

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

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## 6 Abstract

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

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

## 19 Introduction

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

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

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

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

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

51

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

57

58 In this analysis a distinction has been made between physical methods of reducing decomposition (3)  
59 of organic matter which tend to halt turnover, and methods which act on the chemical and biological  
60 processes (2) because these latter tend to slow decomposition down rather than stop it altogether.  
61 For previous reviews of this topic see Smith *et al.* (2000), Powlson *et al.* (2011) and Stockmann *et al.*  
62 (2013).

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

#### 64 *Agroforestry and intercropping*

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

67 levels found in forest soils (Bolin *et al.*, 2000), arable soils usually contain much less C than either  
68 forest or pasture (Bolin *et al.*, 2000). Mixed systems, that is to say trees and arable (known as  
69 silvoarable or agroforestry systems) or trees and grass (known as silvopastoral systems) have been  
70 proposed as a means to extend the benefits of forest to farmed land. Because different species use  
71 resources differently, they can be complementary with one another, often yielding more and  
72 consuming less than corresponding sole crops. It has been suggested recently that agroforestry and  
73 intercropped systems increase the store of carbon in land managed for production (Nair *et al.*,  
74 2009a,b). Nair *et al.* (2009b) report a range of soil C sequestration data with modest values of around  
75 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  
76 years, with little difference in loamy sand and sandy clay soils. Agroforestry and silvopastoral systems  
77 contain more carbon in soil than cropland, but almost all the evidence comes from work in tropical and  
78 sub-tropical soils with little work in temperate systems (Jose, 2009). Even in these studies, few  
79 woodland controls exist so it is not clear if the resource-use complementarity referred to above leads  
80 to extra carbon storage relative to sole species. Quinckenstein *et al.*, 2009; and Montagnini & Nair  
81 (2004) who reviewed C sequestration in soils under temperate agroforestry systems cite a figure of  
82 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  
83 temperate agroforestry systems for increasing soil C

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

92 Intercropping field crops might improve C storage relative to monoculture controls too. Bolin *et al.*  
93 (2000) quote data suggesting that temperate grasslands store 236 C Mg ha<sup>-1</sup> as a global average.  
94 Sequestration rates of 65-70 Mg ha<sup>-1</sup> in 100 years have been quoted (Abberton *et al.*, 2007). On the  
95 other hand Skinner *et al.*, (2006) found that soil C either remained the same with species mixtures or  
96 declined during two years after sowing into a soil that had previously supported winter wheat. The  
97 potential for soil carbon storage in intercropped soils does not appear to have been widely  
98 investigated.

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

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

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

#### 115 *Improved grasses*

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

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

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

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

138 environment. While bacteria are relatively well studied, far less is known about soil fungi (de Boer,  
139 2005). In the vast majority of cases, however, the ultimate source of the carbon that is processed and  
140 exuded by the soil microbes is derived originally from plants and photosynthesis.

141 Some authors suggest that inputs of fresh plant-derived carbon and other root-induced changes in the  
142 soil increase the turnover of existing Soil Organic Matter (SOM, Paterson *et al.*, 2009; Kuzyakov,  
143 2010). Such 'priming' effects are not well understood, and they are not allowed for in most current  
144 models (Wutzler & Reichstein, 2008; Blagodatsky *et al.*, 2010). However, artefacts may account for  
145 many of these observations. Fontaine *et al.* (2007) working with *ex situ* cores found turnover of old  
146 SOM in subsoil was stimulated by addition of fresh organic matter but Salome *et al.* (2009), who  
147 carefully reproduced subsoil conditions, found no priming in soils from below 30cm. While it is  
148 possible that some observed instances of priming are the result of artefacts there is nonetheless  
149 considerable interest in this area (Stockmann *et al.*, 2013)

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

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

### 155 *SOC turnover*

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

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

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

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

## 192 *Biochar*

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

## 200 *Wetlands*

201 Grip (drain) blocking in peat soils is hypothesised to reduce carbon losses through reduced  
202 decomposition and reduced loss of dissolved organic carbon. Billett *et al.* (2010) suggest that current  
203 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  
204 seen during the last 150 years. However, losses of methane may increase and the tradeoff between  
205 reduced emissions of CO<sub>2</sub> and adverse effects of emission of CH<sub>4</sub> are currently being assessed for  
206 the UK (Defra, 2012). Consequently, it is too early to assess restoration of upland peat as a

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

209

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

#### 214 *Tillage*

215 Powlson *et al.* (2011, 2012) have reviewed the scope for increasing soil carbon by reducing tillage  
216 and adding organic materials to soil. In general this work agreed with earlier studies as to the  
217 quantities of carbon involved but differed somewhat in interpretation. Direct drilling probably allows  
218 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  
219 sufficient to say if this figure is statistically greater than zero. Most soils in the UK that are not  
220 ploughed are in some kind of rotational tillage. Here the risk is that even if there is a gain in carbon  
221 stored during the non-inversion rotation, on ploughing this gain will be lost (Conant *et al.*, 2007).  
222 Powlson *et al.* (2011, 2012) also consider the addition of organic waste materials to soil such as  
223 manure or straw. Here the result is less equivocal as regards a change in soil organic carbon status  
224 but with regard to climate change Powlson *et al.* (2011) also caution that the original use of a material  
225 must be considered before its addition to soil can be considered as carbon sequestration in the  
226 service of mitigation of climate change. If the material is simply diverted from one soil to another then  
227 this can hardly be interpreted as genuine sequestration

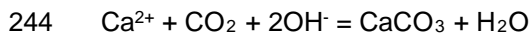
#### 228 **Enhanced mineral weathering in soils to sequester CO<sub>2</sub>**

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

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

#### 241 *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>)



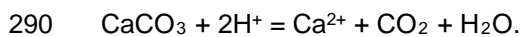
277 dissolution is much faster, and likely to be limited by diffusion and the degree of saturation of the soil  
278 solution (Nye & Ameloko, 1987).

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.

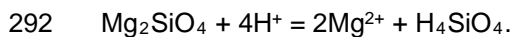
#### 284 *Replacement of agricultural lime with silicates*

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.

308 **Enhanced storage of carbon in urban soils**

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

315 *Organic carbon*

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

330 Further analyses of the SOC data for Coventry and Stoke showed that variations in soil texture cannot  
331 account for the large differences in their median SOC concentrations. Application of the RothC model  
332 to quantitative data for ten of the sites in Stoke-on-Trent suggested that annual carbon inputs required  
333 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  
334 tonnes C ha<sup>-1</sup> yr<sup>-1</sup> which equates to substantial amounts of carbon addition. So either carbon inputs  
335 are particularly large at these sites – which is not suggested by local land use – or the processes  
336 controlling turnover of organic carbon are different to those found in soils under arable or pasture. If  
337 the latter is the case, there are physical, chemical and biological mechanisms which could account for  
338 maintenance of larger SOC concentrations. A possible physical mechanism is that urban soils have  
339 been more severely compacted – due to construction-related activities – which contributes to the  
340 enhanced preservation of SOC as soil microbes cannot mineralize a proportion of soil carbon.  
341 Alternatively, the soil microbial population in urban soils may differ from that in equivalent rural soil  
342 types leading to changes in carbon turnover and increased SOC concentrations. A potential chemical  
343 mechanism is stabilisation of soil organic matter by Ca<sup>2+</sup> (Oades, 1988). Soils of urban areas are

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

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

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

#### 361 *Inorganic carbon*

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

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

382

383

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

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

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

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

405 Studies have shown that, in topsoils, the dominant factors controlling SOC stabilization include  
406 (reviewed by Davidson & Janssens, 2006) texture, mineralogy, base cation content, soil aggregation,  
407 plant litter type and the chemical recalcitrance of soil organic matter, and microbial populations, plus  
408 interactions between these factors. This constitutes an extremely complex system. Stewart *et al.*  
409 (2007) demonstrated that certain topsoils may become carbon saturated. The inherent physical and  
410 chemical characteristics of the soil may determine the maximum quantity of soil organic matter which  
411 can be stabilised (Six *et al.*, 2002). There is strong evidence that iron-oxide content is the dominant  
412 factor controlling stabilisation of organic matter in acid forest soils (Mikutta *et al.*, 2006), whilst the  
413 quantity of clay and silt are most important in the surface horizons of arable and grassland systems  
414 (Hassink & Whitmore, 1997).

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

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

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

447 A recent study from California (Sanderman & Amundson, 2009) demonstrated that DOC movement  
448 and retention in a fine-textured (clay-rich) mineral soil contributes 22% of the annual C inputs below  
449 40 cm in a coniferous forest, whereas only 2% of the C inputs below 20 cm in equivalent grassland  
450 (prairie) soils were accounted for by this process. The authors suggest that in more coarsely textured  
451 soil, the carbon transported to depth may be less effectively stabilised by comparison to clay-rich

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

## 458 **Conclusions**

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

468

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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