

## Article (refereed) - postprint

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Adams, Jessica L.; Tipping, Edward; Bryant, Charlotte L.; Helliwell, Rachel C.; Toberman, Hannah; Quinton, John. 2015. **Aged riverine particulate organic carbon in four UK catchments**. *Science of the Total Environment*, 536. 648-654. [10.1016/j.scitotenv.2015.06.141](https://doi.org/10.1016/j.scitotenv.2015.06.141)

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[10.1016/j.scitotenv.2015.06.141](https://doi.org/10.1016/j.scitotenv.2015.06.141)

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1 *Submitted to Science of the Total Environment, May 2015*

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3 **Aged riverine particulate organic carbon in four UK catchments**

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24

25 **ABSTRACT**

26 The riverine transport of particulate organic matter (POM) is a significant flux in the carbon  
27 cycle, and affects macronutrients and contaminants. We used radiocarbon to characterise POM  
28 in 9 rivers of four UK catchments (Avon, Conwy, Dee, Ribble) over a one-year period. High-  
29 discharge samples were collected on three or four occasions at each site. Suspended particulate  
30 matter (SPM) was obtained by centrifugation, and the samples were analysed for carbon  
31 isotopes. Concentrations of SPM and SPM organic carbon (OC) contents were also  
32 determined, and were found to have a significant negative correlation. For the 7 rivers draining  
33 predominantly rural catchments,  $PO^{14}C$  values, expressed as percent modern carbon absolute  
34 (pMC), varied little among samplings at each site, and there was no significant difference in  
35 the average values among the sites. The overall average  $PO^{14}C$  value for all 7 sites of 91.2  
36 pMC corresponded to an average age of 680  $^{14}C$  years, but this value arises from the mixing of  
37 differently-aged components, and therefore significant amounts of organic matter older than  
38 the average value are present in the samples. Although topsoil erosion is probably the major  
39 source of the riverine POM, the average  $PO^{14}C$  value is appreciably lower than topsoil values  
40 (which are typically 100 pMC). This is most likely explained by inputs of older subsoil OC  
41 from bank erosion, or the preferential loss of high- $^{14}C$  topsoil organic matter by mineralisation  
42 during riverine transport. The significantly lower average  $PO^{14}C$  of samples from the River  
43 Calder (76.6 pMC), can be ascribed to components containing little or no radiocarbon, derived  
44 either from industrial sources or historical coal mining, and this effect is also seen in the River  
45 Ribble, downstream of its confluence with the Calder. At the global scale, the results  
46 significantly expand available information for  $PO^{14}C$  in rivers draining catchments with low  
47 erosion rates.

48

49 *Keywords:* Particulate organic carbon, Radiocarbon, Rivers, Soils

50

51 Abbreviations: AMS, accelerator mass spectrometry; NRCF, NERC Radiocarbon Facility; OC  
52 organic carbon; pMC, percent modern carbon absolute; POC, particulate organic carbon; POM,  
53 particulate organic matter;  $PO^{14}C$  particulate organic radiocarbon; SPM suspended particulate  
54 matter; [SPM] concentration of SPM

55

## 56 1. Introduction

57 Particulate organic matter (POM) transported by rivers is defined as organic matter that  
58 does not pass a filter with sub-micron pore size, and mainly comprises allochthonous inputs  
59 from plant litter, soils and wastes, autochthonous phytoplankton and macrophyte debris, and in  
60 situ production from dissolved organic matter (Ittekkot and Laane, 1991). It plays a significant  
61 role in the carbon cycle, being a loss from the terrestrial environment, a source of C to the  
62 atmosphere due to decomposition during transit, and ultimately a gain to the marine  
63 environment (Raymond and Bauer, 2001; Rosenheim and Galy, 2012; Worrall et al., 2014).  
64 Particulate organic carbon (POC) accounts for approximately 50% of the riverine global  
65 organic carbon export of  $0.4 \text{ Pg a}^{-1}$  (Schlünz and Schneider, 2000; Aufdenkampe et al., 2011).  
66 Particulate organic matter also governs the transport of the macronutrients nitrogen and  
67 phosphorus (Meybeck 1982, Walling 2005), metals (Tipping et al., 1997) and organic  
68 contaminants (Foster et al., 2000). To understand and quantify these POM-associated  
69 processes, and thereby predict how they might respond to changes in land use, climate and  
70 other environmental drivers, we need to delineate the sources of POM in different systems.

71 Because POM is part of suspended particulate matter (SPM), information about sources  
72 can be obtained from more general investigations into SPM, which is known to comprise a  
73 mixture of terrestrial material derived from both surface and sub-surface materials including  
74 bedrock and mineral soil (Blair et al., 2003). The SPM entering the river systems is generally  
75 the result of physical weathering and physical disturbance through anthropogenic activity.  
76 Sediment sourcing techniques, including mineralogy (Klages and Hsieh, 1975), chemistry  
77 (Gaillardet et al., 1999), magnetism (Gruszowski et al., 2003) and radionuclides (Estrany et al.,  
78 2010, Lu et al., 2014; Rosenheim and Galy, 2012) identify sources of SPM as being primarily  
79 topsoil and sub-surface material including erosion of exposed banks. Walling (2013)  
80 summarized sediment source information on 84 UK rivers, and showed that on average topsoil  
81 was the largest contributor of SPM, with relative contributions from surface material and  
82 channel banks contributing between 50% to 99% and <50% respectively.

83 The organic matter components of SPM have been studied by a variety of analytical  
84 techniques and with stable isotopes and element ratios (da Cunha et al., 2000; Onstad et al.,  
85 2000; Kendall et al., 2001; Higuera et al., 2014) to obtain information on molecular structure  
86 and insight into the materials from which the POM is derived. Determination of the  
87 radiocarbon content of POM provides further information, not only on sources but also

88 apparent age. Radiocarbon gives a measure of the time elapsed since C fixation into plants  
89 from the atmosphere, providing an understanding of the residence time of plant-derived C and  
90 losses of C through mechanisms including leaching and erosion (Trumbore, 2009). Naturally  
91 occurring atmospheric  $^{14}\text{C}$  can be used for the measure of C turnover on the centennial and  
92 millennial timescale due to the natural radioactive decay process, while “bomb carbon”  
93 originating from atmospheric weapons testing in the mid-20<sup>th</sup> century, which almost doubled  
94 the atmospheric  $^{14}\text{C}$  levels (Hua et al., 2013), provides information on decadal timescales.  
95 Radiocarbon has been used in studies of POM in rivers in North and South America (Raymond  
96 and Bauer, 2001, Bouchez et al., 2014), Asia (Hilton et al., 2008; Rosenheim and Galy 2012),  
97 Europe (Cathalot et al., 2013, Megens et al., 2001), and Africa (Marwick et al., 2015). Global  
98  $\text{PO}^{14}\text{C}$  (particulate organic radiocarbon) data documented by Marwick et al. (2015) shows that  
99 SPM in highly-eroding catchments is depleted in  $\text{PO}^{14}\text{C}$  and low in OC (organic carbon).

100 The review of Marwick et al. (2015) shows that to date while there are many  $\text{PO}^{14}\text{C}$  data  
101 for catchments with high sediment loads, there are relatively few for riverine  $\text{PO}^{14}\text{C}$  in  
102 temperate, low-erosion European catchments and no known data for catchments of this kind in  
103 the UK. In the wider context, UK data may be of interest because UK soils tend to be rich in  
104 carbon, which may lead to differences from global averages. Therefore understanding UK  
105 sources should improve our ability to model the terrestrial-freshwater C cycle, and its role in  
106 transferring carbon to the atmosphere and ocean. To this end, we carried out a programme of  
107 sampling and analysis to determine the radiocarbon contents of POM from four differing UK  
108 catchments. Since SPM concentrations, and therefore POM transport, are elevated at high  
109 flow, we focused our sample collection on high-discharge events. To interpret the results, we  
110 made use of the extensive soil radiocarbon data available for the UK.

## 111 2. Methods

### 112 2.1. Field sites

113 Table 1 provides information on the individual rivers and their catchments, and their  
114 locations are shown in Figure 1. Data on discharge and rainfall were taken from the National  
115 River Flow Archive (NRFA) (<http://www.ceh.ac.uk/data/nrfa/> accessed January 2015) and Met  
116 Office (<http://www.metoffice.gov.uk/industry/data/commercial/rainfall> accessed March 2015)  
117 respectively. Catchment areas were obtained from the CEH River and Catchment Query and  
118 Extraction Layer (Racquel) (<http://wlwater.ceh.ac.uk/racquel/> accessed March 2015).  
119 Geological information was provided by the British Geological Society online map  
120 (<http://mapapps.bgs.ac.uk/geologyofbritain/home.html>, accessed March 2015). Soil types for  
121 England and Wales were obtained using soil maps (scale 1:250 000). For the Dee catchments,  
122 soil information was obtained from The James Hutton Institute online soils map  
123 ([http://sifss.hutton.ac.uk/SSKIB\\_Stats.php](http://sifss.hutton.ac.uk/SSKIB_Stats.php) accessed March 2015). Land use data were  
124 obtained from the website <http://digimap.edina.ac.uk/> (accessed March 2015).

125 The Ribble catchment is situated in north-west England and has a population density of  
126 989 persons km<sup>-2</sup>. Two major sub catchments, the Rivers Hodder and Calder drain from the  
127 north and south of the catchment respectively. Unlike other tributaries of the Ribble, the Calder  
128 catchment contains extensive conurbations including Burnley and Blackburn, with a history of  
129 industrial and mining activity. The upper parts of the catchment are responsive to rainfall,  
130 exhibiting a flashy flow regime.

131 The River Conwy is one of the major drainage systems in North Wales. The catchment  
132 has a population density of 49 persons km<sup>-2</sup>. The topography is largely mountainous, giving a  
133 high river response during storm events.

134 Situated in the south of England, the Hampshire Avon catchment has a population  
135 density of 108 persons km<sup>-2</sup>. The catchment is largely groundwater dominated due to the  
136 presence of chalk aquifers. Thus, the system at the tidal limit does not significantly respond  
137 during rainfall events.

138 Table 1. Catchment information. Discharge data are from records of between 35 and 50 years up to the present. Geology, soil type and land use are presented in order of importance.

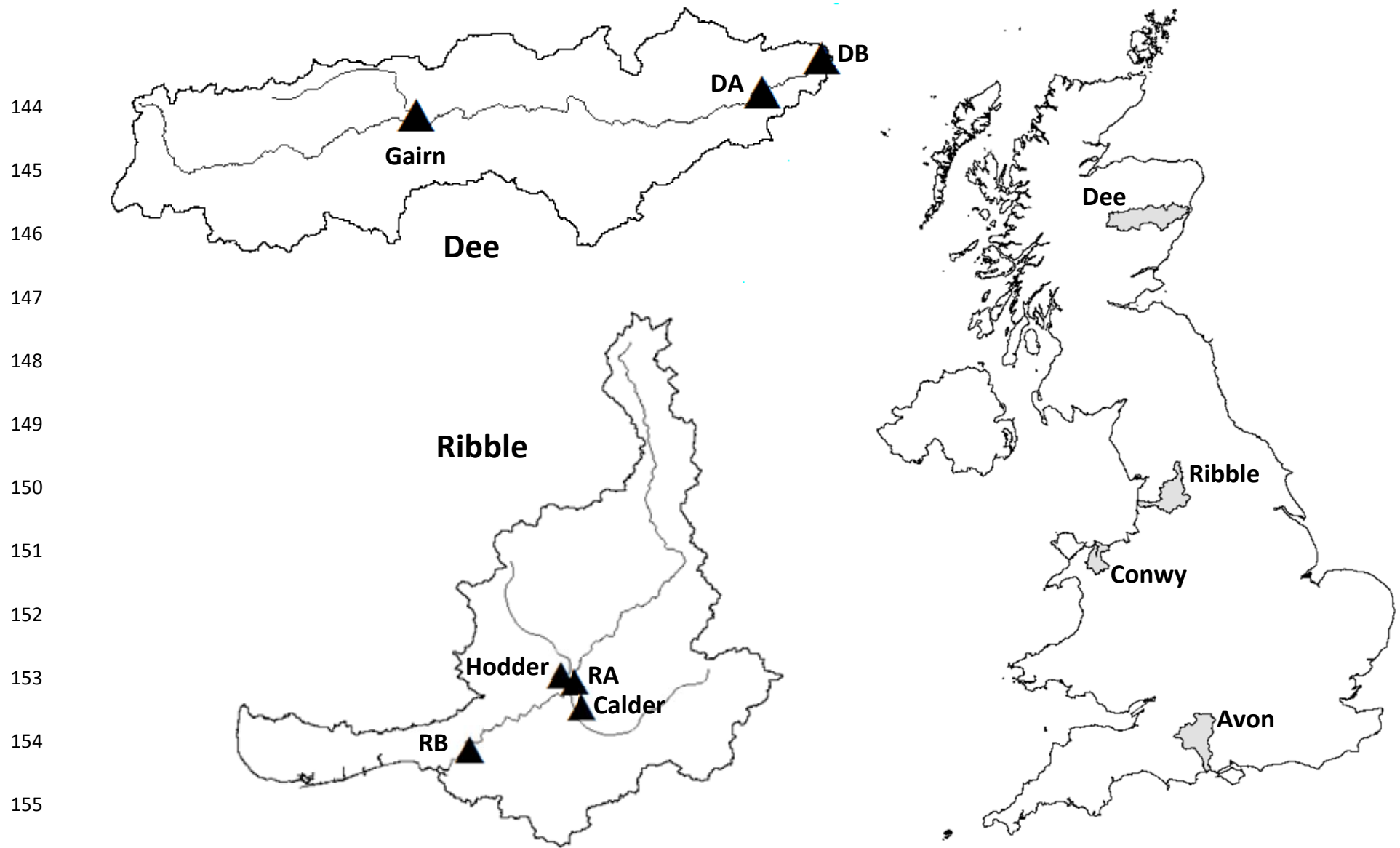
	Calder	Hodder	Ribble A	Ribble B	Conwy	Avon	Gairn	Dee A	Dee B
Catchment drainage area (km <sup>2</sup> )	317	258	446	1144	365	1713	146	2039	2080
Altitude range (masl)	50-560	40-480	20-420	15-560	10-1060	4-240	220-1100	30-1220	20-1220
Mean annual rainfall (m)	1.1	1.5	1.2	1.2	2.1	0.8	1.1	0.9	0.8
Mean annual air temperature (°C)	8.9	7.7	8.8	8.6	8.4	9.6	5.1	7.6	7.7
River discharge (m <sup>3</sup> s <sup>-1</sup> )									
mean	8.6	8.8	13.5	33.2	18.9	20.2	3.9	47.0	no data
95% exceedance	1.9	1.1	1.1	4.6	1.4	6.2	0.8	8.7	no data
10% exceedance	19.5	22.0	34.4	81.2	45.8	39.0	7.4	94.6	no data
Principal bedrock geology <sup>a</sup>	CM MG	MG SSM L	MG CM SSM	MG CM SSM	SSM SC	Ch SSC	Ig VS	VS Ig	VS Ig N
Principal soil types <sup>b</sup>	CS U A	CS SP BE	Sg CS A	Sg CS A	Pz SHG SG	Rz SG SP	P Gs BE	BE Rz A	BE Rz A
Principal land cover <sup>c</sup>	IG U	B HG IG	IG B HG	IG U B	IG B AG	IG W SU	MH H B	H HG MH	MH H HG

139

140 <sup>a</sup> Key to geology: Ch chalk, CM coal measures, Ig igneous intrusion, L limestone, MG millstone grit, N Neogene rocks – gravel sand silt and clay, SC sandstone and conglomerate, SSC  
141 sand silt and clay, SSM sandstone siltstone mudstone, VS volcanic and sedimentary rock.

142 <sup>b</sup> Key to soil type: A alluvisol, BE brown earth, CS cambic stagnogley, Gs gleysol, P peat, Pz podzol, Rz rendzina, SG stagnogley, SHG staghomic gley, SP stagnopodzol, U urban,

143 <sup>c</sup> Key to land cover: AG acid grassland, B bog, H heathland, HG heather grassland, IG improved grassland, MH, montane heathland, SU suburban, U urban, W woodland



156 Figure 1. Location map showing the study catchments. For the Dee and Ribble, black triangles indicate sampling sites. The Avon and Conwy  
 157 sampling sites were at the tidal limits.



158 The River Dee catchment is situated in the north-east of Scotland. The catchment is  
159 sparsely populated above the tidal limit, with a population density of 4 persons km<sup>-2</sup>. The  
160 tributary of the River Gairn is situated in the upper western reaches of the catchment. The upper  
161 mountainous areas respond rapidly to rainfall and snowmelt, producing a flashy flow regime.

## 162 2.2. *Sampling and analysis*

163 To minimise risk of carbon contamination, all equipment used during sampling and  
164 processing was new or acid-washed and all samples were managed in a radiocarbon tracer-free  
165 laboratory. Water samples (5 L) were collected in high-density polyethylene containers from  
166 the tidal limit of the four main catchments, and additional upstream samples were taken in the  
167 Ribble and Dee catchments (Figure 1). For the Ribble, Conwy and Dee sites samples were  
168 collected during high-flow events. For the Avon, which has a much less flashy flow regime,  
169 they were taken at regular intervals throughout one year. High flow events were identified  
170 from daily river levels measured at gauging stations near the sampling sites, and made available  
171 on-line by the Environment Agency of England and Wales and the Scottish Environment  
172 Protection Agency. During the period October 2013 – October 2014, four samples were taken  
173 for most of the sites, but only three each at the Gairn and Dee A sites. Additional 500 or 1000  
174 mL samples were collected for the determination of SPM concentration and the carbon content  
175 of the SPM.

176 The SPM was extracted from the water samples through repeated centrifugation (6 ×  
177 500 mL rotor spinning at 10000 rpm for 30 minutes), removal of supernatant and pooling, until  
178 approximately 100 mL of suspended sediment and water remained. To ensure the absence of  
179 inorganic carbonate, the concentrated suspended sediment was acidified by adding 400 mL of  
180 1M HCl to the extracted sediment and left overnight. Samples were then twice rinsed and  
181 centrifuged with deionised water, and sub-sampled for radiocarbon analysis. Remaining  
182 sediment was frozen for further analysis.

183 Organic carbon content of the SPM was measured using two different techniques.  
184 Firstly a known volume of the additional water sample was filtered through a pre-weighed, pre-  
185 combusted (500 °C) Whatman GF/F filter paper. This was dried at 105°C overnight and  
186 reweighed to determine [SPM], then analysed for total carbon with a Vario EL elemental  
187 analyser at CEH Lancaster (Ribble, Conwy, Avon) and a Thermo Flash 2000 elemental  
188 analyser at the James Hutton Institute. The values obtained would include any inorganic carbon  
189 present in the samples. Secondly a sub-sample of the concentrated SPM was captured on a

190 pre-weighed and combusted GF/F filter paper, and analysed. Results obtained by the two  
191 methods were in good agreement, suggesting that little or no inorganic carbonate had been  
192 present in the samples. Reported values are means from the two methods.

193 Graphite targets for  $^{14}\text{C}$  analysis by AMS were prepared by quantitative recovery of carbon in  
194 sealed quartz tubes followed by cryogenic separation of  $\text{CO}_2$  (Boutton et al., 1983). Aliquots  
195 of  $\text{CO}_2$  were converted to an iron/graphite mix by iron/zinc reduction (Slota et al., 1987). A  
196 sub-sample of  $\text{CO}_2$  was used to measure  $\delta^{13}\text{C}$  using a dual-inlet mass spectrometer with a  
197 multiple ion beam collection facility (Thermo Fisher Delta V) in order to correct  $^{14}\text{C}$  data to –  
198 25 ‰  $\delta^{13}\text{C}_{\text{VPDB}}$ . The mass spectrometer was calibrated with international reference materials  
199 to a precision of  $\pm 0.03$  ‰. For five samples, difficulties were encountered in the measurement  
200 of  $^{13}\text{C}$  by mass spectrometry, and so instead values of  $\delta^{13}\text{C}$  were obtained during AMS analysis,  
201 and used to correct to  $\delta^{13}\text{C} = -25$  ‰ vPDB. In these cases the  $\delta^{13}\text{C}$  values were not considered  
202 representative of the original combusted material.

203 In all but three cases  $^{14}\text{C}$  analysis was carried out at the Scottish Universities  
204 Environmental Research Centre AMS Laboratory, East Kilbride (Xu et al., 2004); these have  
205 publication codes starting SUERC. The other three measurements were on sample sizes of less  
206 than 500  $\mu\text{g}$  carbon and were made at the Keck Carbon Cycle AMS Laboratory at the  
207 University of California Irvine (publication codes UCIAMS). Size matched process  
208 background materials and known age standards were prepared and analysed to check accuracy  
209 and precision. In keeping with international practice, the results are reported as absolute %  
210 modern (pMC) which involves a mathematical adjustment to account for ongoing radioactive  
211 decay of the international reference standard (oxalic acid, provided by the US National Bureau  
212 of Standards), since AD 1950 (Stuiver and Polach, 1977) with conventional radiocarbon ages  
213 (based on radioactive decay and relative to AD1950) provided where results are below 100  
214 pMC. The  $^{14}\text{C}$  enrichment of a sample is measured as a percentage (or fraction) of the  $^{14}\text{C}$   
215 activity relative to the modern standard of oxalic acid where 100% modern is defined as the  
216 value in AD 1950, in the absence of any anthropogenic influences. Radiocarbon contents can  
217 exceed 100 pMC if they contain sufficient “bomb carbon”. Overall analytical precision is  
218 quoted at  $1\sigma$ .

### 219 2.3. Soil radiocarbon data

220 To aid the interpretation of the  $\text{PO}^{14}\text{C}$  data, we assembled soil radiocarbon data for UK sites  
221 under different land use. These comprised 70 data points for agricultural soils from Jenkinson  
222 et al. (2008), 132 values for semi-natural non-forested and forested soils from Mills et al.  
223 (2014), and 87 of our own unpublished data (H Toberman, JL Adams, E Tipping, CL Bryant)  
224 for semi-natural sites and improved grassland. The results are summarised in Table S1. We  
225 used values of  $^{14}\text{C}$  (pMC) for samples taken over the time-period 1999 to 2013. Average values  
226 were calculated to simplify data presentation and provide an overall picture of radiocarbon with  
227 depth. Because  $^{14}\text{C}$  is constantly changing, albeit slowly, the combination of data taken in  
228 different years involves approximation, but the time period for which data were taken was short  
229 in comparison to the turnover rate of bulk soil carbon as estimated by Mills et al. (2014).  
230 Therefore the averages obtained will differ little from those that would apply had all the  
231 sampling been simultaneous.

### 232 3. Results

233 At a UK level, the study catchments vary with respect to size, altitude range, climate,  
234 soil type, and land use (Table 1). The Calder catchment stands out as the only one with a  
235 substantial urban area, and it is also industrialised. The Avon catchment differs in that it lacks  
236 upland area and has more cultivated land. Furthermore, the River Avon discharge varies  
237 relatively little, owing to the dominant influence of groundwater. The other rivers display  
238 much more flashy flow regimes. In the Avon, Conwy and Ribble catchments, the main land  
239 use is livestock grazing, mainly on improved grassland in the Avon and Ribble, but mainly on  
240 unimproved grassland or heather moorland in the Conwy. Much of the Dee catchment is  
241 heather moorland and blanket bog, with significant but smaller areas of coniferous plantation  
242 woodland and improved grassland. None of the catchments contains extensive arable  
243 agriculture. In all cases, the dominant soil types have organic-rich surface horizons.

244 High flow water samples collected across the catchments varied considerably in  
245 average [SPM] and OC content (Table 2). The OC content (%) declines with increasing [SPM],  
246 the relationship following the power law,  $OC(\%) = 26.7 [SPM]^{-0.22}$ , which accounts for 75 %  
247 of the variance in OC content ( $p < 0.005$ ). This is consistent with global-scale data collated by  
248 Marwick et al. (2015), and means that under conditions of high sediment delivery the SPM is  
249 relatively poor in OC.

250 The  $\delta^{13}C$  values of the samples (Table 3) fall in the range -30 to -25 ‰, with all but one  
251 value  $< -27$  ‰. These indicate that the carbon is derived almost exclusively from plants using  
252 the  $C_3$  photosynthetic pathway, which is normal for northern temperate ecosystems like the UK  
253 (Still et al., 2003). The  $^{14}C$  contents of the samples fell in the range 69-100 pMC,  
254 corresponding to conventional  $^{14}C$  ages of 3000 years to modern (Table 3). The overall mean  
255 is 909  $^{14}C$  years with a standard deviation (SD) of 555 years. Comparison of the mean  $^{14}C$   
256 values for the individual rivers (Figure 2) shows that the only two rivers differing significantly  
257 from the others were the River Calder ( $p < 0.01$ ) and Ribble B site ( $p < 0.001$ ). The markedly  
258 low  $^{14}C$  for the Calder is probably related to its urban and industrial character, and the  
259 contribution of the Calder flow to that of the Ribble B is likely the reason for the moderately  
260 low  $PO^{14}C$  of the latter site. If the  $PO^{14}C$  data for the Calder and Ribble B are ignored, the  
261 overall average  $PO^{14}C$  value is 91.2 pMC (SD 3.0), and the average age of POC becomes 681  
262  $^{14}C$  years (SD 246 years), which can be taken as a representative value for predominantly rural  
263 rivers.

264 To put the results into context, we can firstly consider the radiocarbon content of catchment  
265 soils. A systematic survey of soil radiocarbon in proportion to land use or soil type is not  
266 available for each catchment, but a substantial body of radiocarbon data (Table S1) can be used  
267 to summarise land-use and depth variations for the UK (Figure 3). The results show that the  
268 highest  $^{14}\text{C}$  contents are found for topsoils under forest, then for soils under non-forest semi-  
269 natural vegetation, then under agricultural land use. Sub-soil  $^{14}\text{C}$  shows a fairly regular pattern  
270 of decline with depth (Figure 3). The average riverine  $\text{PO}^{14}\text{C}$  of 91.2 pMC is lower than the  
271 average soil organic  $^{14}\text{C}$  values for forest and non-forest semi-natural topsoils, but only slightly  
272 less than the improved grassland average of 93.6pMC, calculated from the two topsoil depths  
273 of 7 and 11cm in figure 3; note that none of our catchments included significant areas of arable  
274 soil.

275 Secondly, our results can be compared with a global dataset published by Marwick et  
276 al. (2015) (Figure 4). These authors identified [SPM] and the OC content (%) of SPM as useful  
277 variables against which to compare the  $^{14}\text{C}$  values. In the global context, the UK [SPM] values  
278 are comparably low and the OC contents are comparatively high. The  $\text{PO}^{14}\text{C}$  values are high  
279 compared with data for high-SPM, low-OC systems, but lower than the previously reported  
280 data for the low-SPM, high-OC range.

281

282

283 Table 2. Mean concentrations of SPM and OC contents of SPM. Values in brackets are  
284 standard deviations, and reflect both natural variation and the averaging of results obtained by  
285 different methods (Section 2.2).

286

River	[SPM] mg L <sup>-1</sup>	OC content %
Calder	52.8 (±63.2)	8.8 (±4.7)
Hodder	13.4 (±6.8)	15.0 (±8.0)
Ribble A	13.8 (±7.6)	14.3 (±5.7)
Ribble B	21.3 (±19.0)	16.1 (±10.3)
Conwy	2.7 (±1.0)	24.6 (±10.3)
Avon	8.1 (±5.4)	19.1 (±6.3)
Gairn	0.8 (±0.2)	35.9 (±19.2)
Dee A	0.8 (±0.5)	14.4 (±14.2)
Dee B	0.9 (±0.5)	35.0 (±17.7)

287

288 Table 3. Isotope data for POM in high-flow samples. Values are given of  $^{14}\text{C}$  (pMC),  $\delta^{13}\text{C}$   
 289 ( $\text{‰}$  vPDB) and conventional radiocarbon age (years BP). The errors in  $^{14}\text{C}$  are expressed as  
 290  $\pm 1\sigma$  (pMC) where  $\sigma$  is the overall analytical uncertainty. Bracketed values of  $\delta^{13}\text{C}$  are not  
 291 necessarily representative of the original combusted material (see Section 2.2).

292

River	Date	$\delta^{13}\text{C}$	$^{14}\text{C}$	$\pm 1\sigma$	Age	Publication No.
Calder	4/10/13	-28.2	75.06	0.35	2243	SUERC-52256
	22/10/13	-27.5	68.86	0.30	2935	SUERC-52262
	2/1/14	-28.2	81.80	0.36	1552	SUERC-52267
	7/1/14	-28.5	80.58	0.37	1672	SUERC-52274
Hodder	4/10/13	-28.6	89.89	0.39	794	SUERC-52257
	22/10/13	-28.6	91.09	0.42	687	SUERC-52263
	2/1/14	-28.8	91.25	0.40	673	SUERC-52268
	7/1/14	(-28.6)	89.92	0.39	792	SUERC-52275
Ribble A	4/10/13	-25.2	88.95	0.41	878	SUERC-52258
	22/10/13	-28.6	87.67	0.40	995	SUERC-52264
	2/1/14	-29.1	89.55	0.41	825	SUERC-52272
	7/1/14	-29.3	89.26	0.41	850	SUERC-52276
Ribble B	4/10/13	-28.6	84.68	0.39	1274	SUERC-52261
	22/10/13	-28.6	84.68	0.39	1273	SUERC-52265
	2/1/14	-28.7	88.15	0.41	951	SUERC-52273
	7/1/14	-28.8	84.34	0.39	1306	SUERC-52277
Conwy	7/1/14	-28.5	90.52	0.42	737	SUERC-52278
	27/1/14	(-23.0)	90.09	0.28	775	UCIAMS-144595
	14/2/14	-29.2	97.90	0.49	108	SUERC-53199
	22/10/14	-28.3	100.07	0.47	Modern	SUERC-58254
Avon	22/10/13	-28.2	90.60	0.40	731	SUERC-52266
	6/2/14	(-28.4)	88.78	0.28	895	UCIAMS-144596
	23/4/14	-29.9	92.63	0.48	553	SUERC-54377
	28/8/14	-30.1	92.62	0.41	554	SUERC-57317
Gairn	7/1/14	-28.5	90.58	0.42	732	SUERC-52283
	26/2/14	(-25.9)	90.92	0.31	700	UCIAMS-144597
	16/3/14	-27.0	95.84	0.45	279	SUERC-54379
Dee A	7/1/14	-27.9	93.74	0.41	457	SUERC-52282
	26/2/14	-28.2	89.52	0.45	827	SUERC-53201
	21/3/14	-27.2	88.09	0.46	957	SUERC-54382
Dee B	7/1/14	-27.9	93.04	0.41	517	SUERC-52281
	26/2/14	(-28.6)	88.88	0.45	885	SUERC-53200
	16/3/14	-27.7	88.95	0.44	878	SUERC-54378
	21/3/14	-27.6	91.76	0.44	628	SUERC-54383

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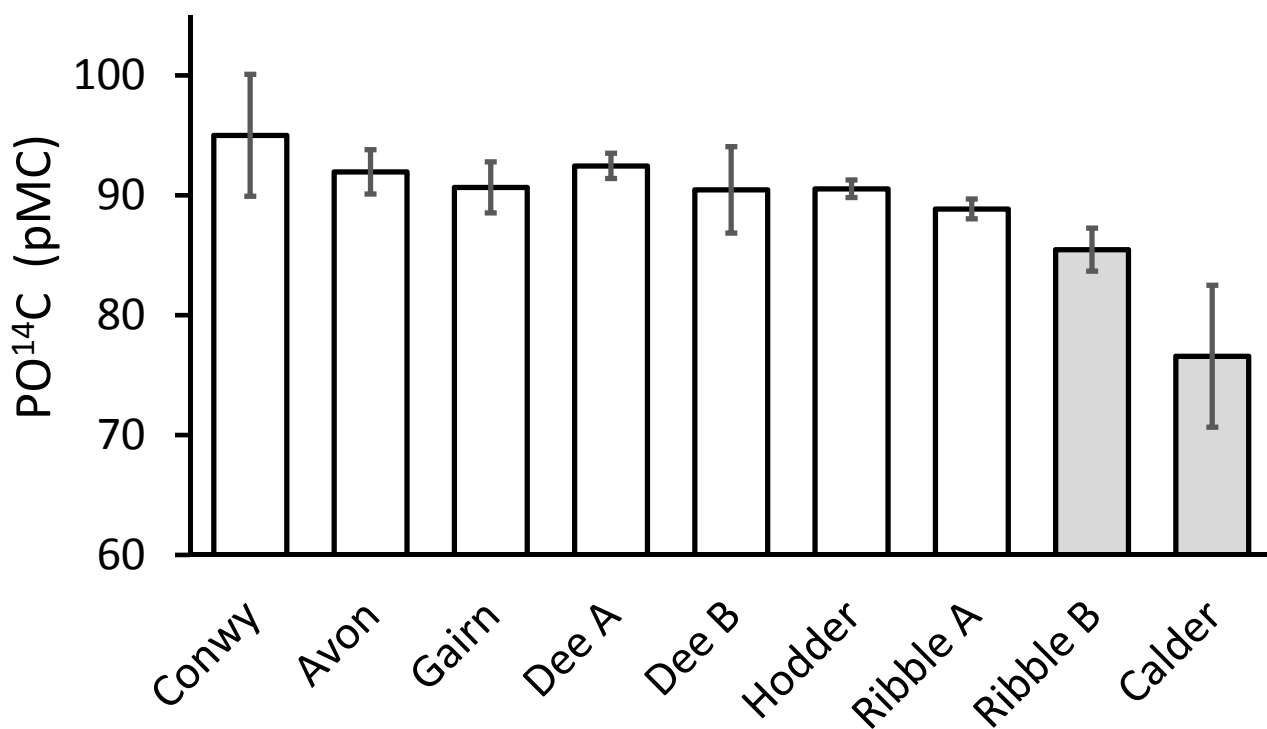
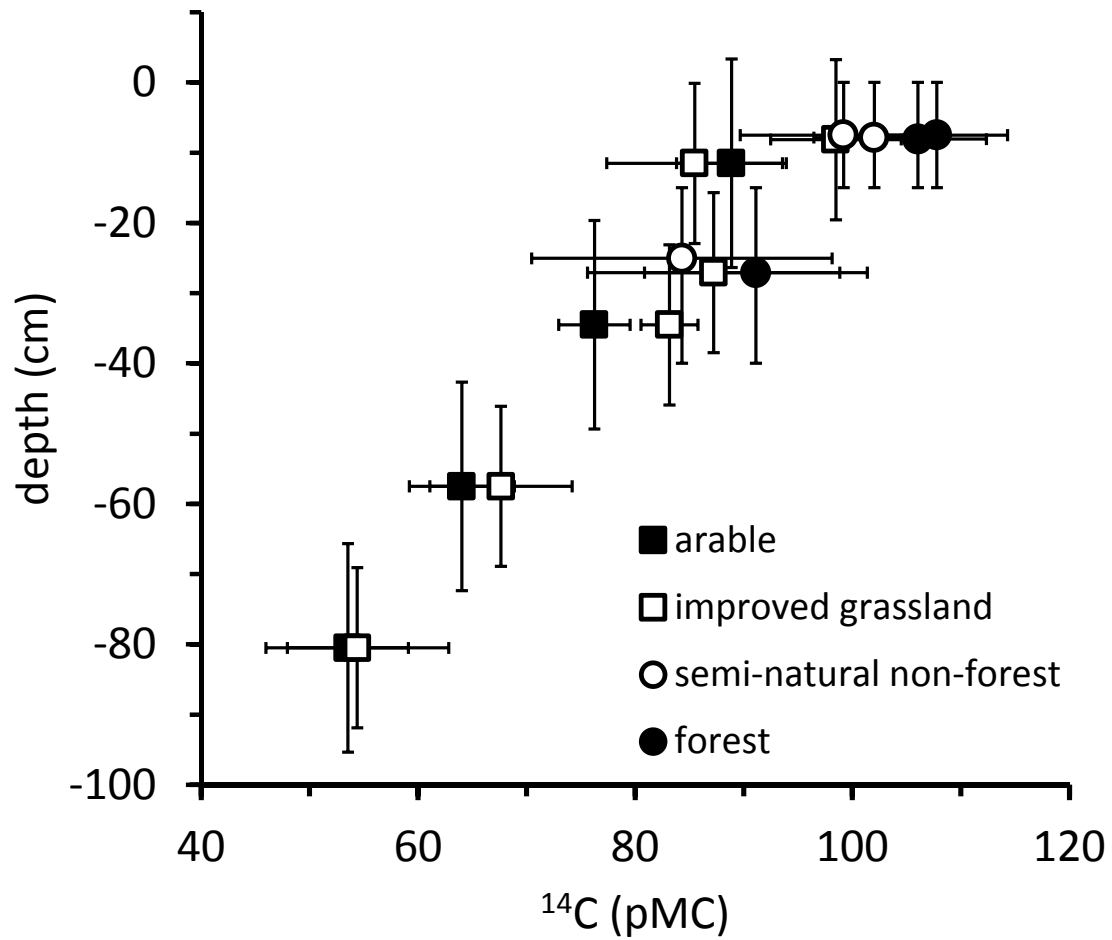


Figure 2. Average PO<sup>14</sup>C (pMC) for suspended sediment collected at high flow at the 9 sampling sites. Error bars represent standard deviations. Greyed bars show the two sites for which the PO<sup>14</sup>C values differ significantly from the others.





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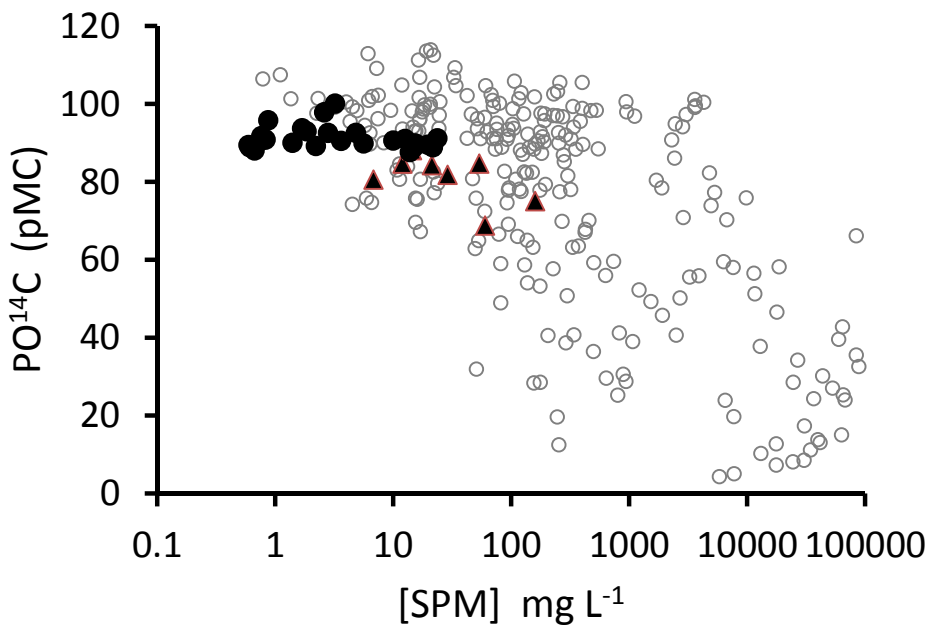
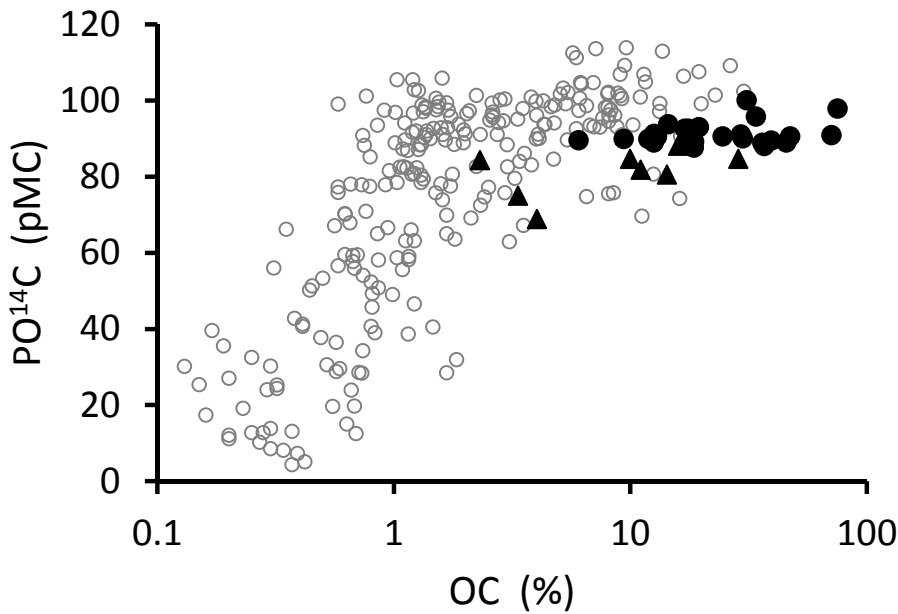
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311 Figure 3. Soil radiocarbon plotted against soil depth for 296 samples of UK soils. Depths are  
 312 plotted as the weighted average of sampling depths. The horizontal bars are standard deviations  
 313 in  $^{14}\text{C}$ , the vertical bars are ranges of sampling depth. See Table S1 for details.

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339 Figure 4. Radiocarbon contents of POM, i.e. PO<sup>14</sup>C, plotted the against OC content of SPM  
340 (%) and [SPM]. Global data collated by Marwick et al. (2015) are represented by the open  
341 circles. Data for the 7 rurally-dominated UK sites are shown by filled circles. Values for the  
342 Rivers Calder and Ribble B are shown by filled triangles.

#### 343 4. Discussion

344 In attempting to interpret the PO<sup>14</sup>C data reported here, it must be borne in mind that  
345 all the measured values arise from the mixing of organic matter from different sources, and that  
346 any calculated ages are only apparent. Therefore, the mean of 680 <sup>14</sup>C years must mean that  
347 both younger and older material is also present. An especially clear effect of mixing is seen  
348 within the present data, for the River Calder sub-catchment and Ribble B site (Table 3, Figure  
349 2). The Calder PO<sup>14</sup>C values (68 – 82 pMC) are lower than at any of the other sites due to  
350 industrial and/or mining activity in the catchment; for example coal (<sup>14</sup>C ~ 0) may be present  
351 in the samples. Mixing of River Calder water with water from the other two Ribble tributaries  
352 (Figure 1) then leads to relatively low PO<sup>14</sup>C (84 – 89 pMC) in the samples from the Ribble B  
353 site.

354 For the 7 rivers other than the Calder and Ribble B, the average value of PO<sup>14</sup>C (91.2  
355 pMC) could arise from the mixing of topsoil material with material from subsoils, exposed at  
356 the bank or via field drains (Chapman et al., 2001, Deasy et al., 2009). For example, if we  
357 assume that average subsoil has a <sup>14</sup>C value of 75 pMC (from Figure 3, the value at a depth of  
358 about 50 cm), and adopt a mid-range value of 100 pMC for the topsoil (Figure 3), then the  
359 value of 91.2 pMC would arise from a mixture comprising 65% topsoil OC and 35% subsoil  
360 OC. But if a topsoil value of 95 pMC were chosen, which might arise if soil under improved  
361 grassland were the main source of riverine POM (Figure 3), the mixture would be 81% topsoil  
362 OC and 19 % subsoil OC. These results bracket the average contributions to riverine SPM of  
363 topsoil and subsoil (73%: 27%) obtained by Walling (2013) from a collation of data for 84 UK  
364 rivers. However, the analysis is complicated by the fact that the OC content of soil decreases  
365 with depth, so that typically for UK soils, the subsoil OC concentration is only about one-fifth  
366 of the topsoil (Table S2, Figure S1). This would mean that to achieve the required amount of  
367 bulk subsoil OC to account for the PO<sup>14</sup>C values, the SPM fractions would have to be weighted  
368 towards the subsoil, which would not agree with Walling's results. A possible explanation is  
369 that soil components that are rich in organic matter are preferentially mobilised from the  
370 subsoil.

371 Another process that might explain why the riverine PO<sup>14</sup>C is depleted relative to  
372 topsoil (i.e. the average value of 91.2 pMC in the 7 rural catchments) is preferential  
373 mineralisation within the river channel of radiocarbon-rich topsoil organic matter (Marwick et  
374 al., 2015). This could arise because topsoil contains organic matter pools with different

375 turnover rates, and therefore with different  $^{14}\text{C}$  contents. On this basis, Mills et al. (2014) used  
376 a steady-state model with two main organic carbon pools having mean residence times of 20  
377 and 1000 years to interpret observed topsoil  $^{14}\text{C}$  data, and estimated that the pools were present  
378 in roughly equal proportions. At the present time, the faster turnover pool has a  $^{14}\text{C}$  content  
379 greater than 100 pMC because of the presence of “bomb carbon”, while the long-lived pool  
380 typically has a  $^{14}\text{C}$  content of about 90 pMC. Furthermore, the topsoil contains plant litter  
381 deposited within the last few years, with a  $^{14}\text{C}$  content slightly greater than 100 pMC. Both the  
382 litter and the 20-year major soil pool are mineralised in the terrestrial environment much faster  
383 than the 1000-year pool, and this difference would also be expected during riverine transport  
384 and temporary storage in the river bed. Loss of the more labile carbon would then reduce the  
385  $\text{PO}^{14}\text{C}$  value compared to that of topsoil. From regression analysis of UK-wide river data,  
386 Worrall et al. (2014) estimated that about 25% of POC is lost to the atmosphere as  $\text{CO}_2$  during  
387 riverine transport. If so, then a substantial reduction in the radiocarbon content of riverine POC  
388 could occur during transit. However, comparisons of sediment storage and annual flux suggest  
389 that residence times of SPM in UK rivers with catchment areas comparable to those of the  
390 present study are short, rarely more than a year (Owens et al., 1999; Collins and Walling, 2007),  
391 and so to achieve the 25 % mineralisation loss suggested by Worrall et al. (2014), rates of  
392 decomposition of POC in rivers would need to be appreciably higher than is generally accepted  
393 for their turnover in the soil. Dispersion of the material and exposure to light during riverine  
394 transport might accelerate the mineralisation process.

395 A possible explanatory factor with respect to our results is the effect of parent geology,  
396 the importance of which was highlighted by Longworth et al. (2007) to interpret  $\text{PO}^{14}\text{C}$  results  
397 for rivers draining small rural catchments in the Hudson-Mohawk watershed in upper New  
398 York State. Like our catchments, this is a low-erosion system as evidenced by the 5-year  
399 average (2004-2008) [SPM] of  $22 \text{ mg L}^{-1}$  for the Mohawk River at Cohoes  
400 (<http://waterdata.usgs.gov/nwis> accessed April 2015). Longworth et al. (2007) did not report  
401 [SPM] and OC content of SPM, and so their results are absent from the plotted values of  
402 Marwick et al. (2015) in Figure 4. Generally, their  $\text{PO}^{14}\text{C}$  values are higher than ours, falling  
403 in the range 89 to 109 pMC, but mostly they exceed 100 pMC. They explained the  
404 geographical distribution of their data, i.e. spatial variations in  $\text{PO}^{14}\text{C}$  values, in terms of  
405 contributions to POM from the physical weathering of shale (containing organic matter low in  
406  $^{14}\text{C}$ ). However, this is an unlikely explanation for the relatively depleted  $\text{PO}^{14}\text{C}$  reported in the  
407 present work, because the 7 rivers that provide the average of 91.2 pMC are in catchments free

408 of rock types containing ancient organic matter (Table 1). Therefore it seems unlikely that the  
409 presence of ancient carbon sources provides a general explanation for depleted PO<sup>14</sup>C in low-  
410 erosion catchments.

411 The present results fit with and extend the data compiled by Marwick et al. (2015). The  
412 plots in Figure 4 show that the global data fall into two zones. One occurs at high [SPM] and  
413 low OC content, for which very low <sup>14</sup>C values are observed, and the data encompass highly  
414 eroding, unstable systems (Smith et al., 2013). As noted by Marwick et al. (2015) this will  
415 reflect the strong dilution of topsoil-derived POC with eroded mineral matter low in OC but  
416 highly-aged, possibly with near-zero <sup>14</sup>C. This zone occurs for [SPM] greater than about 100  
417 mg L<sup>-1</sup> and for OC contents less than about 2%. The other zone is for lower [SPM] and higher  
418 OC content and there appears to be no true trend in the PO<sup>14</sup>C values with either [SPM] or OC  
419 content in this range, especially after the addition of the new data presented here (Figure 4).  
420 Thus we find a range of PO<sup>14</sup>C between about 80 and 110 pMC in the low-SPM, high-OC zone.  
421 Based on the present study and the conclusions of Marwick et al. (2015), variations in PO<sup>14</sup>C  
422 in low-erosion rivers can be attributed to variations in a number of factors. In approximate  
423 order of general importance these are (i) topsoil O<sup>14</sup>C variations across different land uses, (ii)  
424 catchment size and bank erosion, (iii) decomposition of POM during riverine transport, (iv)  
425 inputs of organic matter highly depleted in <sup>14</sup>C (from coal, shale or industry) and (v) in-river  
426 carbon fixation. Different combinations of these factors between rivers, or in the same rivers  
427 at different times, could generate the observed range of PO<sup>14</sup>C values. Progress towards the  
428 precise attribution of POC sources will require all these factors to borne in mind when  
429 designing field surveys and experiments. The fractionation of POM, e.g. by density or particle  
430 size, may also be a useful tool in characterising the PO<sup>14</sup>C. In the meantime, modelling and  
431 forecasting future change in POC fluxes will only be approximate. However, it seems certain  
432 that the riverine transport of carbon fixed many centuries ago, arising from both topsoil and  
433 subsoil, is contributing appreciably to carbon budgets in the UK and other low-erosion  
434 locations, and will continue to do so.

435 The high degree of consistency among the rivers (Figure 2) means that the results  
436 presented here are probably representative of pasture and upland catchments of similar size or  
437 greater across the UK. Catchments dominated by arable agriculture are missing from this study  
438 and should be considered in future research. We would expect that their rivers would have  
439 lower PO<sup>14</sup>C, in view of the available data on arable topsoils showing them to be relatively low  
440 in <sup>14</sup>C (Figure 3). The likely lower PO<sup>14</sup>C values in arable-dominated catchments, together

441 with contributions of POC from catchments with coal mining and industry, will tend to make  
442 the average age of POC entering the sea from the whole UK, somewhat greater than the average  
443 value of 680 <sup>14</sup>C years derived for the rural catchments of the present study.

444

445 **5. Conclusions**

- 446 • Particulate organic matter transported at high flow by 7 UK rivers draining pastoral rural  
447 landscapes had an average  $^{14}\text{C}$  content of 91.2 pMC, corresponding to an apparent average  
448 age of 681  $^{14}\text{C}$  years. These rivers show no significant difference ( $p > 0.05$ ) in their average  
449  $^{14}\text{C}$  values.
- 450 • Owing to industrial and mining activity in its catchment, the River Calder's POM was  
451 significantly more depleted in  $^{14}\text{C}$  (average 76.6 pMC). The Ribble B site, of which the  
452 River Calder is a tributary, also showed depleted  $\text{PO}^{14}\text{C}$  as a result of the contribution from  
453 the Calder catchment.
- 454 • Erosion of topsoil is an obvious major source of riverine POM. The most likely  
455 explanations for the relatively low  $\text{PO}^{14}\text{C}$  in the 7 rural rivers compared to topsoil  $\text{O}^{14}\text{C}$   
456 (range 94 – 109 pMC depending upon land-use) are firstly, inputs of older subsoil OC due  
457 to bank erosion and secondly, preferential mineralisation of  $^{14}\text{C}$ -rich organic matter during  
458 riverine transport.
- 459 • The present results are probably typical of other UK rivers with similar catchment soils and  
460 land uses. We expect that catchments dominated by arable soils would have lower  $\text{PO}^{14}\text{C}$   
461 values because of lower topsoil radiocarbon levels.

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464 **Acknowledgements**

465           The research was funded by the UK Natural Environment Research Council  
466   Macronutrient Cycles Programme (LTLS project, Grant No. NE/J011533/1), and the Scottish  
467   Government. We are grateful to A Panton (National Oceanography Centre, University of  
468   Southampton), EC Rowe (CEH Bangor) and C Somerville for assistance with sampling, P  
469   Scholefield (CEH Lancaster) for providing catchment area values, the analytical chemistry  
470   teams at CEH Lancaster and the James Hutton Institute (Rural and Environment Science and  
471   Analytical Services Division of the Scottish Government) for organic carbon measurements,  
472   and K Howarth (Environment Agency, North-West England) for facilitating access to sampling  
473   sites in the Ribble catchment. Thanks are due to the staff at the SUERC AMS Laboratory,  
474   East Kilbride for carbon isotope measurements, and to Dr Xiaomei Xu at the Keck Carbon  
475   Cycle AMS Laboratory, University of California, Irvine for analysis of three of the samples  
476   (Table 3).

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