequences of large silicate applications at the site of application.  
280 Of concern are the consequences for (a) plant growth, e.g. via deficiencies of P and micronutrients at  
281 high pH in calcifuge plants; (b) soil structure and sealing of the soil by SiO<sub>2</sub> precipitation; and (c) the  
282 turnover of soil organic matter and leaching of dissolved organic carbon. Equally we know little about  
283 the consequences of increased HCO<sub>3</sub><sup>-</sup> fluxes downstream in rivers, local seas, and the deep ocean.

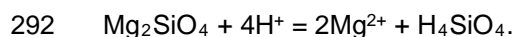
#### 284 *Replacement of agricultural lime with silicates*

285 In theory, there is a significant potential for avoiding carbon emissions by replacing current agricultural  
286 lime applications with ground silicates, assuming the C costs of production and transport are the  
287 same.

288 Liming to balance acidity produced in nitrogen transformations, crop off-take, acid deposition etc.  
289 releases 1 mol of CO<sub>2</sub> to the atmosphere per 2 mol of acid (i.e. H<sup>+</sup>) neutralised.



291 Whereas, with silicates there would be no CO<sub>2</sub> release, e.g. for the simple olivine Mg<sub>2</sub>SiO<sub>4</sub>:



293 According to Defra (2008), average annual lime rates are of the order of 250, 100 and 25 kg CaO ha<sup>-1</sup>  
294 on arable land, managed grassland and semi-natural grassland, respectively, and the respective  
295 areas of these land uses in England and Wales are 64, 39 and 13 × 10<sup>3</sup> km<sup>2</sup>. If 2/56 kmol OH<sup>-</sup> are  
296 produced per kg CaO reacting, and 1 kmol CO<sub>2</sub> is saved per kmol H<sup>+</sup> neutralised by silicate rather  
297 than lime, then the total annual avoided emission is close to 1 million t CO<sub>2</sub>-C.

298 Data compiled by Renforth et al. (2009, 2011) indicate there are many times the required amounts of  
299 silicate wastes available from various sources across UK and globally. This includes wastes from  
300 igneous rock quarry fines, concrete demolition, slags and fly ash, which amount to several tens of  
301 million t CO<sub>2</sub>-C equivalents.

302 Therefore, in principle this is a real possibility. The consequences for soil conditions would require  
303 further investigation. In particular, the extent to which SiO<sub>2</sub> would accumulate in soils over the long  
304 term, and the consequences of this for soil conditions; and also the extent of contaminant additions  
305 with waste materials. Given that the acidity of the oceans is rising as atmospheric CO<sub>2</sub> concentrations  
306 rise, the resulting increase in alkalinity might be beneficial. However the ecological consequences are  
307 highly uncertain.

## Enhanced storage of carbon in urban soils

Urban soils include any soil of natural or imported origin (e.g. made ground, including engineered fill) or soil that has been modified, for example by the removal of topsoil or its mixture with the subsoil. Urban land accounts for around 9.0% of land in England, whilst the equivalent percentage for Wales is 4.3% (Morton et al., 2011). It has been suggested that urban soils develop a distinct biogeochemistry from their rural equivalents (Kaye et al. 2006). There is some evidence from England that organic carbon storage may be enhanced in urban soil.

### *Organic carbon*

Analyses of urban soil samples from three locations across the UK showed substantial variations in organic carbon concentrations between centres and no consistent relationships with local, grassland soils (Rawlins et al., 2008). These data, in combination with unpublished data for other centres suggest that the relative importance of the factors which influence soil organic carbon (SOC) concentrations in urban soils may differ from those in rural soils. The wide variation in SOC concentrations in urban topsoil across eight UK urban centres is shown in Table 1. It is notable that median SOC concentrations are particularly large in Leicester (7%) and Stoke-on-Trent (6.8%). These values are larger than for both permanent grassland (5.7%) and ley grassland (3.6%) in topsoil across England and Wales (data from the Landis database ([www.landis.org.uk](http://www.landis.org.uk))). The total quantity of SOC in urban topsoil (0-15 cm depth) in England is around 8.5 MtC. This calculation was based on an estimate of built up areas and garden land area (11 690 km<sup>2</sup>; Morton et al., 2011) assuming that (Wood et al., 2006) 50% has zero carbon due to replacement by a sealed layer. We applied a pedotransfer function to compute bulk density from SOC (Alexander, 1980) using the urban SOC analyses for those data summarised in Table 1.

Further analyses of the SOC data for Coventry and Stoke showed that variations in soil texture cannot account for the large differences in their median SOC concentrations. Application of the RothC model to quantitative data for ten of the sites in Stoke-on-Trent suggested that annual carbon inputs required to maintain SOC concentrations were between 1 and 5.4 tonnes C ha<sup>-1</sup> yr<sup>-1</sup>; three sites had values >5 tonnes C ha<sup>-1</sup> yr<sup>-1</sup> which equates to substantial amounts of carbon addition. So either carbon inputs are particularly large at these sites – which is not suggested by local land use – or the processes controlling turnover of organic carbon are different to those found in soils under arable or pasture. If the latter is the case, there are physical, chemical and biological mechanisms which could account for maintenance of larger SOC concentrations. A possible physical mechanism is that urban soils have been more severely compacted – due to construction-related activities – which contributes to the enhanced preservation of SOC as soil microbes cannot mineralize a proportion of soil carbon. Alternatively, the soil microbial population in urban soils may differ from that in equivalent rural soil types leading to changes in carbon turnover and increased SOC concentrations. A potential chemical mechanism is stabilisation of soil organic matter by Ca<sup>2+</sup> (Oades, 1988). Soils of urban areas are

known to be enriched in exchangeable  $\text{Ca}^{2+}$  relative to rural soils due to the dispersal of construction wastes (see next section). The other major factor which could account for the variations observed are the frequency and timing of historical soil disturbance at these sampling sites which impact carbon turnover. At present we do not have sufficient information on historic land use change to determine whether this might account for the large observed differences.

In urban areas, architects are increasingly incorporating 'green roofs' into buildings Schrader and Böning (2006) found between 1.8 and 4.6% carbon in the soils in such roofs in Hannover, depending on age. It is not clear, however, if organic matter was incorporated with a mineral substrate at the start of the experiment and to what extent the observed carbon storage reflects these starting values.

To summarise, it appears there may be a mechanism which is leading to the enhanced storage of organic carbon in urban soil, but to date we do not have sufficient knowledge to explain it. With the data available, we can make some estimates of its potential magnitude for enhancing carbon storage in urban soil. Two urban centres (Stoke-on-Trent and Leicester) have median topsoil organic carbon concentrations of around 7%, which is between 1 and 2.5 % greater than in the other urban areas. It may be possible to increase SOC concentrations in some urban areas by this quantity, but further research is needed to understand the mechanisms before a soil management strategy or other interventions could be implemented.

#### *Inorganic carbon*

The contribution that mineral carbonation – the addition of certain minerals to soils to remove  $\text{CO}_2$  as carbonates – could make to enhanced carbon storage in soils is discussed above. The essential requirements are the availability of calcium ( $\text{Ca}^{2+}$ ) or magnesium ( $\text{Mg}^{2+}$ ) cations and a source of base to convert dissolved  $\text{CO}_2$  to  $\text{CO}_3^{2-}$ . Certain silicate minerals may be suitable for this, and urban soils may be particularly suited because of the local availability of such silicates as wastes from the construction industry. The potential for this has been demonstrated by Renforth *et al.* (2009) and Washbourne *et al.* (2012) who measured rates of *de novo*  $\text{CaCO}_3$  formation of up to  $25 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  over 10 years in urban brownfield sites receiving demolition waste from concrete buildings. Urban soils are known to be enriched in Ca due to the dispersal of construction wastes, including hydrated cement minerals, the mineral portlandite ( $\text{Ca}(\text{OH})_2$ ), and, to a lesser extent, gypsum ( $\text{CaSO}_4$ ) from plasterboard wastes. These minerals are prone to weathering in the soil environment, yielding  $\text{Ca}^{2+}$ . Using data from the British Geological Survey's geochemistry database for seven urban centres in south and eastern England, we found the concentrations of total Ca were on average  $4000 \text{ mg kg}^{-1}$  greater in urban topsoil (0–15 cm depth) compared with equivalent, adjacent rural topsoil, with typical enrichments of between 150 and 200% (Defra, 2010). We restricted our analysis to urban soils in south-east England because we considered mean annual rainfall in these areas (<550 mm) would not be sufficient to

leach dissolved  $\text{Ca}^{2+}$  beyond depths of around 1 metre. Based on these data and some simplifying assumptions, we computed the capacity of the soils in these urban areas to sequester C (based on excess Ca) to be 0.5 MtC (megatonnes of carbon).

#### **Enhanced carbon storage in subsoils**

Kleber (2010) and Dungait et al. (2012) suggest that turnover of organic materials in soil is less about what SOM is and more about where it is. Some geological parent materials contain small but significant concentrations of fossil carbon which is incorporated into the soil during its formation. This could be either inorganic, geogenic or organic carbon. An example of the former is the carbon present as carbonate derived from the weathering of chalk parent materials. Organic carbon is also often present in the clay-rich soil parent materials of southern England and also the recalcitrant organic carbon derived from coal-bearing strata. It is not possible to increase the quantities of fossil carbon in soil and so this fossil carbon is outside the scope of our study. However, stabilisation of carbon on the surfaces of minerals derived from weathering of parent material can enhance C storage in the subsoil.

The question we pose here is whether it is possible to increase the quantities of organic carbon stored in the subsoils (> 25 cm depth) of England and Wales either through different land management practices (changes in land use or cultivation), or possibly the application of organic amendments to the topsoil. Before we can address this question it is useful to review both the knowledge and knowledge gaps concerning the carbon stored in subsoil of England and Wales and the mechanisms which control it.

Bradley *et al.* (2005) have estimated that subsoils in England and Wales contain approx. 0.5% C by weight (Table 2). On average, soil organic carbon becomes both more recalcitrant and older with increasing depth as soil biota have utilised the simpler organic compounds, leaving behind the more resistant, energy-poor fractions.

Studies have shown that, in topsoils, the dominant factors controlling SOC stabilization include (reviewed by Davidson & Janssens, 2006) texture, mineralogy, base cation content, soil aggregation, plant litter type and the chemical recalcitrance of soil organic matter, and microbial populations, plus interactions between these factors. This constitutes an extremely complex system. Stewart *et al.* (2007) demonstrated that certain topsoils may become carbon saturated. The inherent physical and chemical characteristics of the soil may determine the maximum quantity of soil organic matter which can be stabilised (Six *et al.*, 2002). There is strong evidence that iron-oxide content is the dominant factor controlling stabilisation of organic matter in acid forest soils (Mikutta *et al.*, 2006), whilst the quantity of clay and silt are most important in the surface horizons of arable and grassland systems (Hassink & Whitmore, 1997).

Far less research has been undertaken on subsoil systems. One study showed that when fresh carbon is added to subsoil it has a priming effect which leads to the degradation of previously stable subsoil carbon (Fontaine *et al.*, 2007), though a subsequent study (Salome *et al.*, 2009) observed greater spatial heterogeneity in factors which determine carbon turnover in subsoil compared to topsoil and suggested that controls on carbon turnover may be different between topsoil and subsoil. Observations that the microbial biomass or activity in subsurface soil is more variable than in topsoil suggest that spatial relationships between organic matter and microbial communities may be more significant in the former. This is consistent with observations of distinct flow paths along which younger and less recalcitrant carbon is located, adjacent to the subsoil matrix containing smaller quantities of more recalcitrant carbon (Chabbi *et al.*, 2009). This young carbon is likely to become mineralised in the short or medium-term and may not contribute to long-term carbon storage.

There is evidence that the association between mineral surfaces and organic matter in subsoils differs from that in topsoil. Organic matter coatings on subsoil mineral surfaces tend to be thin and patchy whilst those in topsoil samples are thicker and often completely cover mineral particles. So the potential for stabilising organic matter by adsorption to mineral surfaces in subsoil may be substantially less than in topsoil (Wagai *et al.*, 2009). This may in part be explained by the nature of the organic carbon; in subsoil it has undergone more microbial processing by comparison to that in topsoil. The quantity of carbon stored in the subsoil may therefore depend more on its inherent recalcitrance than the mechanisms of its stabilisation on mineral surfaces. Watts *et al.* (2005) suggested that the action of the microbial biomass was crucial in the binding of organic matter and the formation of soil aggregates and so it is possible that the reduced microbial activity in the subsoils has an effect on carbon stabilisation.

Increasing the storage of organic carbon in subsoil (> 30 cm depth) requires: i) a mechanism for its emplacement at depth, and ii) confidence that this carbon will stay in the soil (i.e. be stabilised), and will not be degraded by soil biota or lead to enhanced losses of existing soil carbon. We consider that methods involving direct emplacement of fresh organic carbon into subsoil will not lead to enhanced storage of carbon, and could be counter-productive through disturbance and mineralisation losses of topsoil carbon. An alternative to direct emplacement is to enhance the natural process of migration of carbon from surface to depth; this is dominated by leaching of dissolved organic carbon (DOC). Leaching of DOC is known to be greater under forests than grassland and arable land. Minerals deeper in the soil profile, such as iron oxides, have a large capacity to stabilise this carbon (Mikutta *et al.*, 2006). Plant breeding might also enhance access to these stabilising sites (Kell, 2012)

A recent study from California (Sanderman & Amundson, 2009) demonstrated that DOC movement and retention in a fine-textured (clay-rich) mineral soil contributes 22% of the annual C inputs below 40 cm in a coniferous forest, whereas only 2% of the C inputs below 20 cm in equivalent grassland (prairie) soils were accounted for by this process. The authors suggest that in more coarsely textured soil, the carbon transported to depth may be less effectively stabilised by comparison to clay-rich

lithologies. Another study (Arevalo *et al.*, 2009) which compared the storage of carbon in deeper soil horizons under different land use types also demonstrated that long-term forested sites store more carbon at 20-50 cm depth than recent forest plantation (2-9 years), grassland or crops. The majority of the organic carbon in the subsoil was associated with the finer fractions. Hence, there is evidence that conversion of grassland or arable land use to forest could enhance carbon storage in subsoil where it has a fine texture or large quantities of Fe-oxide phases (Mikutta *et al.*, 2006).

## **Conclusions**

Most means to store carbon in soil suffer from slow build up or restrictions in general use based on climate, soil type or the need to grow food on the land. Those technologies show that promise for widespread, rapid manipulation of the carbon cycle such as (i) the use of polyphenols to complex SOM or inhibit enzymes that decompose it, (ii) enhancing storage in topsoil based on mechanisms of physical protection that currently operate in the subsoil, or (iii) mineral carbonation, all require research before they could be used or their potential deployment in practice be assessed. Increased use of improved grasses where possible could increase carbon storage now; breeding might provide additional perennial crops or varieties in the future that divert carbon to the subsoil. Interventions on urban soils are necessarily restricted to a small percentage of the land area.

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**Table 1** Median soil organic C contents of urban top soils (0–15 cm depth) from eight urban centres in the UK

Urban centre	Sample counts (n)	Median OC* (g kg <sup>-1</sup> )	Median OC* (%)
Glasgow	1382	52	5.2
Stoke-on-Trent	747	68	6.8
Coventry	396	34	3.4
Derby	276	43	4.3
Manchester	301	49	4.9
Leicester	309	70	7.0
Belfast	1198	41	4.1
London**	6468	43	4.2

\* estimated from loss on ignition analysis – may include a component of recalcitrant (black) carbon

\*\*?

Source of data?

Q why both g/kg and %, Also shouldn't 43 g/kg be 4.3%?

**Table 2** Average organic C contents of subsoils at two depth ranges in different land uses across England and Wales

Soil depth range (cm)	Organic C content (g kg <sup>-1</sup> )			
	Arable	Ley grass	Permanent grass	Other
25–50	13.0	13.6	15.7	18.5
50–100	3.6	4.0	4.4	4.3