

Rapid removal of atmospheric CO₂ by urban soils

Carla-Leanne Washbourne^{a1}, Elisa Lopez-Capel^a, Phil Renforth^b, Philippa L. Ascough^c and David A. C. Manning^{a}*

^aSchool of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU.

^bSchool of Earth & Ocean Sciences, Cardiff University, Cardiff, CF10 3AT.

^cScottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, UK, G75 0QF.

¹Present address: Department of Science, Technology, Engineering and Public Policy, University College London, 36-36 Fitzroy Square, London, UK, W1T 6EY

*for correspondence: School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU. Phone: +44 (0) 191 208 6610. Fax: +44 (0) 191 208 5322. Email: david.manning@ncl.ac.uk

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1 **TOC/Abstract art**



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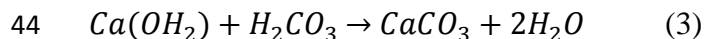
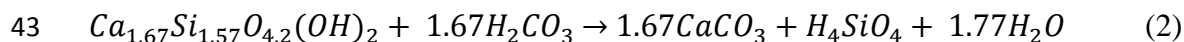
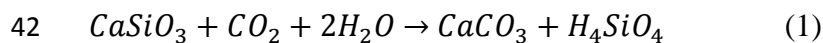
4 **Abstract**

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 CO₂ per hectare (ha⁻¹) (8.5 kg CO₂ m⁻²) 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 CO₂ ultimately
10 derived from the atmosphere, precipitating as calcite. Stable isotope data confirm an
11 atmospheric origin for carbonate-carbon, and ¹⁴C 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 CO₂ from the atmosphere
17 annually. The maximum global potential is estimated to be approximately 700-1,200 Mt
18 CO₂ 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 CO₂ a⁻¹ by 2050 of CO₂ 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 CO₂ a⁻¹ 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.^{1,2}

31 Soils emit almost 275 Gt CO₂ a⁻¹ 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.³ During weathering, Ca and Mg silicate and carbonate minerals naturally react
35 with dissolved carbon dioxide (CO₂) to increase local alkalinity. Given the right conditions,
36 some of this dissolved CO₂ 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 CO₂.^{4,5,6}
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 CO₂ over geological time periods^{4,7} and also contributes
47 to the formation of pedogenic carbonates in both natural⁸ and artificial soils⁹ over much
48 shorter timescales. Limited information is available for the formation of pedogenic
49 carbonates in UK soils, with Rawlins (2011)¹⁰ 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^{9,11-20} 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 CO₂ a⁻¹,
59 representing 2.0-3.7% of contemporary global CO₂ emissions (currently global annual CO₂
60 emissions account for approximately ~33 Gt CO₂ a⁻¹), or one sixth to one third of a
61 stabilisation wedge.^{1,21} Natural silicates present a carbon capture potential orders of
62 magnitude greater.²⁰

63 Studies in urban soils^{9,16} demonstrate a carbon capture potential of 12.5 kg CO₂ tonne
64 soil⁻¹ a⁻¹ 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^{9,12,14-19} 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 CO₂
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 CO₂ from the atmosphere.

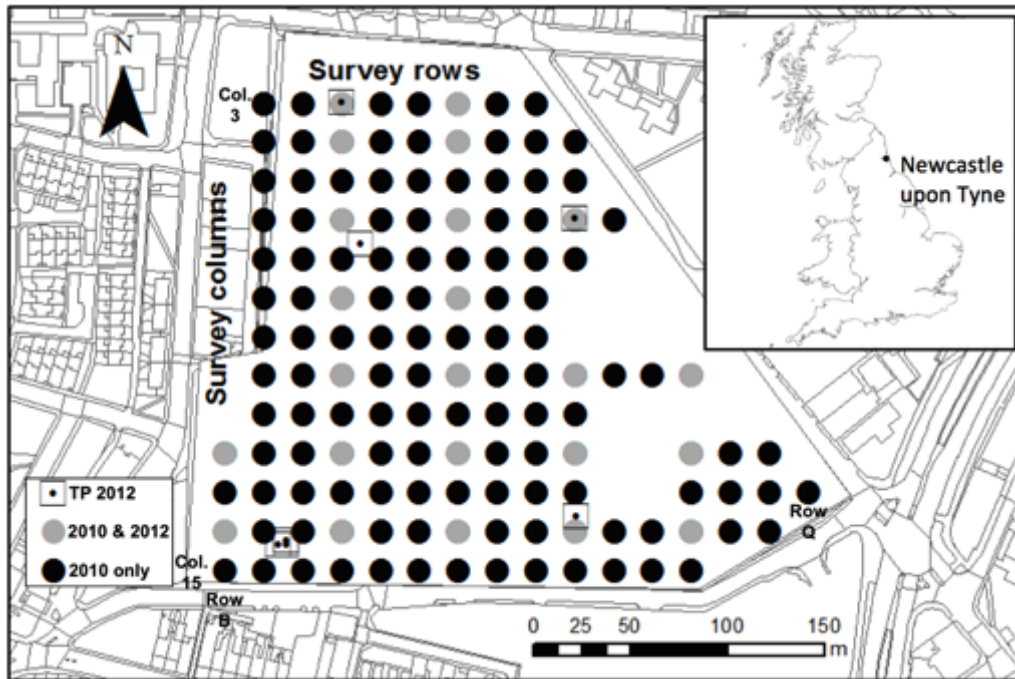
78 **Materials and methods**

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.²² 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 16th September 2010¹⁷ and again at 23 of these
92 points on 13th 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).¹⁷ 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 13th 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, 2010¹⁷ (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)²³, 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 (¹⁴C) 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.^{24,25} 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 previously¹⁷. Soil pH was consistently high (>9.5) with values up to 11.7¹⁷.

134 Two methods of determination, calcimeter and Leco analysis (total carbon – organic
135 carbon), give closely corresponding soil CaCO₃ contents. Calcimeter analysis reported bulk
136 equivalent CaCO₃ 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 = ±

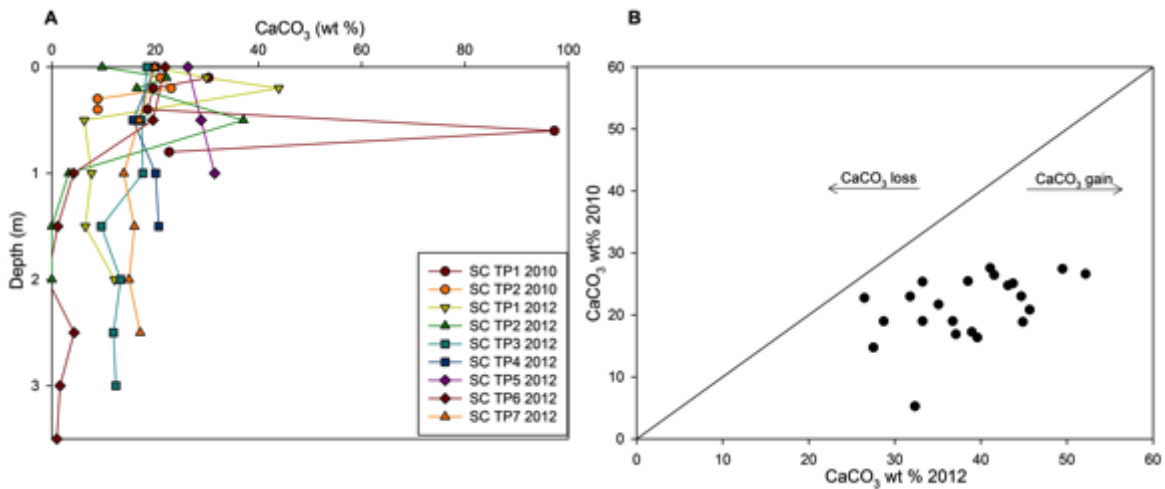
138 0.21 wt%). Leco analysis reported an average inorganic carbon content of 4.1 ± 1.2 wt%
139 (range 3.0 - 7.1 wt%; SEM ± 0.48 wt%), corresponding to CaCO_3 concentrations of $38.9 \pm$
140 15.6 wt% (range 25.2 - 59.1 wt%; equivalent analytical precision ± 4.0 wt%).

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.¹⁷ Trial pit samples to approx. 1 m depth have CaCO_3 contents
144 varying from 0.0 to 97.3 wt% CaCO_3 , with an average value of 19.1 wt% excluding a
145 single outlier (97.3 wt% 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 ± 9.7 wt% CaCO_3 . 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 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 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 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 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% CaCO_3 in 2010 and for the repeat samples
172 26.5 to 61.4 wt% 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 CaCO₃ 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 studies²⁶⁻²⁸ have illustrated that the stable isotope signatures of carbon and
 183 oxygen can be used to assess sequestration of CO₂ 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)₂, which
 187 releases hydroxyl ions into solution (hydroxylation), thereby increasing pH. Hydroxylation
 188 occurs at high pH (pH > 11.5)²⁶, 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 CO₂ into aqueous solution and subsequent
 191 precipitation of CaCO₃. The rate of hydroxylation exerts the greatest influence on the

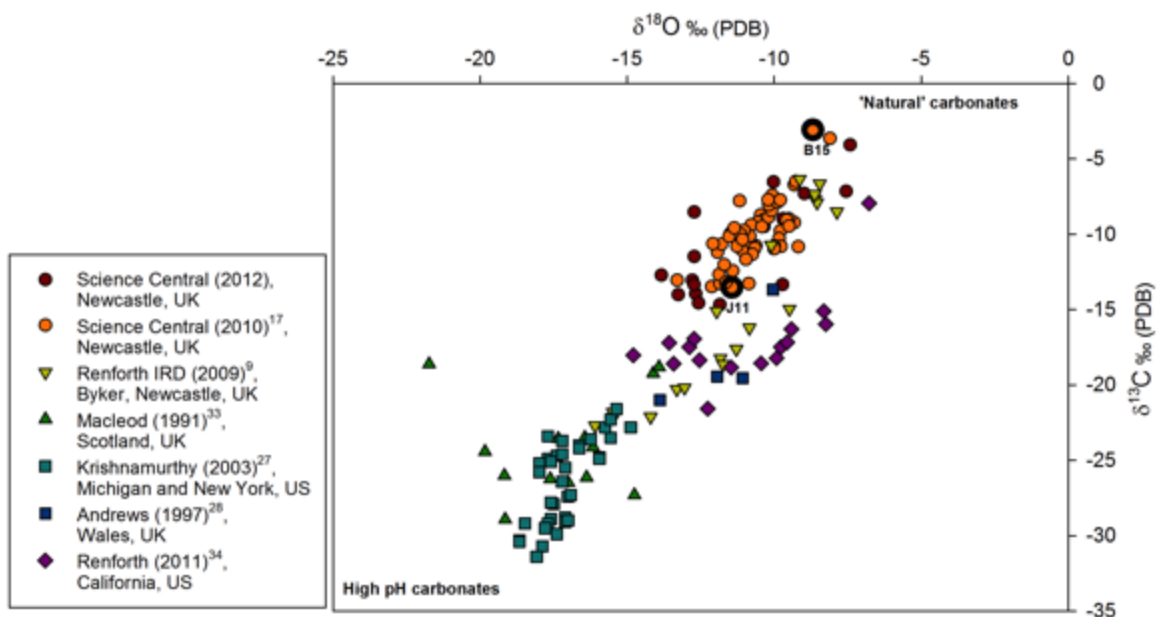
192 isotope signature of high pH solutions and can be assigned a large role in determining the
193 isotopic composition of carbonates formed from the weathering of artificial minerals in soil
194 settings. Stable isotopic analysis of secondary carbonate minerals forming under ambient
195 conditions that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

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 CaCO_3 derived from geological (lithogenic) sources (such as
204 limestone aggregate in construction materials) and carbonate that originates through
205 hydroxylation of CO_2 at high pH⁹, forming a linear plot representing mixing between
206 lithogenic and pedogenic carbonates⁹. Similar arrays of data are reported for mortar²⁷ and
207 carbonate precipitates from the underside of concrete structures.³³

208 A mixing line is superimposed on the data¹⁷, 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), $\delta^{13}\text{C} = -25.3\%$.^{9,17,26,28,30,31} (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.^{9,32} 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 CaCO_3 derived from geological (lithogenic)
 219 sources and carbonate that is assumed to have originated more recently through the
 220 hydroxylation of CO_2 at high pH.⁹ ^{14}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}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}C sample points B15 and J11 indicated.

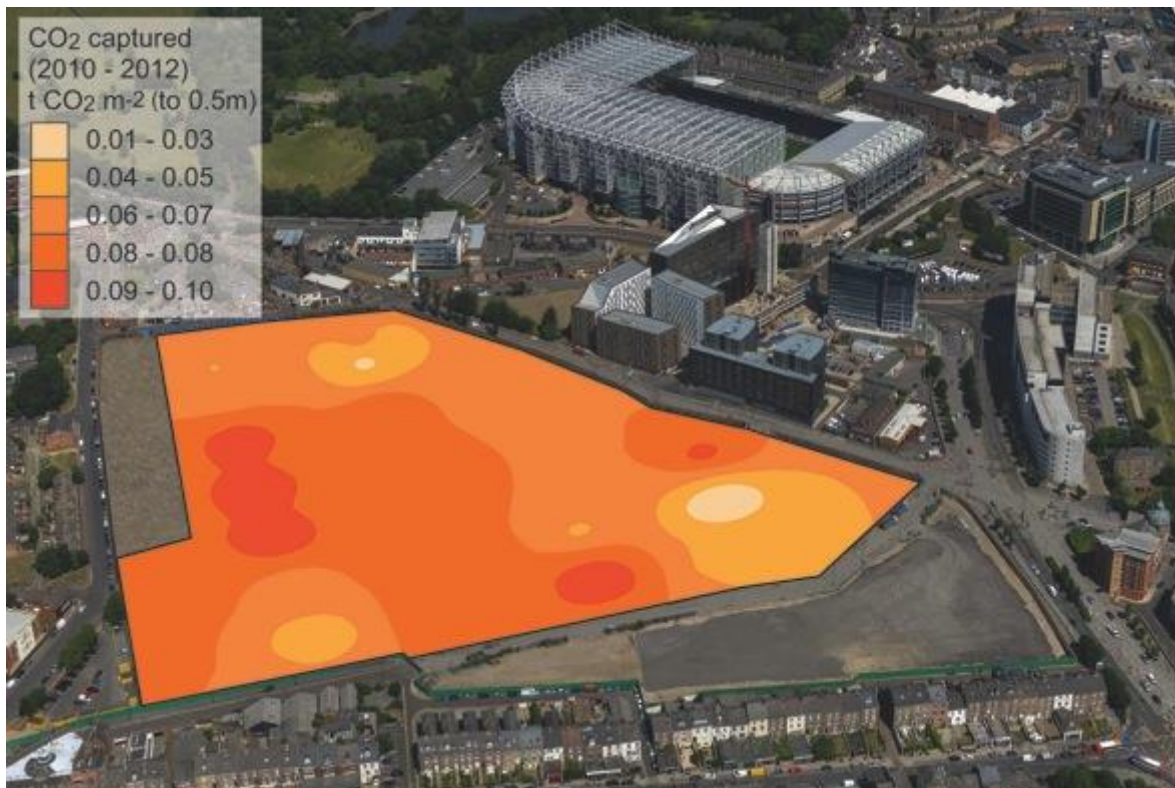
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232 Variation in CaCO_3 content with depth depends on ground conditions, as noted in previous
233 sections. In general, homogeneously crushed demolition material was found to depths of at
234 least 1 m, extending deeper than this in some cases. Based on the observed change between
235 2010 and 2012 in CaCO_3 content of surface samples from 370 to 660 t ha^{-1} ($0.037 - 0.066 \text{ t m}^{-2}$)
236 m^{-2}), the rate of precipitation of calcium carbonate in the top 100 mm of soil is estimated to
237 be 16 t ha^{-1} (0.0016 t m^{-2}) per month, or 192 t ha^{-1} (0.0192 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 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 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 t C ha^{-1} ($0.0085 \text{ t C m}^{-2}$)).³⁵ 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).³⁶ 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.¹⁰ Figure 4
248 summarises CO_2 removal, extrapolating to 0.5 m depth on the basis of the consistent
249 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 CaCO_3 content of 20 ± 12.3 wt% (mean 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).³⁷ 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 SiO₂ and CaO, consistent
266 with the formation of calcite and proportionate reduction in the silicate minerals fraction.
267 However, once normalised to TiO₂ (assuming Ti to be immobile during weathering)³⁸, the
268 loss of SiO₂ exceeds that corresponding to dilution by newly-formed carbonate minerals.
269 The observed loss of 20% of the SiO₂ content is equivalent to a weathering rate of 10^{-12.7}
270 mol (Si) cm⁻² s⁻¹ (normalised to a nominal mineral surface area of 1m² g⁻¹, conservatively
271 estimated from particle size distribution¹⁷ and assuming 1 Mt of material onsite²²) or
272 16,000 t (Si) km⁻² a⁻¹ (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^{-8.0} mol (Ca) cm⁻² s⁻¹)¹⁷, 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⁻² a⁻¹,³³ or 100s t
278 km⁻² a⁻¹ for tropical volcanic arcs.⁴⁰ Enhanced SiO₂ 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.⁴¹

281 The significance of the results reported here is the demonstration of the very rapid and
282 substantial rate of removal of CO₂ 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 CO₂ removal has been estimated based on the

285 assumption that calcium carbonate content in soil was zero at the time of demolition⁹ or soil
286 formation¹⁴. In urban soils, the dominant calcium silicate flux to soil is by incorporation of
287 demolition materials. Carbonation of artificial cement replaces CO₂ lost during
288 manufacture which involves calcining limestone (globally 5% of anthropogenic
289 emissions)⁴², thus closing one loop of the carbon cycle but not compensating for CO₂
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 area⁴³. 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 CO₂ 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.⁴⁴

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 CO₂ to depth
306 via plant root systems and associated metabolism) is likely to increase carbonation rates

307 throughout the site.^{14,45,46} There is evidence that this carbon capture process occurs at other
308 sites where topsoil has been emplaced.⁹ 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.⁴⁷

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 CO₂ from firing
315 carbonate raw materials (around 50% of the total CO₂ emissions of a kiln).⁴⁸ 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 3×10^9 t of cement is produced annually, emitting
321 approximately 1.5×10^9 t CO₂ from chemical decarbonation.⁴⁹ 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.¹⁴ 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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340 Supporting information available. This information is available free of charge via the
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