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# Rapid removal of atmospheric CO<sub>2</sub> by urban soils

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## **Keywords:**

Mineral carbonation, soil, climate change

1 TOC/Abstract art



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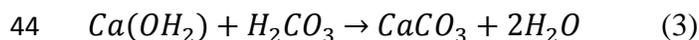
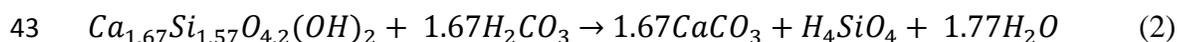
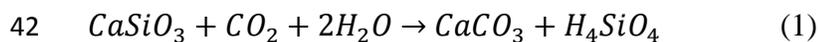
4 **Abstract**

5 The measured calcium carbonate content of soils to 100 mm depth at a large urban  
6 development site has increased over 18 months at a rate that corresponds to the  
7 sequestration of 85 tonnes CO<sub>2</sub> per hectare (ha<sup>-1</sup>) (8.5 kg CO<sub>2</sub> m<sup>-2</sup>) annually. This is a  
8 consequence of rapid weathering of calcium silicate and hydroxide minerals derived from  
9 demolition of concrete structures, which releases Ca that combines with CO<sub>2</sub> ultimately  
10 derived from the atmosphere, precipitating as calcite. Stable isotope data confirm an  
11 atmospheric origin for carbonate-carbon, and <sup>14</sup>C dating indicates the predominance of  
12 modern carbon in the pedogenic calcite. Trial pits show that carbonation extends to depths  
13 of 1 m or more. Work at other sites shows that the occurrence of pedogenic carbonates is  
14 widespread in artificially created urban soils containing Ca and Mg silicate minerals.  
15 Appropriate management of less than 12,000 hectares of urban land to maximise calcite  
16 precipitation has the potential to remove 1 million tonnes of CO<sub>2</sub> from the atmosphere  
17 annually. The maximum global potential is estimated to be approximately 700-1,200 Mt  
18 CO<sub>2</sub> per year (representing 2.0-3.7% of total emissions from fossil fuel combustion) based  
19 on current rates of production of industry-derived Ca and Mg-bearing materials.

## 20 **Introduction**

21 There is a global commitment to reduce greenhouse gas emissions; the UK Government is  
22 currently committed to an 80% reduction by 2050 (against a 1990 baseline). A number of  
23 approaches envisage ways in which climate mitigation could be achieved practically.  
24 Pacala and Socolow (2004) estimated that 26 Gt CO<sub>2</sub> a<sup>-1</sup> by 2050 of CO<sub>2</sub> would need to be  
25 removed from the atmosphere in order to compensate wholly for anthropogenic emissions.  
26 They propose that a number of individual mitigation approaches may potentially be used in  
27 unison to remove equally sized ‘stabilisation wedges’ of 4 Gt CO<sub>2</sub> a<sup>-1</sup> each by 2050. This  
28 view is revised by Davis et al (2013), who recognise that continued growth in annual  
29 emissions since 2003 required more wedges than previously considered, and stress the  
30 importance of supporting energy technology innovation to achieve the required targets.<sup>1,2</sup>

31 Soils emit almost 275 Gt CO<sub>2</sub> a<sup>-1</sup> as a consequence of plant root respiration and the  
32 mineralisation of organic carbon, and so they have an important influence on climate. The  
33 inorganic carbon content in soils is dominated by calcium and magnesium carbonate  
34 minerals.<sup>3</sup> During weathering, Ca and Mg silicate and carbonate minerals naturally react  
35 with dissolved carbon dioxide (CO<sub>2</sub>) to increase local alkalinity. Given the right conditions,  
36 some of this dissolved CO<sub>2</sub> precipitates as secondary carbonate minerals in the soil. If the  
37 Ca or Mg in the carbonate is derived from silicate weathering, and weathering products,  
38 this process provides a means of effectively capturing and fixing atmospheric CO<sub>2</sub>.<sup>4,5,6</sup>  
39 Examples of carbonation reactions are given below, using for illustrative purposes  
40 wollastonite, a natural calcium silicate (reaction 1), jennite, a hydrated cement mineral  
41 (reaction 2), and portlandite, a component of Portland cement (reaction 3):



45 The precipitation of carbonate minerals as a consequence of silicate weathering contributes  
46 to the stabilisation of atmospheric CO<sub>2</sub> over geological time periods<sup>4,7</sup> and also contributes  
47 to the formation of pedogenic carbonates in both natural<sup>8</sup> and artificial soils<sup>9</sup> over much  
48 shorter timescales. Limited information is available for the formation of pedogenic  
49 carbonates in UK soils, with Rawlins (2011)<sup>10</sup> estimating the total inorganic carbon stock  
50 of soil (0–30 cm depth) to be 186 Mt C, around 5.5% of the estimated total soil carbon  
51 stock (organic and inorganic) across the UK.

52 Work on the in situ weathering of natural and artificial silicates<sup>9,11-20</sup> has shown that  
53 artificial silicates and mineral wastes (such as construction and demolition waste, iron and  
54 steel slag and mine tailings) in soil settings rapidly weather with the associated formation of  
55 carbonate minerals. This process is influenced by a number of physical and environmental  
56 factors including small particle size and high surface area, poor crystallinity and degree of  
57 exposure through proximity to the ground surface or position relative to the water table. In  
58 this way, artificial silicates have the global potential to capture 700-1200 Mt CO<sub>2</sub> a<sup>-1</sup>,  
59 representing 2.0-3.7% of contemporary global CO<sub>2</sub> emissions (currently global annual CO<sub>2</sub>  
60 emissions account for approximately ~33 Gt CO<sub>2</sub> a<sup>-1</sup>), or one sixth to one third of a  
61 stabilisation wedge.<sup>1,21</sup> Natural silicates present a carbon capture potential orders of  
62 magnitude greater.<sup>20</sup>

63 Studies in urban soils<sup>9,16</sup> demonstrate a carbon capture potential of 12.5 kg CO<sub>2</sub> tonne  
64 soil<sup>-1</sup> a<sup>-1</sup> by this process, showing that formation of these pedogenic carbonate minerals in  
65 urban soils may be a significant and exploitable storage route for soil carbon. An increasing  
66 number of studies<sup>9,12,14-19</sup> have focussed on the carbonation of artificial and waste minerals  
67 in this context, due to their abundance and ability to provide a readily available and  
68 accessible analogue for the intentional carbonation of natural minerals.

69 In the present study we measured soil carbonate formation over 18 months, with accurate  
70 resampling of a subset of the original sample points achieved using high resolution GPS.  
71 This is the first time that a study of this kind has directly measured changes in soil  
72 inorganic carbon content in urban soils over time. We quantifiably show that CO<sub>2</sub>  
73 sequestration from the atmosphere can occur rapidly over months to years, even where sites  
74 are not intentionally managed for this purpose. Using stable and radiogenic isotope analysis,  
75 we unambiguously demonstrate the sequestration of modern atmospheric carbon dioxide.  
76 The results of this study suggest that the management of urban soils constitutes a promising  
77 and relatively inexpensive process for removing CO<sub>2</sub> from the atmosphere.

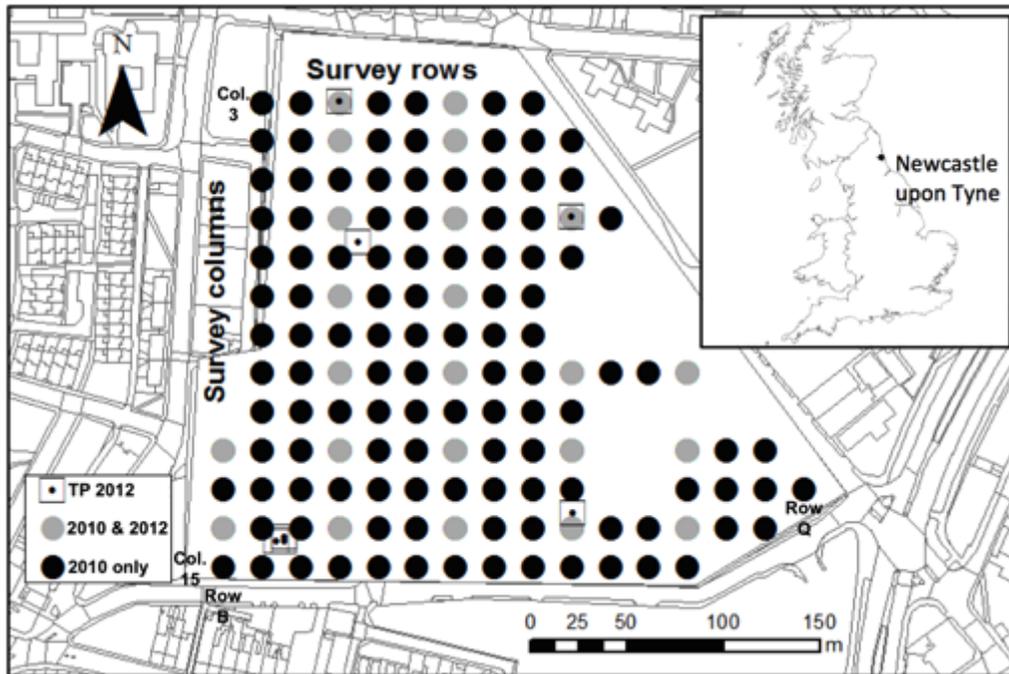
## 78 **Materials and methods**

79 Newcastle Science Central (World Geodetic System coordinates UK; 54.970406 –  
80 1.626477 (WGS84)) is a 10 ha site that is currently being developed by Newcastle  
81 University and Newcastle City Council into a multi-use ‘science, business, living and  
82 leisure’ complex.<sup>22</sup> The pre-existing complex of brewery buildings was demolished in  
83 December 2007, at which point the site was completed with a surface layer (0.2 – 6 m thick)  
84 of ‘made ground’ composed of material derived from demolition, including fines from the

85 onsite production of crushed concrete secondary aggregates. This is typical of modern  
86 development practice, which frequently involves on-site crushing to recover a secondary  
87 aggregate product while retaining crusher ‘fines’ on site as part of the soil. After demolition,  
88 the site remained undisturbed, allowing sparse growth of primary colonising plants (e.g.  
89 *Buddleia* sp.), until early 2013 when ground stabilisation work was carried out to remove,  
90 replace and compact all material to a depth of 20 m.

91 Soil samples were collected at 72 points on 16<sup>th</sup> September 2010<sup>17</sup> and again at 23 of these  
92 points on 13<sup>th</sup> March 2012, located to 25 mm accuracy using Leica GPS equipment (Leica  
93 GS15 with a CS16 controller with a Smartnet RTK correction; Fig. 1). At each location,  
94 the soil consisted of demolition rubble containing fragments of building materials grading  
95 into fines resulting from processing during demolition. 0.5-1.0 kg of this material was  
96 collected between 0-100mm depth using hand tools and sieved to <2mm onsite (eliminating  
97 large fragments of bricks and concrete, and representing a sub-sample of 30% of the total  
98 soil mass).<sup>17</sup> In parallel, 7 trial pits, to investigate carbonate formation with depth, were  
99 excavated to a depth (where possible) of up to 3 m, on 13<sup>th</sup> March 2012, taking samples of  
100 0.5-1.0 kg at approximate intervals of 0.5 m. All samples were air dried, crushed and  
101 sieved to <63µm prior to analysis.

102



103

104 **Figure 1.** Location of study site, 2010<sup>17</sup> (2010 spatial data points used in this figure are  
 105 taken from Washbourne et al 2012) and 2012 sample points, and 2012 trial pit (TP)  
 106 locations.

107

108 Methods used are described fully in Supporting Information (SI), with full details of  
 109 analytical accuracy and precision. Bulk carbonate was determined for 95 samples (72 for  
 110 2010, 23 for 2012) using an Eijkelkamp calcimeter (BS 7755-3.10:1995)<sup>23</sup>, and organic  
 111 (not reported here) and inorganic carbon content determined using a Leco CS-244 Carbon /  
 112 Sulfur Determinator. Stable isotope ratios of C and O were determined for 18 (9 for 2010, 9  
 113 for 2012) samples by Iso-Analytical, Cheshire UK, using a Europa Scientific 20-20  
 114 continuous-flow isotope ratio mass spectrometer (IRMS). Radiocarbon (<sup>14</sup>C) measurement  
 115 was carried out on 2 samples (2010 sampling round) at the Scottish Universities  
 116 Environmental Research Centre (SUERC) using an NEC Single Stage Accelerator Mass

117 Spectrometer.<sup>24,25</sup> X-Ray Fluorescence (XRF) analysis was conducted on 14 samples (7 =  
118 2010, 7 = 2012) at the University of Leicester Department of Geology using a PANalytical  
119 Axios Advanced XRF spectrometer. X-Ray Diffraction (XRD) analysis was carried out on  
120 4 samples (2 = 2010, 2 = 2012) at Newcastle University School of Chemical Engineering  
121 and Advanced Materials using a PANalytical X'Pert Pro Multipurpose Diffractometer fitted  
122 with an X'Celerator detector and a secondary monochromator. Thermogravimetry-  
123 differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC-  
124 QMS) was conducted for 6 samples (3 = 2010, 3 = 2012) using a Netzsch Jupiter STA449C  
125 TG-DSC system connected to a Netzsch Aeolos 403C QMS.

## 126 **Results and discussion**

127 Surface soils (0-100 mm) were sampled systematically on two occasions 18 months apart,  
128 with very precise location (within 25 mm). All samples were analysed immediately  
129 following collection (SI, Table 1). Where analyses were carried out on smaller subsets of  
130 surface samples these were selected primarily to provide spatially even, distributed  
131 coverage across the study site.

132 The soil samples are similar in colour and particle size distribution to those reported  
133 previously<sup>17</sup>. Soil pH was consistently high (>9.5) with values up to 11.7<sup>17</sup>.

134 Two methods of determination, calcimeter and Leco analysis (total carbon – organic  
135 carbon), give closely corresponding soil CaCO<sub>3</sub> contents. Calcimeter analysis reported bulk  
136 equivalent CaCO<sub>3</sub> contents of 39.4 ± 8.1 wt% (range 26.5 - 61.4 wt%; 2010 samples  
137 analytical precision (standard error of the mean; SEM) ± 0.73 wt%; 2012 samples SEM = ±

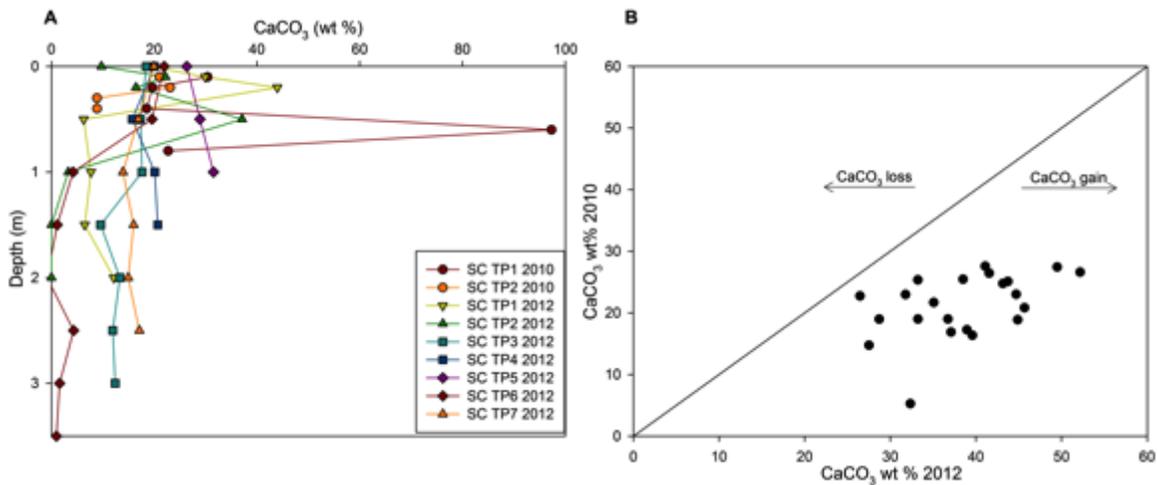
138 0.21 wt%). Leco analysis reported an average inorganic carbon content of  $4.1 \pm 1.2$  wt%  
139 (range 3.0 - 7.1 wt%; SEM  $\pm 0.48$  wt%), corresponding to  $\text{CaCO}_3$  concentrations of  $38.9 \pm$   
140  $15.6$  wt% (range 25.2 - 59.1 wt%; equivalent analytical precision  $\pm 4.0$  wt%).

141 Fig. 2A illustrates data from the depth to which trial pit samples could be taken during the  
142 sampling programme, however the total depth of material greatly exceeds this at some  
143 points across the site.<sup>17</sup> Trial pit samples to approx. 1 m depth have  $\text{CaCO}_3$  contents  
144 varying from 0.0 to 97.3 wt%  $\text{CaCO}_3$ , with an average value of 19.1 wt% excluding a  
145 single outlier (97.3 wt%  $\text{CaCO}_3$ ), which likely corresponds to inclusion of limestone  
146 aggregate (Fig. 2A; variability with depth is due to changes in ground conditions). The  
147 average carbonate content for trial pits from approx. 0 - 3 m depth, calculated from Leco  
148 total inorganic carbon data, is  $15.9 \pm 9.7$  wt%  $\text{CaCO}_3$ .  $\text{CaCO}_3$  content does not vary with  
149 depth in a consistent manner across the site; nevertheless, the trial pit data generally show  
150 little variation with depth to 1.5m or greater. A number of the trial pits have anomalously  
151 high concentrations of  $\text{CaCO}_3$  close to the surface (<1.0m), and two exhibit a decline in  
152 concentration deeper than 1.0m. These observations could indicate a carbonation front  
153 moving to greater depth with time. Reasons for the observed variability can be attributed to  
154 heterogeneity in material composition and properties, and to site-specific properties such as  
155 drainage patterns.

156 Thermogravimetry-differential scanning calorimetry coupled with quadrupole mass  
157 spectrometry (TG-DSC-QMS) and X-Ray diffraction (XRD) analysis (SI, Fig. 1 and 2)  
158 confirm the presence of calcite as the dominant calcium carbonate mineral, and  
159 demonstrate the presence of portlandite ( $\text{Ca}(\text{OH})_2$ ).

160 Between sampling dates, the surface soil samples show a consistent and statistically  
161 significant increase in  $\text{CaCO}_3$  content (Fig. 2B). A Shapiro-Wilk test was conducted on the  
162 data, which found a non-normal distribution for 2010 and normal distribution for 2012.  
163 Given this discrepancy a non-parametric test was run (Wilcoxon Signed Rank Test which is  
164 used to assess whether the rank of population mean values differ between related samples)  
165 producing a significance value of 0.000, allowing the rejection of the null hypothesis (at 95%  
166 confidence) that the difference in the samples was due to chance. The starting composition  
167 of the material with respect to  $\text{CaCO}_3$  is not known, but can be assumed to be small (but  
168 non-zero) due to possible inclusion of limestone aggregate or concrete carbonation  
169 occurring over the life of the now demolished structures. Overall, the  $\text{CaCO}_3$  content to 100  
170 mm depth over 18 months (2010-2012) increases from 22.0 wt% to 39.0 wt%. The range of  
171 the entire sample data is from 5.3 to 43.0 wt%  $\text{CaCO}_3$  in 2010 and for the repeat samples  
172 26.5 to 61.4 wt%  $\text{CaCO}_3$  in 2012. Standard deviations are higher (8.3 wt%) in 2012 (6.9 wt%  
173 in 2010), which may reflect variable progress of the carbonation reaction occurring in a  
174 geochemically heterogeneous environment.

175



176

177 **Figure 2.** Calcium carbonate contents of urban soils determined by calcimeter analysis. A)  
 178 variation in calcium carbonate content with depth from trial pit samples (N = 51) ; B)  
 179 Increase in CaCO<sub>3</sub> concentration from 2010 to 2012 from surface samples; analytical error  
 180 within size of symbol in both plots (comparative data 2010/12 N = 23).

181

182 A number of studies<sup>26-28</sup> have illustrated that the stable isotope signatures of carbon and  
 183 oxygen can be used to assess sequestration of CO<sub>2</sub> in recently formed pedogenic inorganic  
 184 carbonates. Non-equilibrium stable isotope signatures are common in carbonate minerals  
 185 formed from high pH brines. Thus, non-equilibrium isotope fractionation must be  
 186 considered in studies of weathering and carbonation of portlandite, Ca(OH)<sub>2</sub>, which  
 187 releases hydroxyl ions into solution (hydroxylation), thereby increasing pH. Hydroxylation  
 188 occurs at high pH (pH > 11.5)<sup>26</sup>, in environments corresponding to those dominated by the  
 189 weathering of artificial minerals in construction materials, as at Science Central. The C  
 190 isotope signature is governed by diffusion of CO<sub>2</sub> into aqueous solution and subsequent  
 191 precipitation of CaCO<sub>3</sub>. The rate of hydroxylation exerts the greatest influence on the

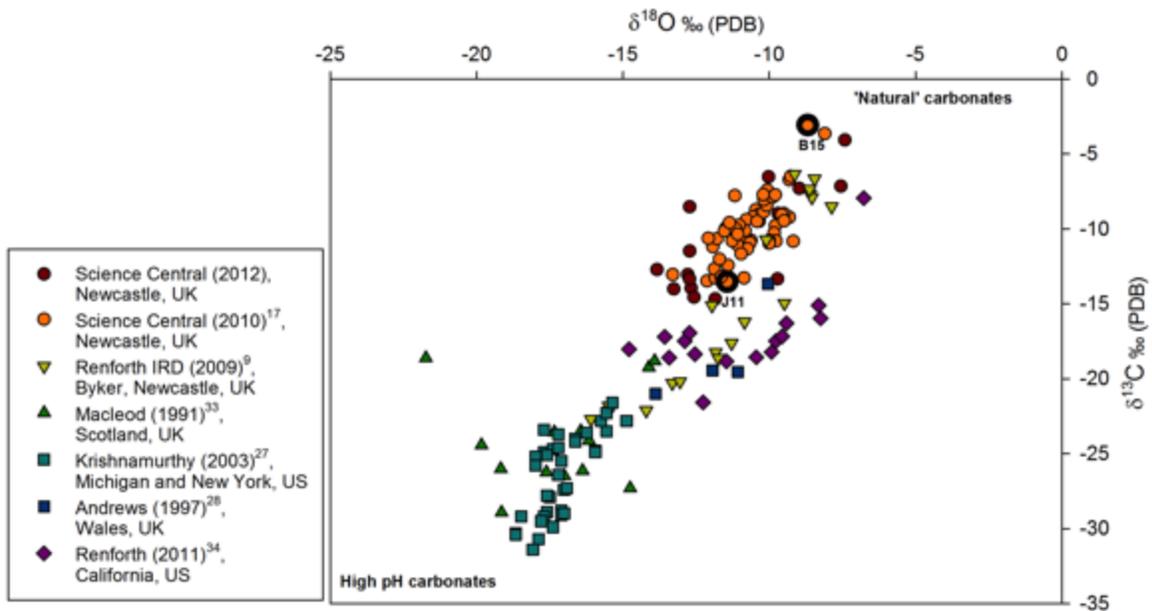
192 isotope signature of high pH solutions and can be assigned a large role in determining the  
193 isotopic composition of carbonates formed from the weathering of artificial minerals in soil  
194 settings. Stable isotopic analysis of secondary carbonate minerals forming under ambient  
195 conditions that are relevant to soils confirms that a significant proportion of the carbonate  
196 carbon has been sequestered from the atmosphere in this way.<sup>29</sup>

197 C and O isotope data for Science Central have  $\delta^{18}\text{O}$  values between -10.0‰ and -13.8‰  
198 and  $\delta^{13}\text{C}$  values between -6.5‰ and -14.6‰ (all V-PDB; 2010 samples SE =  $\pm 0.03\%$  for  
199  $\delta^{13}\text{C}$  and  $\pm 0.06\%$  for  $\delta^{18}\text{O}$ ; 2012 samples SE =  $\pm 0.04\%$  for  $\delta^{13}\text{C}$  and  $\pm 0.03\%$  for  $\delta^{18}\text{O}$ ). Between  
200 the two sampling dates, the mean  $\delta^{13}\text{C}$  values change from -9.9 to -12.6‰, and  $\delta^{18}\text{O}$  from -  
201 10.7 to -12.6‰. The shift towards more negative values is expected if the carbonate present  
202 includes a higher proportion produced following hydroxylation. The data shown in Fig. 3  
203 represent mixtures of  $\text{CaCO}_3$  derived from geological (lithogenic) sources (such as  
204 limestone aggregate in construction materials) and carbonate that originates through  
205 hydroxylation of  $\text{CO}_2$  at high pH<sup>9</sup>, forming a linear plot representing mixing between  
206 lithogenic and pedogenic carbonates<sup>9</sup>. Similar arrays of data are reported for mortar<sup>27</sup> and  
207 carbonate precipitates from the underside of concrete structures.<sup>33</sup>

208 A mixing line is superimposed on the data<sup>17</sup>, which assumes a lithogenic end member value  
209 for  $\delta^{18}\text{O} = -0.0\%$ ,  $\delta^{13}\text{C} = -0.0\%$ , and a hydroxylation (high pH) end member  $\delta^{18}\text{O} = -20.5\%$   
210 (assuming meteoric water  $\delta^{18}\text{O} = -7.8\%$  vs SMOW),  $\delta^{13}\text{C} = -25.3\%$ .<sup>9,17,26,28,30,31</sup> (SI, Fig.  
211 3). Other studies consider mixing between lithogenic carbonate and a ‘biogenic’ end  
212 member, with  $\delta^{18}\text{O} = -6.8\%$  and  $\delta^{13}\text{C} = -8.0\%$ , attributed to photosynthesis.<sup>9,32</sup> As the  
213 soils investigated in this study have little plant cover, and the observed range of  $\delta^{18}\text{O}$  and

214  $\delta^{13}\text{C}$  extends to more negative values, it is assumed that photosynthetic inputs to newly  
 215 formed soil carbonate are negligible. Thus on the basis of mixing between lithogenic and  
 216 pedogenic carbonate formed at high pH, proportions of each component vary from 42 - 80%  
 217 lithogenic and 58 - 20% hydroxylation (mean hydroxylation = 50%).

218 The data shown in Fig. 3 represent mixtures of  $\text{CaCO}_3$  derived from geological (lithogenic)  
 219 sources and carbonate that is assumed to have originated more recently through the  
 220 hydroxylation of  $\text{CO}_2$  at high pH.<sup>9</sup>  $^{14}\text{C}$  measurements (2 samples selected from the extremes  
 221 of the observed range of the  $\delta^{13}\text{C}$  data) suggest that a significant proportion of the C present  
 222 in carbonates originates from the modern atmosphere (i.e. non-lithogenic sources). A value  
 223 of  $30.4 \pm 0.1\%$  Modern Carbon was found for a sample with  $\delta^{13}\text{C} = -3.13\text{‰}$  (B15) and  $80.7$   
 224  $\pm 0.4\%$  Modern Carbon for a sample with  $\delta^{13}\text{C} = -13.55\text{‰}$  (J11; points are indicated in  
 225 Figure 3) Full  $^{14}\text{C}$  data in SI, Table. 2. This is consistent with increased incorporation of  
 226 carbon from the modern atmosphere in samples that show most reaction.



227

228 **Figure 3.** Stable isotopic data of samples from Science Central:  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  ‰ (V-  
229 PDB) (repeatability error bars are within point, in comparison with IRMS values from other  
230 sites (UK: 8, 26, 28; US: 25, 29)) (N = 185).  $^{14}\text{C}$  sample points B15 and J11 indicated.

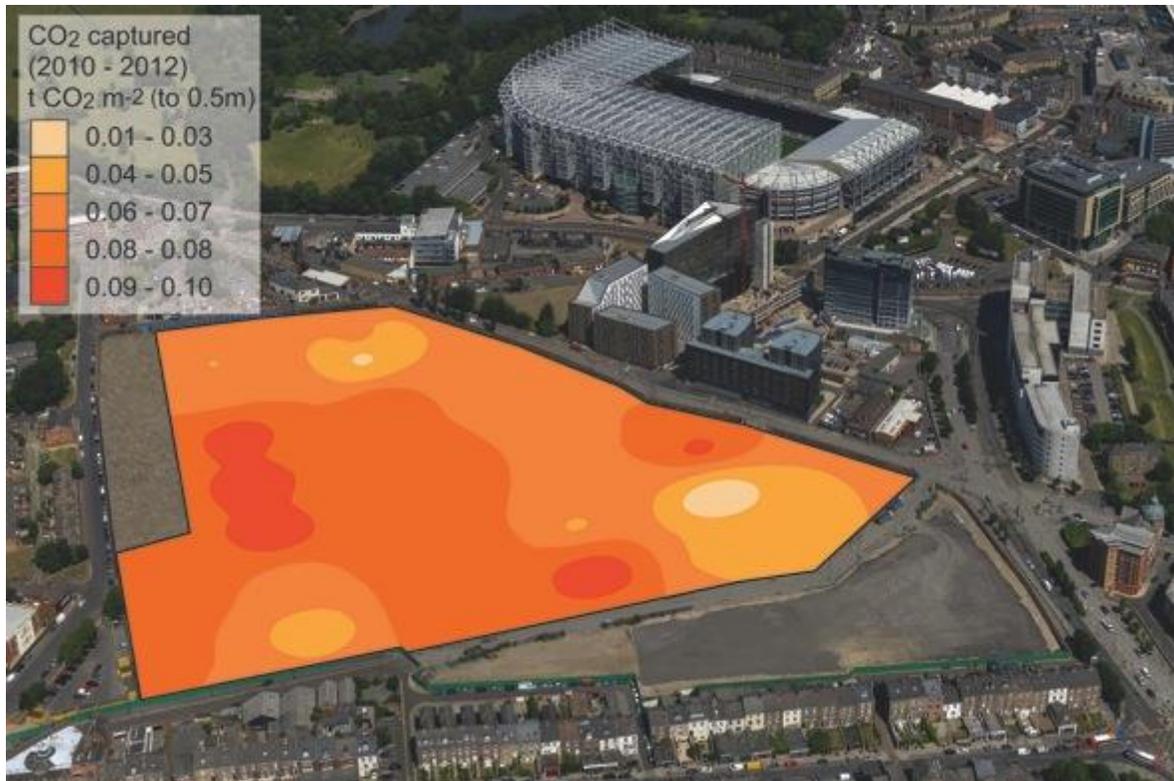
231

232 Variation in  $\text{CaCO}_3$  content with depth depends on ground conditions, as noted in previous  
233 sections. In general, homogeneously crushed demolition material was found to depths of at  
234 least 1 m, extending deeper than this in some cases. Based on the observed change between  
235 2010 and 2012 in  $\text{CaCO}_3$  content of surface samples from 370 to 660  $\text{t ha}^{-1}$  ( $0.037 - 0.066 \text{ t m}^{-2}$ ),  
236 the rate of precipitation of calcium carbonate in the top 100 mm of soil is estimated to  
237 be 16  $\text{t ha}^{-1}$  ( $0.0016 \text{ t m}^{-2}$ ) per month, or 192  $\text{t ha}^{-1}$  ( $0.0192 \text{ t m}^{-2}$ ) annually. This corresponds  
238 to carbon removal from the atmosphere equivalent to 85  $\text{t CO}_2 \text{ ha}^{-1}$  ( $0.0085 \text{ t CO}_2 \text{ m}^{-2}$ )  
239 annually, or an annual increase in soil C content of 23  $\text{t C ha}^{-1}$  ( $0.0023 \text{ t C m}^{-2}$ ).

240 The measured soil inorganic carbon stock to 100 mm depth increased from 44 to 79  $\text{t C ha}^{-1}$   
241 ( $0.0044 - 0.0079 \text{ t C m}^{-2}$ ) in 18 months, approaching values similar to those reported for  
242 organic carbon in arable land ( $84 \text{ t C ha}^{-1}$  ( $0.0085 \text{ t C m}^{-2}$ )).<sup>35</sup> The rate of increase inferred  
243 from the observed change at Science Central exceeds estimates for soil carbon increases in  
244 rural land use (e.g.  $3.63 \text{ t C ha}^{-1} \text{ a}^{-1}$  ( $0.363 \text{ kg C m}^{-2} \text{ a}^{-1}$ ) through establishment (for example)  
245 of new woodlands).<sup>36</sup> It is likely that the observed rate will change with time, but it is not  
246 possible to measure changes at the site since 2012 due to more recent construction activity.

247 Soil carbon stocks are conventionally reported to greater depths than 100 mm.<sup>10</sup> Figure 4  
248 summarises  $\text{CO}_2$  removal, extrapolating to 0.5 m depth on the basis of the consistent  
249  $\text{CaCO}_3$  contents to that depth from trial pit samples (see Fig. 2A) The extrapolation in

250 Figure 4 is based upon trial pit data to 0.5m and analytical data, assuming a contemporary  
251 mean  $\text{CaCO}_3$  content of  $20 \pm 12.3$  wt% (mean  $\text{CaCO}_3$  content from trial pits to 0.5m and  
252 surface samples = 19.5wt %) and assuming that the proportion of carbonate newly formed  
253 (shortly prior to, or since demolition) through hydroxylation is 50% overall.



254  
255 **Figure 4.** Observed carbon capture at Science Central, Newcastle (N = 23) (Contour map  
256 plotted using ArcGIS 10. Overlay created in Adobe Photoshop and Illustrator)

257

258 The calcium required for the carbonation reaction derives from two sources. First,  
259 dissolution of the cement mineral portlandite ( $\text{Ca}(\text{OH})_2$ ) can provide readily-available Ca.  
260 The portlandite content of the samples was not quantified, but is typically around 15% in  
261 hydrated cement (~ 5% in concrete).<sup>37</sup> Secondly, dissolution of artificial Ca-bearing

262 silicates (amorphous or poorly crystalline phases; part of the cement clinker) occurs as  
263 cement weathers within the soil. An estimate of the rate of weathering of the silicate  
264 components of the soil has been made using the change in bulk composition determined by  
265 XRF (SI, Table 3), which shows a negative correlation between SiO<sub>2</sub> and CaO, consistent  
266 with the formation of calcite and proportionate reduction in the silicate minerals fraction.  
267 However, once normalised to TiO<sub>2</sub> (assuming Ti to be immobile during weathering)<sup>38</sup>, the  
268 loss of SiO<sub>2</sub> exceeds that corresponding to dilution by newly-formed carbonate minerals.  
269 The observed loss of 20% of the SiO<sub>2</sub> content is equivalent to a weathering rate of 10<sup>-12.7</sup>  
270 mol (Si) cm<sup>-2</sup> s<sup>-1</sup> (normalised to a nominal mineral surface area of 1m<sup>2</sup> g<sup>-1</sup>, conservatively  
271 estimated from particle size distribution<sup>17</sup> and assuming 1 Mt of material onsite<sup>22</sup>) or  
272 16,000 t (Si) km<sup>-2</sup> a<sup>-1</sup> (when normalised to the site area). It is assumed that Si is removed  
273 from the site in drainage waters, although some may have been retained in the formation of  
274 clay minerals (identified by XRD analysis). This is several orders of magnitude slower than  
275 dissolution rates for hydrated cement minerals determined through laboratory experiments  
276 (10<sup>-8.0</sup> mol (Ca) cm<sup>-2</sup> s<sup>-1</sup>)<sup>17</sup>, but is two orders of magnitude faster than the greatest  
277 weathering rates for natural catchments (e.g. a global average of 24 t km<sup>-2</sup> a<sup>-1</sup>,<sup>33</sup> or 100s t  
278 km<sup>-2</sup> a<sup>-1</sup> for tropical volcanic arcs.<sup>40</sup> Enhanced SiO<sub>2</sub> removal is consistent with the high pH  
279 of this anthropogenic soil, and may explain the elevated weathering rate measured from  
280 rivers draining urbanised catchments.<sup>41</sup>

281 The significance of the results reported here is the demonstration of the very rapid and  
282 substantial rate of removal of CO<sub>2</sub> from the atmosphere by carbonation reactions that take  
283 place within soils that contain reactive calcium minerals. Similar observations have been  
284 found other sites, where the rate of CO<sub>2</sub> removal has been estimated based on the

285 assumption that calcium carbonate content in soil was zero at the time of demolition<sup>9</sup> or soil  
286 formation<sup>14</sup>. In urban soils, the dominant calcium silicate flux to soil is by incorporation of  
287 demolition materials. Carbonation of artificial cement replaces CO<sub>2</sub> lost during  
288 manufacture which involves calcining limestone (globally 5% of anthropogenic  
289 emissions)<sup>42</sup>, thus closing one loop of the carbon cycle but not compensating for CO<sub>2</sub>  
290 produced by combustion of fuel used in the calcining process. Science Central represents a  
291 single 10 ha site, but is typical of modern development practice that involves on-site  
292 crushing of materials and the retention of crusher ‘fines’ on site as part of the soil. Urban  
293 land in the UK represents 7% (or 1.7 million ha) of the country’s 25-million ha area<sup>43</sup>. If  
294 only 12,000 ha (or 0.7%) of urban soils in the UK were managed in a similar way to  
295 Science Central, they could have the potential to remove 1 Mt CO<sub>2</sub> annually over the period  
296 in which they are sequestering carbon dioxide, contributing to the requirement for the UK  
297 carbon account for 2050 to be at least 80% lower than the 1990 baseline.<sup>44</sup>

298 There are several considerations around the effective management of these sites to  
299 maximise carbon capture, including the rate and thickness at which materials are emplaced,  
300 how long the site remains undeveloped and the manner in which it might be covered by  
301 buildings or by landscaped topsoil. Science Central is typical of redevelopment land, where  
302 demolition materials are emplaced to variable depth (1 to 10’s of metres) on sites that may  
303 remain undeveloped for 5 years or more. Carbonation appears to decrease with depth, likely  
304 due to the isolation of materials from the atmosphere, therefore management which  
305 increases atmospheric exposure (e.g. through appropriate planting that takes CO<sub>2</sub> to depth  
306 via plant root systems and associated metabolism) is likely to increase carbonation rates

307 throughout the site.<sup>14,45,46</sup> There is evidence that this carbon capture process occurs at other  
308 sites where topsoil has been emplaced.<sup>9</sup> If the soil is covered by a building or impermeable  
309 pavements it will be isolated from the atmosphere, due to a ‘capping’ effect. By analogy  
310 with natural systems carbonate material formed whilst sites are undeveloped is likely to be  
311 stable and remain in the soils during and after redevelopment has taken place.<sup>47</sup>

312 Globally, appropriate management of land as part of the development or reconstruction of  
313 sites where concrete structures have been demolished or destroyed should be considered as  
314 a way of partly compensating for emissions associated with the loss of CO<sub>2</sub> from firing  
315 carbonate raw materials (around 50% of the total CO<sub>2</sub> emissions of a kiln).<sup>48</sup> However, the  
316 cement industry will have to rapidly decarbonise in the coming decades to meet emission  
317 reduction targets (including wide-scale deployment of carbon capture and storage of kiln  
318 flue gasses). The post-use recarbonation of cement at the end of life of a structure, through  
319 soil processes, could result in a net negative carbon life cycle if combined with mitigation  
320 at the kiln. Approximately  $3 \times 10^9$  t of cement is produced annually, emitting  
321 approximately  $1.5 \times 10^9$  t CO<sub>2</sub> from chemical decarbonation.<sup>49</sup> Given the average building  
322 lifespan is around 50 years, this material could become available by mid century,  
323 representing a substantial carbon capture opportunity for the industry.

324 Although reported here for urban soils with artificial mineral inputs, calcite precipitation  
325 has also been observed in artificial soils prepared by blending natural calcium silicate rocks  
326 with compost.<sup>14</sup> In the long term, a proportion of the calcite may dissolve, contributing to  
327 bicarbonate in groundwater and surface water (fluxes similar to those from outcropping  
328 natural carbonate-cemented sandstones). The potential for carbon capture as calcite

329 precipitated in soils with added calcium silicates has the potential to provide a passive  
330 carbon dioxide removal mechanism, analogous to the use of reed beds to clean  
331 contaminated surface waters.

332

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339

340 Supporting information available. This information is available free of charge via the  
341 Internet at <http://pubs.acs.org/>

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