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Science of the Total Environment

DOI:

[10.1016/j.scitotenv.2017.12.179](https://doi.org/10.1016/j.scitotenv.2017.12.179)

Published: 15/05/2018

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

de Sosa, L. L., Glanville, H. C., Marshall, M. R., Williams, A. P., & Jones, D. L. (2018).

Quantifying the contribution of riparian soils to the provision of ecosystem services. *Science of the Total Environment*, 624, 807-819. <https://doi.org/10.1016/j.scitotenv.2017.12.179>

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1 **Quantifying the contribution of riparian soils to the provision of ecosystem services**

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16

17 **Funding information**

18 This research was supported by the UK Natural Environment Research Council under the
19 Macronutrients Programme as part of the ‘Multi-Scale Response of Water Quality,
20 Biodiversity and Carbon Sequestration to Coupled Macronutrient Cycling from Source to Sea’
21 project (NE/J011967/1). This research was also supported by a Knowledge Economy Skills
22 Scholarship (KESS 2) awarded to LDS funded via the European Social Fund (ESF) through
23 the European Union's Convergence program administered by the Welsh Government.

24 **ABSTRACT**

25 Riparian areas, the interface between land and freshwater ecosystems, are considered to play a
26 pivotal role in the supply of regulating, provisioning, cultural and supporting services. Most
27 previous studies, however, have tended to focus on intensive agricultural systems and only on
28 a single ecosystem function. Here, we present the first study which attempts to assess a wide
29 range of ecological processes involved in the provision of the ecosystem service of water
30 quality regulation across a diverse range of riparian typologies. Specifically, we focus on 1)
31 evaluating the spatial variation in riparian soils properties with respect to distance with the river
32 and soil depth in contrasting habitat types; 2) gaining further insights into the underlying
33 mechanisms of pollutant removal (i.e. pesticide sorption/degradation, denitrification, etc) by
34 riparian soils; and 3) quantify and evaluate how riparian vegetation across different habitat
35 types contribute to the provision of watercourse shading. All the habitats were present within
36 a single large catchment and included: (i) improved grassland, (ii) unimproved (semi-natural)
37 grassland, (iii) broadleaf woodland, (iv) coniferous woodland, and (v) mountain, heath and
38 bog. Taking all the data together, the riparian soils could be statistically separated by habitat
39 type, providing evidence that they deliver ecosystem services to differing extents. Overall,
40 however, our findings seem to contradict the general assumption that soils in riparian area are
41 different from neighbouring (non-riparian) areas and that they possess extra functionality in
42 terms of ecosystem service provision. Watercourse shading was highly habitat specific and was
43 maximal in forests (ca. 52% shade cover) in comparison to the other habitat types (7-17%).
44 Our data suggest that the functioning of riparian areas in less intensive agricultural areas, such
45 as those studied here, may be broadly predicted from the surrounding land use, however, further
46 research is required to critically test this across a wider range of ecosystems.

47

48 *Keywords:* *E. coli* O157; Freshwater corridors; Land use; Riverbanks, Nutrient removal;
49 Wetlands.

50

51 **HIGHLIGHTS**

- 52 • Habitat type is the main driver explaining riparian soil physicochemical variability.
- 53 • Riparian areas do not necessarily deliver greater ecosystem services.
- 54 • LiDAR data can support the identification of key areas to target to increase riparian
55 shade. Riparian function can be largely predicted from neighbouring land use/soil type.
- 56 • Riparian function can be largely predicted from neighbouring land use/soil type.

57

58 **1. Introduction**

59 Ecosystem service-based approaches have been increasingly used to reduce pressure on natural
60 resources and implement better land-management practices with respect to the environment
61 (Van Looy et al., 2017). Riparian areas, the interface between land and freshwater ecosystems,
62 are considered to play a pivotal role in the supply of regulating, provisioning, cultural and
63 supporting services (Jones et al., 2010; Clerici et al., 2011; Aguiar et al., 2015). However,
64 despite the fact that the number of studies referring to ecosystem services has increased by 38%
65 in Europe over the last 20 years (Adhikari and Hartemink, 2016), riparian zones have received
66 less attention than other land use types from an ecosystem services perspective. The few
67 publications which have integrated an ecosystem service approach to the assessment of riparian
68 areas have tended to address this from a modelling perspective (Clerici et al., 2014; Tomscha
69 et al., 2017; Sharps et al., 2017). McVittie et al. (2015) proposed a model which aims to outline
70 the fundamental ecological processes that deliver ecosystem services within riparian areas.
71 Models provide a powerful and cost-effective tool to assess and map ecosystem services at the
72 landscape scale, however, they do not always provide a mechanistic process-level

73 understanding. It is therefore important that models are supported and developed with robust
74 underpinning data to correctly identify and describe the main factors affecting ecosystem
75 services delivery within complex landscapes (i.e. those which may contain a diverse array of
76 different riparian typologies). Little is known, however, about how inherent riparian properties
77 and ecosystem functioning vary across different habitats within a catchment area (Burkhard et
78 al., 2009). This uncertainty is largely due to the majority of riparian studies being focused on
79 single sites, typically intensive agricultural systems (i.e. arable and grasslands) as these
80 represent a major source of pollution (e.g. from fertilizers, livestock and pesticides) and
81 because riparian zones associated with agriculture present pollution mitigation potential
82 (Pierson et al., 2001; Rasmussen et al., 2011; Broetto et al., 2017). However, these studies tend
83 to overlook the fact that riparian areas are inter-related systems and therefore changes (both
84 natural and anthropogenic) occurring in headwater riparian zones across different habitat types
85 could also affect riparian processes occurring downstream (Harper and Everard, 1998; Charron
86 et al., 2008).

87 Among the many ecosystem services attributed to riparian areas, their role in water
88 quality enhancement has grown in recognition over the years. Water quality has become a
89 universal problem (Stephenson and Pollard, 2008) and is nowadays considered a priority
90 objective for EU environmental sustainability (EEA, 2012). Increased loss of phosphorus (P)
91 and nitrate (NO_3^-) from agricultural fertilizers has led to extensive eutrophication of surface
92 and groundwaters (EEA, 2005), and contamination by pesticides and biological contaminants
93 (e.g. bacteria) are regularly reported (Klapproth and Johnson., 2000; Troiano et al., 2001).
94 Riparian areas are frequently proposed as a management strategy to reduce freshwater nutrient
95 pollution (e.g. Coyne et al., 1995; O'Donnell and Jones, 2006; Stutter et al., 2009; Aguiar et
96 al., 2015; Sgouridis and Ullah, 2015) and could also reduce the cost of drinking water
97 purification (Klapproth and Johnson., 2000; Meador and Goldstein, 2003; Chase et al., 2016).

98 This pollution mitigation potential is often attributed to specific characteristics within riparian
99 soils (Mikkelsen and Vesho, 2000; Naiman et al., 2010). Table 1 summarizes the link between
100 riparian soil properties and the provision of ecosystem services found in the literature. A better
101 understanding of the causal factors for ecosystem services delivery will provide an improved
102 knowledge base on which to make land management decisions and protection policies.

103 Many regulating services are highly affected by environmental conditions. For example,
104 temperature is known to directly and indirectly affect biological activity through its impact on
105 gaseous concentrations in soil (e.g. CO₂/O₂) and in the water column (Beschta, 1997; Verberk
106 et al., 2016). It also plays an important role in determining the rate of key ecosystem processes
107 such as denitrification (Bonnett et al., 2013). Riparian buffers have increasingly been used as
108 a eutrophication mitigation tool by temperature regulation through provision of shade (Nisbet
109 and Broadmeadow, 2004; Burrell et al., 2014; Johnson and Wilby, 2015). Ghermandi et al.
110 (2009) suggested that shading could viably be used as a management option to improve water
111 quality conditions in small and moderately-sized watercourses. However, finding a cost-
112 effective way to target vulnerable areas is challenging and has been poorly explored to date.

113 The main focus of this study is to assess the link between riparian areas and the regulating
114 service of water purification through a wide range of ecological processes. In particular, we
115 aim to: 1) evaluate the spatial variation in riparian soils properties (i.e. general nutrient status,
116 soil acidity and conductivity, and microbial community size) with respect to distance with the
117 river and soil depth in contrasting habitat types; 2) gain further insights into the underlying
118 mechanisms of pollutant removal (i.e. pesticide sorption/degradation, denitrification, etc) by
119 riparian soils; and 3) quantify and evaluate how riparian vegetation across different habitat
120 types contribute to the provision of shade. This could help identify areas especially vulnerable
121 to excessive solar radiation and offer a cost-effective way to improve ecosystem service
122 provision (Ghermandi et al., 2009; De Groot et al., 2012). We hypothesized that riparian areas

123 would support a greater delivery of ecosystem services in comparison to the upslope area, but
124 that the balance of these services would be land use specific within a catchment area.

125

126 **2. Methodology**

127 *2.1. Site description*

128 The Conwy catchment was chosen as a demonstration test site for this study due to its
129 extensive use in previous ecosystem service monitoring studies (Emmett et al., 2016). It is
130 located in North Wales, UK (3°50'W, 53°00'N) and comprises a total area of 580 km² (Fig. 1).
131 The elevation ranges from sea level to 1060 m, with rainfall ranging between 500 to 3500 mm
132 y⁻¹ and the catchment has a mean annual temperature of 10 °C. Together, the topography,
133 parent material and climate have given rise to a wide range of soil types within the catchment
134 of which the dominant ones include Eutric Cambisols, Endoskeletic Umbrisols, Albic Podzols
135 and Sapric Histosols (WRB, 2014). It is predominantly a rural catchment, with livestock
136 farming (sheep and cattle) being the main land-uses. The two main habitat types are improved
137 (predominantly limed and fertilised) and unimproved grassland in the lower altitudes to the
138 east and mountain (exposed rock), heathland and bog in the western part of the catchment.
139 Extensive areas of coniferous (plantation) forestry and semi-natural deciduous woodland can
140 also be found in the upper reaches of the catchment.

141

142 *2.2. Field sampling*

143 Five dominant habitat types (MHB = mountain, heath and bog; BW = broadleaf
144 woodland; CW = coniferous woodland; SNG = semi-natural grassland; IG = improved
145 grassland) were selected for soil sampling throughout the catchment. Habitat classification was
146 derived from the new Phase 1 National Vegetation Survey (Lucas et al., 2011) and

147 subsequently grouped, for simplicity, into the same broad habitat classes (see Appendix 1 for
148 details of groupings) defined in the UK's Land Cover Map 2007 (Morton et al., 2014).

149 Independent riparian sampling areas ($n = 5$) were selected from each of the 5 dominant
150 habitat types. At all sites, soil was collected at 2 m distance from a river and 50 m from a river,
151 which is regarded as the maximum extent of the riparian buffer zone and which contained a
152 different vegetation from that close to the river (De Sosa, 2017, unpublished data). The
153 sampling was designed to enable a direct comparison of how soil properties are influenced by
154 proximity to the river.

155 Intact soil cores (5 cm diameter, 30 cm long) were collected using a split tube sampler
156 (Eijklecamp Soil and Water, Giesbeek, The Netherlands) and separated into top- and sub-soil
157 fractions (0-15 cm and 15-30 cm depths respectively), stored in gas-permeable plastic bags and
158 transported to the laboratory for immediate analysis. These depths reflect the main rooting
159 zones in the soil profile (Glanville et al., unpublished data). In addition, the depths were chosen
160 to be consistent with those used in the national surveys for assessing changes in soil ecosystem
161 service delivery and which are used to directly inform land use policy at the national-level
162 (Countryside Survey, Glastir Monitoring and Evaluation Programme; Emmett et al., 2010,
163 2016; Norton et al., 2012).

164

165 *2.3. Soil characterisation*

166 Soil samples were sieved (< 2 mm) to remove stones and any visible plant material and
167 to ensure sample homogeneity (Jones and Willett, 2006). Samples were then stored at 4 °C
168 prior to laboratory analysis. Soil water content was determined gravimetrically (24 h, 105 °C)
169 and soil organic matter (SOM) content was determined by loss-on-ignition (LOI) (450 °C, 16
170 h). Soil pH and electrical conductivity (EC) were measured using standard electrodes in a 1:2.5
171 (w/v) soil-to-deionised water mixture. Total available ammonium (NH₄-N) and nitrate (NO₃-

172 N) were determined with 0.5 M K₂SO₄ extracts (Jones and Willett, 2006) with colorimetric
173 analysis following the salicylate-based procedure of Mulvaney (1996) and the VCl₃ method
174 of Miranda et al. (2001), respectively. Available P was quantified with 0.5 M acetic acid
175 extracts (1:5 w/v) following the ascorbic acid-molybdate blue method of Murphy and Riley
176 (1962) and total C (TC) and N (TN) were determined with a TruSpec[®] elemental analyser
177 (Leco Corp., St Joseph, MI). Dissolved organic C (DOC) and total dissolved N (TDN) were
178 quantified in 1:5 (w/v) soil-to-0.5 M K₂SO₄ extracts using a Multi N/C 2100 TOC analyzer
179 (AnalytikJena, Jena, Germany)(Jones and Willett, 2006). Microbial biomass C and N was
180 assayed by chloroform fumigation-extraction after a 72 h incubation using conversion factors
181 of $k_{ec} = 0.45$ and $k_{en} = 0.54$ (Vance et al., 1987).

182

183 *2.4. Process-level studies to measure ecosystem services*

184 A series of process-level studies were conducted to investigate how soils across different
185 habitats contribute to the regulation of important ecosystem services involved in pollutant
186 attenuation. In addition, we aimed to assess how habitat influences the provision of shade and
187 the impacts on temperature regulation. For all experiments, field-moist soil ($n = 5$) was used to
188 best represent field conditions.

189

190 *2.4.1. Phosphorus sorption to soil*

191 P adsorption isotherms were determined to estimate the soil's capacity for removing
192 dissolved P from solution, and hence assess the potential for soils to reduce the amount of P
193 entering freshwaters. Sorption of P was determined following an adapted method of Nair et al.
194 (1984). In brief, 2.5 g of field-moist soil was shaken in 0.01 M CaCl₂ (1:5 w/v soil-to-extractant
195 ratio) containing known concentrations of P (0, 0.3, 1, 5, 10, 20 mg P l⁻¹ as KH₂PO₄) spiked
196 with ³³P (PerkinElmer Inc., Walham, MA) (0.2 kBq ml⁻¹). These concentrations were selected

197 due to their likelihood of being encountered in the catchment (DeLuca et al., 2015). Samples
198 were shaken (2 h, 150 rev min⁻¹, 25 °C) on an orbital shaker. This time was chosen to assess
199 intermediate equilibrium conditions (Santos et al., 2011). After 2 h, 1.5 ml of supernatant was
200 removed, centrifuged (10,000 g, 5 min), and subsequently, 1 ml of supernatant was mixed with
201 4 ml of Optiphase HiSafe 3 liquid scintillation fluid (PerkinElmer Inc.). The amount of ³³P
202 activity remaining in solution measured using a Wallac 1404 liquid scintillation counter
203 (Wallac EG&G, Milton Keynes, UK) and the total amount of P adsorbed was determined as
204 the difference between the initial ³³P activity added and the final amount of ³³P remaining in
205 solution. Any P not recovered in the solution was assumed to be sorbed onto the soil's solid
206 phase.

207 Sorption isotherms were examined according to the linearized form of the Langmuir
208 equation to estimate the P adsorption maxima and the P sorption binding energy for P (Reddy
209 and Kadlec, 1999; Mehdi et al., 2007):

$$210 \quad C/S = (1 / k \times S_{\max}) + (C/S_{\max}) \quad (\text{Eqn. 1})$$

211 where S is the amount of P adsorbed (mg P adsorbed kg⁻¹), C is the equilibrium solution
212 concentration after 2 h (mg P l⁻¹), S_{\max} is the P adsorption maximum (mg kg⁻¹), and k is a
213 constant related to the bonding energy (l mg⁻¹ P).

214

215 2.4.2. Bacterial pathogen survival

216 Soils from different habitat types were inoculated with human-pathogenic *Escherichia*
217 *coli* O157:H7 to investigate pathogen persistence in soils with respect to proximity to
218 waterbodies. Faecal samples, collected from a commercial beef farm in North Wales in January
219 2016, were inoculated with *E. coli* O157:H7 to reproduce the natural vector by which the
220 pathogen is introduced into the environment (Jones, 1999; Williams et al., 2008). Samples were
221 transported to the laboratory and stored at 4.0 ± 0.1 °C prior to use. Both faecal and soil samples

222 were previously screened for the background *E. coli* O157:H7 cells using an enrichment
223 technique (Avery et al., 2008) and absence of *E. coli* O157:H7 was confirmed by latex
224 agglutination (Oxoid DR620; Oxoid Ltd., Basingstoke, UK). Prior to the start of the experiment
225 a basic characterization of the faecal samples was undertaken and moisture content, organic
226 matter, EC, pH, NO₃-N, NH₄-N and P determined as previously described. The bacterial
227 inoculum was prepared from a fresh overnight culture (LB broth; 18 h, 37 °C, 150 rev min⁻¹ on
228 an orbital shaker) of two environmental isolates of *E. coli* O157:H7 (strains #2920 and #3704)
229 (Campbell et al., 2001; Ritchie et al., 2003). A 40 ml aliquot of the *E. coli* O157:H7 was added
230 to 360 g of cow faecal samples and thoroughly mixed to deliver a final concentration of
231 approximately 10⁸ cfu g⁻¹ faeces (to reproduce the highest natural concentration encountered;
232 Besser et al., 2001; Fukushima and Seki, 2004). In brief, 5 g of faeces spiked with *E. coli*
233 O157:H7 was added to 5 g of soil in a sterile 50 ml polypropylene tube and incubated at 10 °C
234 (mean annual temperature for the catchment) for 1, 3, 7 and 14 d. After each incubation time,
235 samples were placed on an orbital shaker (150 rev min⁻¹, 15 min, 37 °C) with 20 ml of sterile
236 quarter-strength Ringers solution (Oxoid Ltd.), followed by 4 × 3 s bursts on a vortex mixer.
237 Serial dilutions were plated in duplicate onto Sorbitol MacConkey agar (SMAC) (Oxoid Ltd.),
238 then incubated (37 °C, 20 h) and colonies enumerated. Presumptive *E. coli* O157:H7 colonies
239 were confirmed via latex agglutination as described previously.

240

241 2.4.3. Pesticide sorption and degradation in soil

242 The s-triazine herbicide, simazine (C₇H₁₂ClN₅; Water solubility, 5 mg l⁻¹; K_{ow}, 2.2; pKa,
243 1.6), was selected to investigate the fate of a common pesticide when applied to soils influenced
244 by different environmental factors.

245 Simazine sorption followed the procedure of Jones et al. (2011). Briefly, 5 ml of ¹⁴C-
246 labelled simazine (final concentration 0.5 mg l⁻¹; 0.02 kBq ml⁻¹) was added to 2.5 g of soil

247 contained in 20 ml polypropylene vials. The samples were then shaken (15 min, 200 rev min⁻¹) to reflect instantaneous equilibrium conditions (Kookana et al., 1993). The extracts were
248 then centrifuged (10,000 g, 5 min) and the supernatant mixed with Scintisafe 3[®] scintillation
249 cocktail (Fisher Scientific, Leicestershire, UK). The ¹⁴C activity remaining in solution was then
250 determined as described before. The simazine partition coefficient, K_d , was determined as
251 follows:

$$253 \quad K_d = C_{\text{ads}} / C_{\text{sol}} \quad (\text{Eqn. 2})$$

254 where C_{ads} is the amount of simazine sorbed (mg kg⁻¹) and C_{sol} is the equilibrium solution
255 concentration (mg l⁻¹).

256 To determine how soil influences pesticide degradation, 5 g of soil was placed in
257 individual 50 ml polypropylene tubes and ¹⁴C-labelled simazine was added to the soil at a rate
258 of 0.05 mg l⁻¹ (0.25 μM; 0.2 kBq ml⁻¹). A 1 ml NaOH trap (1 M) was then placed into the tube
259 to capture any ¹⁴CO₂ evolved. The tubes were hermetically sealed and placed at room
260 temperature (25 °C). The first NaOH traps were replaced after 24 h and then every 5 d for 30
261 d. On removal, NaOH traps were immediately mixed with Optiphase HiSafe 3 scintillation
262 fluid (PerkinElmer Inc.) and the amount of ¹⁴CO₂ captured was determined using a Wallac
263 1404 liquid scintillation counter. Total simazine degradation was calculated as the cumulative
264 percentage of ¹⁴C labelled CO₂ evolved at the end of the incubation period.

265

266 *2.4.4. Nitrate loss from soil*

267 Loss of nitrate via denitrification represents a major N loss pathway (Sgouridis and Ullah,
268 2015). Denitrification capacity was estimated using the acetylene inhibition technique (AIT)
269 as described in Abalos and Sanz-Cobena (2013). Although the application of this technique
270 presents limitations (i.e. poor diffusion of C₂H₂ into the soil and inhibition of NO₃⁻ production

271 via nitrification), it has been widely used to give a qualitative estimate of denitrification activity
272 (Estavillo et al., 2002; Groffman and Altabet, 2006; Tellez-Rio and García-Marco, 2015)).

273 In brief, 20 g of field-moist soil was placed in 150 ml gas-tight polypropylene containers.
274 Subsequently, KNO₃ (8 ml, 42.9 mM) was added to the soil to remove NO₃⁻ limitation, the
275 containers sealed and placed under vacuum and filled with O₂-free N₂ gas to induce anaerobic
276 conditions. Ten percent of the container headspace was then replaced with acetylene to block
277 the conversion of N₂O to N₂ gas. The containers were put on a reciprocating shaker at 25 °C.
278 After 0, 8 and 24 h, gas samples (10 ml) were removed with a syringe and stored in pre-
279 evacuated 20 ml glass vials, refilled with O₂-free N₂ gas. Nitrous oxide was analysed by gas
280 chromatography (GC) using a Clarus 500 GC equipped with a headspace autoanalyzer
281 Turbomatrix (HS-40) (PerkinElmer Inc.). Emission rates and cumulative fluxes were
282 determined as described by MacKenzie (1998) and Menéndez et al. (2006), respectively.

283

284 *2.5. Water temperature regulation and riparian shading provision*

285 A GIS-based methodology was used to determine the extent to which vegetation
286 contributes to water channel shading in the different habitats. Based on the UK Environment
287 Agency ‘Keeping River Cool’ programme (Lenane, 2012), a LiDAR dataset (2 m resolution
288 Natural Resources Wales composite dataset) (Table 2) was used to provide a riparian shade
289 map to quantify how different habitat types and their associated riparian zones contribute to
290 shade provision. Using the ArcGIS Solar Radiation tool, we calculated the difference in
291 average incoming solar radiation during the summer months (1st May to 30th Sept.) between
292 two different elevation datasets to produce a measure of relative shade for the catchment. A
293 Digital Terrain Model (DTM) provided the ‘bare earth elevation’ whereas a Digital Surface
294 Model (DSM) provided the earth’s surface data including all objects on it. Differences in
295 incoming solar radiation between these datasets indicates the likely amount of shade created

296 by vegetation. Although the relative shade was calculated for the whole catchment, only the
297 parts which overlap with rivers were considered. The Zonal Statistics function (Arc GIS) was
298 used to attach the difference in solar radiation from the DTM and DSM to the water body
299 features (clipped using a 25×25 m grid in order to make small but similar sized units to attach
300 results) extracted from the OS Open Rivers dataset (Ordnance Survey, Southampton, UK). The
301 resultant shapefile was exported to Excel where shading differences were ranked (1-20, with 1
302 being the least shaded and 20 the most shaded). The term “relative shading” was used to refer
303 to those areas that appear to have more or less than others due to the effect of the vegetation.
304 Finally, those areas which scored >10 on the ranking scale (higher provision of shade) were
305 then analysed to assess the influence of the habitat type on shade provision. A 2 m margin was
306 applied to each river, to ensure accurate intersection with the adjacent Phase 1 habitat
307 classification (Lucas et al., 2011) to estimate the percentage occurrence of each habitat in
308 relation to provision of shade.

309

310 *2.6. Statistical analyses*

311 For physicochemical soil properties, principal component analysis (PCA) was used to
312 explore the spatial relationships of selected soil properties for the different habitat types. A
313 two-way ANOVA was used to evaluate the interactions between physicochemical properties
314 with distance from river and soil depth within each habitat type. For each ecosystem process,
315 an independent t-test was performed to assess the influence of proximity to the river in terms
316 of ecosystem service provision. Pearson correlations were used to explore the relationships
317 between physicochemical properties and the results from the processing studies. All data were
318 analysed for normality and homogeneity of variance with Shapiro Wilk’s tests and Levene’s
319 statistics, respectively. Transformations to accomplish normality were done when necessary.

320 For all statistical tests, $P < 0.05$ was selected as the significance cut-off value. Statistical
321 analyses were performed with SPSS version 22 for Windows (IBM Corp., Armonk, NY).

322

323 **3. Results**

324 *3.1. Soil properties*

325 Principal Component Analysis (PCA) of the soil physicochemical variables of all
326 samples across the five dominant habitat types (see Methods for acronyms) ($n = 100$,
327 irrespective of distance or depth) identified two principal components (PC) which, together,
328 explain 66% of the total variance within the dataset (Fig. 2). Soil pH, available P, total C, total
329 N, DOC and TDN correlated significantly ($P < 0.001$) with the positive axis of PC1, whilst
330 microbial-N correlated significantly ($P < 0.001$) with the positive axis of PC2. Soil moisture,
331 organic matter, available $\text{NH}_4\text{-N}$ and microbial-C correlated significantly ($P < 0.01$) with both
332 PC1 and PC2.

333 Results of the PCA showed that habitat type (represented by cluster centroids, average
334 score on each PC1 and PC2 with standard errors) was an important predictor of soil
335 physicochemical variables. In terms of soil properties, BW and CW, and IG were closely
336 associated to each other in the Conwy catchment, although IG displayed overall higher total C
337 and N content (Table 3). At the other end of the spectrum (positive axis of PC1), the MHB
338 habitat was driven by moisture content (2.5 times more compared to woodlands and IG and 1.5
339 times greater than SNG) and total C (ranging between 3.5 times greater than IG and 9.5 for
340 BW) (Table 3). The SNG habitat resembled MHB in the sense that it had a greater moisture
341 content, total C and N compared to woodlands and IG habitats. However, they were more
342 influenced by microbial biomass showing larger variability in their vertical component. The
343 sites IG, SNG and BW were characterized by more alkaline pH values (ca. 5.2), whilst MHB
344 and CW displayed a more acidic pH (ca. 4.5) (Table 3).

345 As the objective of this work was to assess the influence of the river and soil depth in
346 terms of ecosystem service provision and not to compare different habitats, from this point
347 onwards we will focus on the influence of these factors within each habitat type.

348 The influence of soil depth and distance from river on physicochemical properties within
349 each habitat type is summarised in Tables S1-S5. Overall, soil depth showed no significant
350 effect on any of the soil physicochemical properties across habitat types, with some exceptions.
351 Microbial biomass-C was three times greater in the topsoil than subsoil in MHB ($P < 0.01$)
352 while microbial biomass-N differed approximately two-fold in the topsoil compared to the
353 subsoil in CW and SNG ($P < 0.05$). Total C showed a 72% change from top- to sub-soil in IG
354 ($P < 0.001$).

355 Available P was three times greater close to the river than 50 m away ($P < 0.01$) in MHB
356 but it was in the topsoil where the most noticeable difference was seen. The BW habitat
357 displayed the greatest difference when comparing physicochemical properties with respect to
358 distance. The BW habitat displayed 1.5 times greater EC away from the river, whereas total N
359 decreased by 1.5 times with distance from the river. Inorganic N ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) showed
360 a statistically significant increase (27% ($P = 0.042$) and 64% ($P = 0.004$) respectively) away
361 from the river whereas microbial biomass-N was 1.7 times less close to the river.

362 The pH within the CW habitat showed a significant variation ($P = 0.002$) with a 10%
363 increase close to the river, whereas DOC was 1.5 times greater away from the river. Distance
364 had no effect in physicochemical properties in SNG and IG habitats with the exception of
365 microbial biomass-C in SNG which was 6-times greater close to the river, although the standard
366 error was quite high. Total N within the IG habitat showed an increase of 62% close to the river
367 ($P < 0.05$).

368 As depth was shown to have very little effect on soil physicochemical properties, this
369 factor was removed from the subsequent assessment of ecosystem services delivery.

370 3.2. Ecosystem service provisioning

371 3.2.1. Phosphorus sorption to soil

372 P sorption across all habitat types was generally well described by the Langmuir model
373 ($r^2 = 0.92 \pm 0.01$). P sorption maxima, S_{\max} , ranged on average from 85 to 382 mg P kg⁻¹ across
374 the five habitat types, showing the lowest sorption capacity with BW and the highest in MHB.
375 Results showed that MHB had consistently higher values of maximum P sorption than the other
376 habitats. Nonetheless, the binding parameter, k , that reflects the strength of P sorption, was
377 found to be highly variable and reduced for MHB whilst the rest of the habitat types displayed
378 a similar trend (Table 4).

379 Although river proximity did not have a significant effect on S_{\max} ($P > 0.05$), SNG and
380 IG showed a tendency of greater P sorption closer to the river (Table 4). Significant positive
381 correlations ($P < 0.001$) were observed between S_{\max} and moisture content, organic matter,
382 available forms of N and P, C content and microbial biomass. In contrast, S_{\max} correlated
383 negatively with bulk density ($P < 0.001$). The most striking relationship was between S_{\max} and
384 DOC and TDN, suggesting that organic matter might play a key role in P sorption capacity.

385

386 3.2.2. Human bacterial pathogen survival in soil

387 Overall numbers of *E. coli* O157:H7 declined significantly ($P < 0.001$) between the first
388 and the second harvest dates across all habitat types. After 24 h post-inoculation, a decrease of
389 ca. 20% of pathogen numbers were observed at all sites. Numbers then remained relatively
390 stable in the soil for all habitat types with the exception of SNG in which the final percentage
391 ($49 \pm 2\%$) differed significantly from the rest of the habitat types. The final percentage decrease
392 across the other sites was ~ 70%, suggesting different controlling factors within SNG sites. In
393 terms of distance from river, there was no significant effect ($P > 0.05$) on persistence of *E. coli*
394 O157:H7 colony counts and therefore, both values (close and far) were amalgamated (Fig. 3).

395 3.2.3. *Pesticide sorption to soil*

396 Average K_d values, irrespective of distance to river, ranged from 11 to 484 l kg⁻¹ across
397 all habitat types. The pesticide sorption capacity in MHB soils was 45 and 23 times greater
398 than in the woodland (BW and CW, respectively) soils and between 6 and 30 times greater
399 than SNG and IG sites (Fig. 4). Woodland (BW, CW) and IG habitats showed similar K_d values
400 (11 ± 2 , 21 ± 3 and 16 ± 6 kg⁻¹, respectively) and the average K_d value for SNG was 79 ± 28
401 kg⁻¹ which is midway between the MHB and woodland habitats. K_d values displayed fairly
402 similar trends ($P > 0.05$) when comparing results from close and far away from the river (Fig.
403 4). Organic matter and moisture content correlated significantly ($P < 0.001$) with K_d which
404 might explain the higher sorption capacities within MHB and SNG habitat types.

405

406 3.2.4. *Pesticide degradation in soil*

407 After 30 d of incubation, the total percentage of simazine degradation ranged from 2.7 to
408 8.8% of the total ¹⁴C-simazine activity added across habitat types irrespective of distance from
409 the river. The amount of simazine mineralized was noticeably less in the MHB sites compared
410 with the rest of the habitats. Across all habitats and distances, the rate of simazine
411 mineralization was maximal in the first week of incubation and then progressively decreased
412 over the 30 d incubation period. No significant differences were noted for MHB and IG with
413 respect to distance from the river. In contrast, significant differences with distance from the
414 river were observed in the two woodland habitats (Fig. 5; $P = 0.041$ for BW and $P = 0.035$ for
415 CW). However, while the final percentage of simazine mineralized tended to be higher close
416 to the river in CW, the opposite trend was seen for BW. Across habitat types, the most striking
417 relationships between simazine degradation and soil physicochemical properties were a
418 positive correlation with pH ($P < 0.01$) and negative correlation with DOC ($P < 0.001$).

419 Simazine degradation also correlated negatively with N inorganic forms ($\text{NH}_4\text{-N}$, $P = 0.002$,
420 $\text{NO}_3\text{-N}$, $P = 0.003$) and available P ($P = 0.008$).

421

422 3.2.5. Denitrification potential in soil

423 Denitrification potential (DP) ranged between 0.25 and 1.94 mg $\text{N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ across
424 habitat types based on a 24 h incubation. Overall, IG showed the highest DP, being 3 and 7.5
425 times higher than the MHB and the woodlands, respectively.

426 The influence of river proximity revealed no significant differences in N_2O emissions (P
427 > 0.05). Very different emission patterns were observed within each habitat, as indicated by
428 the large error bars in Figure 6, reflecting the spatial complexity and the presence of
429 denitrification hot spots across all habitat types. When hot spot values were removed from the
430 analysis, N_2O emissions were the same irrespective of proximity to the river for MHB, BW
431 and CW habitat types. Although not significant, emissions rates tended to be higher further
432 away from the river for SNG and CW whereas the opposite trend was found for MHB and BW.

433 Overall, significant positive correlations ($P < 0.05$) were found between N_2O emissions
434 ($n = 50$) and bulk density and pH. Higher denitrification rates were found between pH 5 and 6
435 and bulk densities of 0.6 and 0.8 g cm^{-3} .

436

437 3.2.6. Provision of riparian shade

438 When evaluated across the whole catchment, the presence of woodland (CW and BW)
439 shaded 52.4% of the water channel. In contrast, in the MHB habitat the vegetation only
440 provided 7.6% shade cover. In the IG and SNG habitats the vegetation provided 17.4% and
441 12.9% shading respectively, however, this was partially due to the presence of isolated hedges,
442 trees and shrubs which were present within these habitats (Fig. 7).

443

444 **4. Discussion**

445 *4.1. General approach*

446 Our study investigated the spatial diversity of riparian soils and the ecological processes
447 that regulate the ecosystem service related to improving water quality. Soil physicochemical
448 properties were compared between samples taken close to (2 m) and distant (50 m) from the
449 river to further our understanding of how riparian specific soil characteristics vary across
450 different habitat types. Additionally, we explored different mechanisms of pollutant removal
451 (i.e. sorption, degradation and denitrification) and shading involved in water quality
452 enhancement with respect to riparian areas. We acknowledge that significant gradients may
453 exist across riparian areas, however, our sampling approach was designed to simply compare
454 soils in and out of the riparian zone. This approach reflects existing broad-scale soil surveys
455 which are used to measure and predict ecosystem service delivery at the national scale (Emmett
456 et al., 2010, 2016; Norton et al., 2012; Jones et al., 2014)

457 *4.2. Riparian soil physicochemical properties*

458 Many studies have linked the provision of riparian ecosystem services to their unique
459 intrinsic characteristics (Vought et al., 1994; Natta and Sinsin, 2002; Groffman and Crawford,
460 2003). Riparian soils may have higher organic C contents (Figueiredo et al., 2016; Graf-
461 Rosenfellner, 2016), greater amounts of nutrients and fine-grained sediments (Lee et al., 2000;
462 Mayer et al., 2007), increased moisture contents (Lewis et al., 2003; Zaines et al., 2007) and
463 microbial biomass (Naiman et al., 2010) than adjacent non-riparian areas. Contrary to
464 expectations, our findings contradict the frequently held assumption of riparian area
465 ‘uniqueness’. We observed little or no effect of the proximity to the river on the soil
466 physicochemical properties measured, despite major differences in vegetation community
467 composition and exposure to different hydrological regimes. General soil physicochemical
468 properties across habitat types followed the same trends as previous studies undertaken in the

469 catchment (Ullah and Faulkner, 2006; Sgouridis and Ullah, 2014; ;2015) and the inherent
470 habitat characteristics proved to be the main drivers explaining soil physicochemical variability
471 in riparian areas. In support of our findings, Richardson et al. (2005) also noticed little
472 difference in soil properties between riparian and upslope areas along small streams in
473 temperate forested areas of the Pacific Northwest. In addition, riparian studies have commonly
474 focussed on agriculturally-managed grasslands and more specifically on riparian buffer strips
475 as management tools (Pierson et al., 2001; Hefting and Bobbink, 2003; Hickey and Doran,
476 2004), even though this habitat type has shown less value in terms of ecosystem service
477 provision (Maes et al., 2011; 2012). Stutter et al. (2012) and Smith et al. (2012) found
478 significant differences when comparing soil physicochemical properties of riparian buffers
479 versus adjacent fields. However, the comparison was undertaken between areas which
480 possessed vastly different management regimes and in which the vegetation cover changed
481 dramatically. Similarly, Burger et al. (2010) also showed differences in soil properties between
482 agriculturally impacted riparian areas and ones conserved in pristine natural conditions. Most
483 of the habitats assessed in our study have little or no management intervention so natural or
484 semi-natural habitat conditions remained consistent across the upslope and riparian area. This
485 was true even for the areas subject to agricultural practices (improved and to a lesser extent
486 semi-natural grassland), although it should be stated that these agricultural areas generally have
487 good soil quality (unlike those under arable cropping; Emmett et al., 2016). It is possibly for
488 this reason that we did not identify any significant change in soil physicochemical properties
489 as reported by others. Further studies are therefore needed to take into account management
490 intensity and to include seasonal patterns as they may also represent an important component
491 in riparian dynamics (Dhondt et al., 2002; Greet et al., 2011).

492

493 *4.3. Ecosystem service provision*

494 In comparison to the surrounding region, riparian areas are usually considered to have
495 extra functionality in terms of ecosystem service provision through enhanced flood control,
496 water purification or biodiversity (Salo and Theobald, 2016; Sutfin et al., 2016; Xiang et al.,
497 2016). However, in our study there was no evidence that fundamental differences exist between
498 riparian zones and the adjacent land. This is supported by the clear segregation of results
499 according to habitat types and not by riparian areas (Fig. 8). Main habitat characteristics and
500 not distance from the river was the driving factor in all cases. In this respect, Table S6
501 summarizes the soil habitat physicochemical properties which are most likely to be driving the
502 ecosystem service delivery in this study. Together with that, we also include other factors that,
503 despite not being measured, should be considered in future riparian studies to predict the spatial
504 and temporal variation in ecosystem service delivery. These processes could be responsible for
505 creating ‘hot spots and moments’ within riparian zones (McClain et al., 2003; Vidon et al.,
506 2010). For example, erosion is more prevalent in riparian areas due to the exposure to a more
507 dynamic water regime (McCloskey, 2010). This can cause a large release of N, P and C into
508 the water column producing similar loads to those induced by fertilizer application (Quinton et
509 al., 2010). Likewise, water table fluctuations that modifies oxygen levels and nutrient
510 availability, and the presence of macrophytes are also good examples that could potentially
511 alter ecosystem service delivery dynamics in riparian areas (Naiman and Decamps, 1997; Hill,
512 2000; Lewis et al., 2003; Ng and Chan, 2017).

513

514 *4.3.1 Pollutant removal via sorption*

515 Values of S_{\max} (P sorption) and K_d (simazine sorption) resulted in good agreement with
516 other values found in the literature across habitat types (Dunne et al., 2005; Flores et al., 2009).
517 Analysis suggested that simazine and P sorption was driven by high organic matter content as
518 has been highlighted in previous studies (Li et al., 2003; Hogan et al., 2004; Kang and

519 Hesterberg, 2009; Alister and Kogan, 2010). Particularly for P sorption, some authors attribute
520 this affinity of P for organic matter to the co-occurrence of Al and Fe oxides, which can sorb
521 high amounts of P (Pant et al., 2001; Kang and Hesterberg, 2009). We had expected that the
522 riparian areas would be wetter, have a lower redox status and would contain a lesser amount of
523 oxidised forms of Fe and thus a lower P retention capacity, however, this was not apparent in
524 our soils. Barrow (2017) illustrated different pathways for P sorption according to soil pH but
525 due to the relatively small shifts in pH relative to the distance to the river, no such effect was
526 found in this study.

527 Comparing the results obtained in this study is challenging as most studies within riparian
528 areas try to identify the most cost-effective buffer width depending on the pollutant load in
529 agricultural systems or constructed wetlands. This is motivated by the fact that land managers
530 do not want to sacrifice more productive land than they have to (Wenger, 1999; Shearer and
531 Xiang, 2007). Consequently, the centre of attention has been on comparing inputs versus
532 outputs of pollutants in runoff through vegetative buffer strips (Schultz et al., 2000; Maillard
533 and Imfeld, 2014). Results found in the literature about the long-term effectiveness of riparian
534 buffers in trapping pollutants are contradictory as riparian areas can vary from being sources
535 to sinks depending mostly on physicochemical soil properties and hydrology (Hickey and
536 Doran 2004; Fisher and Acreman, 2004; Stutter et al., 2009; Maillard and Imfeld, 2014). Some
537 studies (e.g. Miller et al., 2016) reported different P retention capacities with distance from the
538 river. However, it was only true for samples included inside a concentrated flow path that was
539 visually identified prior to sampling. In contrast, samples outside this concentrated flow path
540 did not reveal any differences in P retention across the transect.

541 The similar pollutant sorption capacities relative to distance from the river found in this
542 study, combined with fact that simazine and P retention by soil can only occur when they are
543 in direct contact with the adsorbent suggest that the soil potential data alone is not very useful

544 in predicting the pollutant retention capacity (Reddy and Kadlec, 1999). Thus, the study of
545 transport pathways, potential sources of pollutant loads, ease of degradation, desorption
546 potential from the soil, shifts in temperature that controls simazine solubility or pH that controls
547 P precipitation may contribute more efficiently to understanding riparian pollutant attenuation.

548

549 *4.3.2 Pollutant removal through degradation*

550 Degradation, together with sorption, is one of the main processes determining the fate of
551 pollutants within the environment (Gunasekara et al., 2007; Maillard and Imfeld, 2014). In our
552 study, we investigated the degradation of a pesticide and loss of the biological contaminant, *E.*
553 *coli* O157, which are of concern in terms of their impact on human health (Holden et al., 2017).
554 Sorption and transport of pollutants, and the extension of buffer strips on agricultural and
555 wetland systems has often been the focus of attention (Vellidis et al., 2002; Hickey and Doran
556 2004; Rasmussen et al., 2011), but processes influencing pollutant degradation in riparian areas
557 are much less well understood (Vidon et al., 2010). Microbial activity has long been identified
558 as a critical factor determining the fate of pesticides in the environment (Kaufman and Kearney,
559 1976; Anderson, 1984), and it is suggested that microbial populations within riparian areas are
560 able to degrade pesticides due to their continuous exposure to such chemicals through runoff
561 from agricultural lands (Vidon et al., 2010). Overall, simazine degradation in this study showed
562 a similar percentage decrease (of the total of ¹⁴C-simazine added) to other studies (Laabs et al.,
563 2002; Gunasekara et al., 2007; Jones et al., 2011). Laabs et al. (2002) and Cox et al. (2001)
564 found a negative correlation between simazine degradation rates and organic matter content
565 due to the residue binding to organic matter reducing herbicide movement in the soil. This fact
566 could explain the minimal amount of simazine degraded in MHB sites in this study. Previous
567 studies have demonstrated enhanced pesticide degradation within riparian areas (Mudd et al.,
568 1995; Staddon et al., 2001). However, the riparian buffer strips in these previous studies

569 differed considerably from the adjacent habitat (i.e. bare or highly modified fields versus
570 vegetated buffer strips). In our study, only the woodlands showed a different pattern in terms
571 of pesticide degradation when comparing sites close and distal to the river. However, we
572 hypothesized that the negative correlation between simazine degradation and N and P inorganic
573 forms content could explain this spatial variability as the use of pesticides as a source of energy
574 in areas with low nutrient status has been identified (Błaszak et al., 2011). In addition, it has
575 been shown that some organisms (e.g. *Pseudomonas*) are able to mineralise simazine more
576 rapidly (Regitano, 2006; Błaszak et al., 2011) and therefore a more diverse microbial
577 population associated with a higher above-ground plant diversity could be involved in different
578 ecosystems. Our results may therefore reflect the spatial heterogeneity of microbial populations
579 within these habitat types rather than a specialization of microbial population in riparian areas.
580 This fact is endorsed by studies like Widenfalk et al. (2008) where an effect on microbial
581 composition due to pesticide exposure could not be identified. Our results reveal that there is a
582 need for linking functional soil biota groups with the maintenance of ecosystem services to
583 better explain the inherent spatial heterogeneity (Brussaard, 1997; Graham et al., 2016).

584 Along with pesticides, biological contaminants, in particular faecal coliform bacteria
585 (FCB), have become an important source of water contamination from human and animal
586 wastes applied to land (Bai et al., 2016). Although the use of riparian buffer strips for reducing
587 FCB transport into streams has been explored (Coyne et al., 1995; Parkyn et al., 2003; Sullivan
588 et al., 2007), bacterial survival and behaviour in terrestrial systems has received less attention
589 than in water ecosystems (Jones, 1999). Our results corroborate previous studies that show *E.*
590 *coli* O157 can survive for long periods (more than 120 d) in a diverse range of soils and under
591 a wide range of environmental conditions (Bogosian et al., 1996; Kauppi and Tatini, 1998;
592 Jones, 1999). Some studies have suggested that moisture status and organic matter are the
593 principal factors controlling *E. coli* survival (Jamieson et al., 2002). However, the lack of

594 correlation between soil properties and pathogen survival in this study suggest that other
595 factors, such as predation or the presence of elements highlighted in other studies (Al, Zn;
596 Avery et al., 2008), might better explain the lower survival rate found in semi-natural grassland
597 sites.

598

599 *4.3.3 Pollutant removal through denitrification*

600 Denitrification, as a mechanism for permanent removal of NO_3^- from ecosystems, has
601 important implications for both water quality and greenhouse emissions (Groffman et al.,
602 2009). It has been extensively studied in riparian areas due to the frequency of locally anoxic
603 conditions and labile organic C which trigger denitrification (Bettez and Groffman, 2012). In
604 our study, rates of N_2O emissions across habitat types followed similar trends to those
605 described in Sgouridis and Ullah (2014). However, we could not find any clear evidence that
606 leads us to identify more efficient patterns of NO_3^- removal by denitrification with proximity
607 to the river. We also observed a high degree of spatial variability in denitrification with some
608 extremely high rates as has been observed in other studies and described as ‘hot spots or
609 moments’ controlled by oxygen, NO_3^- and C availability (Parkin, 1987; McClain et al., 2003;
610 Groffman et al., 2009; Vidon et al., 2010). Previous riparian studies have also reported no clear
611 spatial patterns in denitrification rates (Martin et al., 1999). In our study, it was clear that the
612 addition of NO_3^- was not sufficient to trigger large amounts of N_2O production, indicating that
613 factors other than NO_3^- limitation were playing a key role. Sgouridis and Ullah (2015) describe
614 significant relationships between denitrification rates and pH and bulk density, and the same
615 pattern was found in our study. However, those factors do not explain the high variability
616 encountered within habitat types, and it was not possible to demonstrate significantly increased
617 N_2O production rates within riparian areas as demonstrated in previous studies (Hanson et al.,
618 1994; Groffman et al., 2000; Groffman and Crawford, 2003). Further research is therefore

619 required to better understand why denitrification is so spatially variable and the
620 spatial/temporal existence of ‘hot spots or moments’.

621

622 *4.3.4 Riparian shading*

623 Riparian shading is gaining increased recognition for its potential to alleviate water
624 pollution (Ghermandi et al., 2009; Warren et al., 2017). For example, Hutchins et al. (2010)
625 found that the reduction of nutrient pollution was less effective at suppressing phytoplankton
626 growth than establishing riparian shading. Bowes et al. (2012) also noticed a potential reduction
627 of 50% of periphyton accrual rate through shading in the River Thames.

628 The shade mapping approach presented here provides an easy tool to identify watercourse
629 exposure to solar radiation. As described in Lenane (2012), the maps generated using this
630 approach, offer the guidance necessary to help with riparian management plans and decision-
631 making strategies. Identifying whether riparian vegetation is providing effective shade is
632 fundamental for environmental protection. Furthermore, the size of this area required to
633 provide shade has economic implications as it takes the land out of production (Sahu, 2010).
634 The shade evaluation undertaken in this study differs from others in which field monitoring are
635 required (Boothroyd et al., 2004; Halliday et al., 2016) and consequently it avoids excessive
636 costs associated with field measurement campaigns. However, it does not predict water quality
637 changes as proposed by Ghermandi et al. (2009) which combines available flow measurements
638 with biochemical and shade models.

639 As expected, in our study the effects of shading were more significant in woodlands than
640 in any other habitat type. Woodland riparian zones are likely to offer the greatest influence on
641 water temperature within a catchment. Any assessment, however, should also consider
642 excessive shading, mostly caused by abandoned woodlands (Suzuki, 2013) which can be
643 detrimental to aquatic ecosystems by excessively reducing water temperature. This can have a

644 direct impact on aquatic fauna and result in a loss of shade-intolerant plants (Forestry
645 Commission, 2004; Hédli et al., 2010). Shading may also reduce the UV radiation-induced
646 photooxidation of many pesticides within the water column.

647

648 **5. Conclusions**

649 Recommendations and guidance about riparian zone management are frequently
650 undertaken without an accurate evaluation of their status and the ecosystem services that they
651 actually provide. Consequently, many previous environmental protection measures involving
652 riparian management remain too general and untargeted and may offer little environmental
653 benefit. Through a series of laboratory experiments and GIS-based mapping, this study has
654 shown that across a diverse range of habitats, riparian soils diverge from their capacity to
655 deliver the specific ecosystem service of water purification. However, contrary to expectation,
656 riparian soils did not differ greatly in their ability to provide this service in comparison to
657 neighbouring upslope (non-riparian) soils. We ascribe this to our habitats being in a close to
658 natural or semi-natural state rather than the more frequently studied riparian areas in degraded
659 agricultural systems. Further work should focus on validating our findings using an even
660 greater range of ecosystem services (e.g. inclusion of CH₄/CO₂ emissions, metal attenuation,
661 biodiversity), using in situ measurements, encompassing inter-annual variation and over a
662 wider range of ecosystem types.

663

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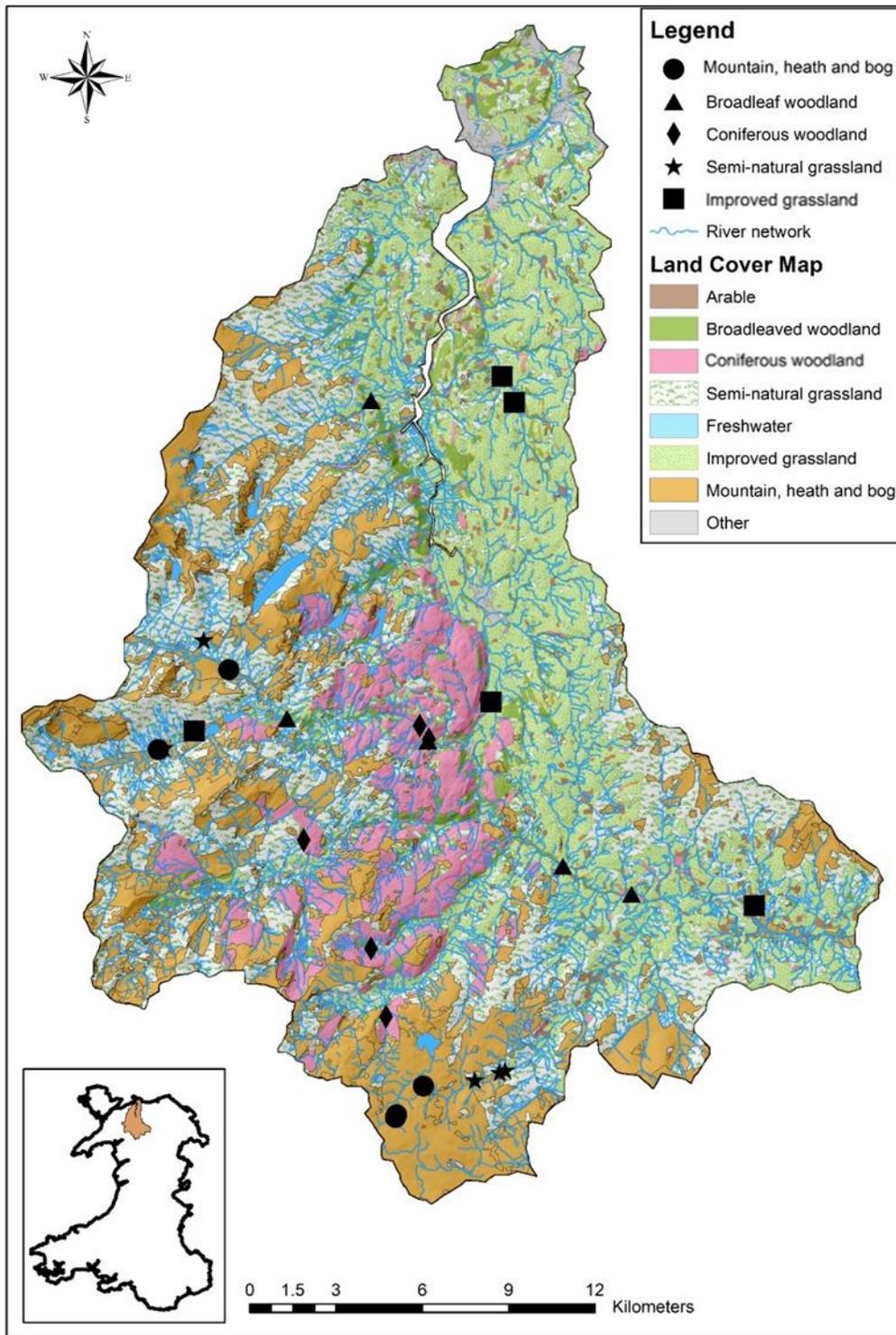
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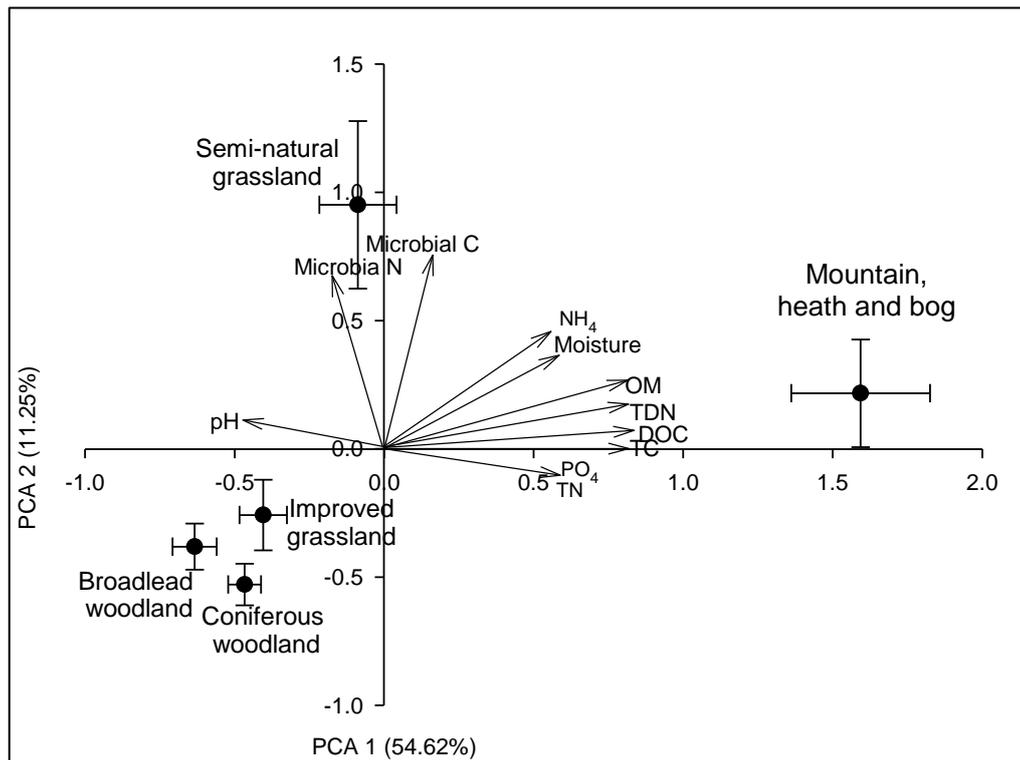
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1093 **Figure 1.** The Conwy catchment, North Wales, UK showing location of sample points, land
 1094 cover classes (Lucas et al., 2011) and river network. Samples sites were distributed within the
 1095 five dominant habitat types in the Conwy catchment (mountain, heath and bog, broadleaf and
 1096 coniferous woodlands, semi-natural grassland and improved grassland) and each symbol
 1097 represents a pair of sample points, one at 2 m and another at 50 m distance from the river
 1098 system ($n = 10$).



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1101 **Figure 2.** Correlation bi-plot from the principal component analysis (PCA) on soil
 1102 physicochemical variables according to their dominant habitat type and irrespective of distance
 1103 and depth ($n = 100$). Correlation of soil properties with the main axes are given by arrows and
 1104 habitat types by cluster centroids (average score on each horizontal principal component (PC1)
 1105 and vertical principal component (PC2) with standards errors). Organic matter (OM). Total
 1106 carbon (TC). Total nitrogen (TN). Dissolved organic carbon (DOC). Total dissolved nitrogen
 1107 (TDN).

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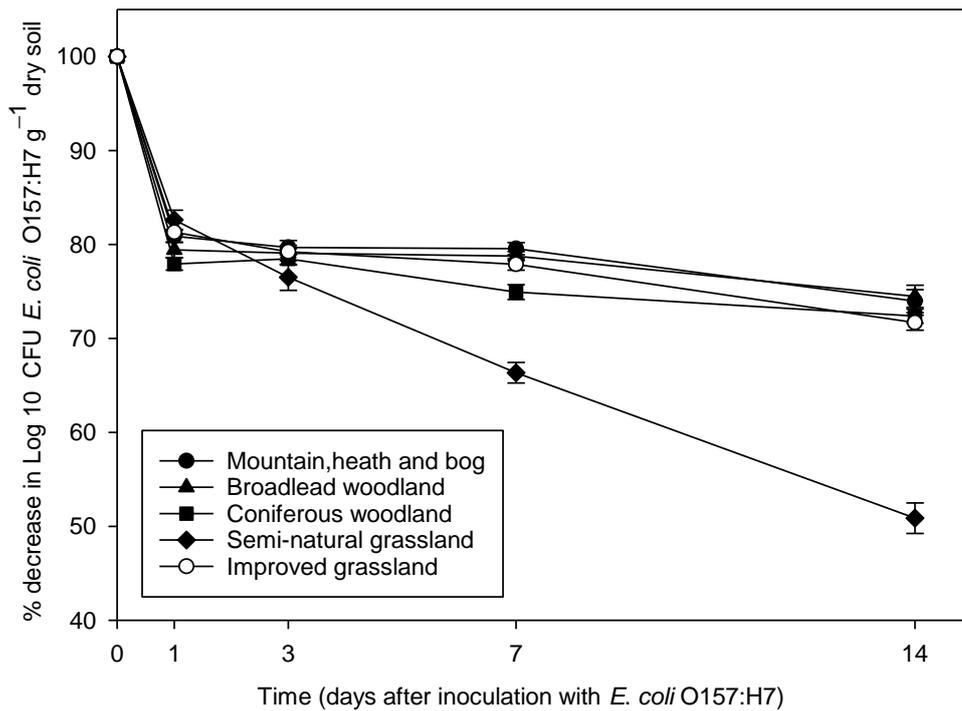
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1122 **Figure 3.** Survival of *Escherichia coli* O157:H7 following the application of pathogen-
 1123 contaminated cattle slurry to the soil from different habitat types amalgamating distance from
 1124 the river. Data points represent mean values ($n = 10$) \pm standard error of the mean (SEM).

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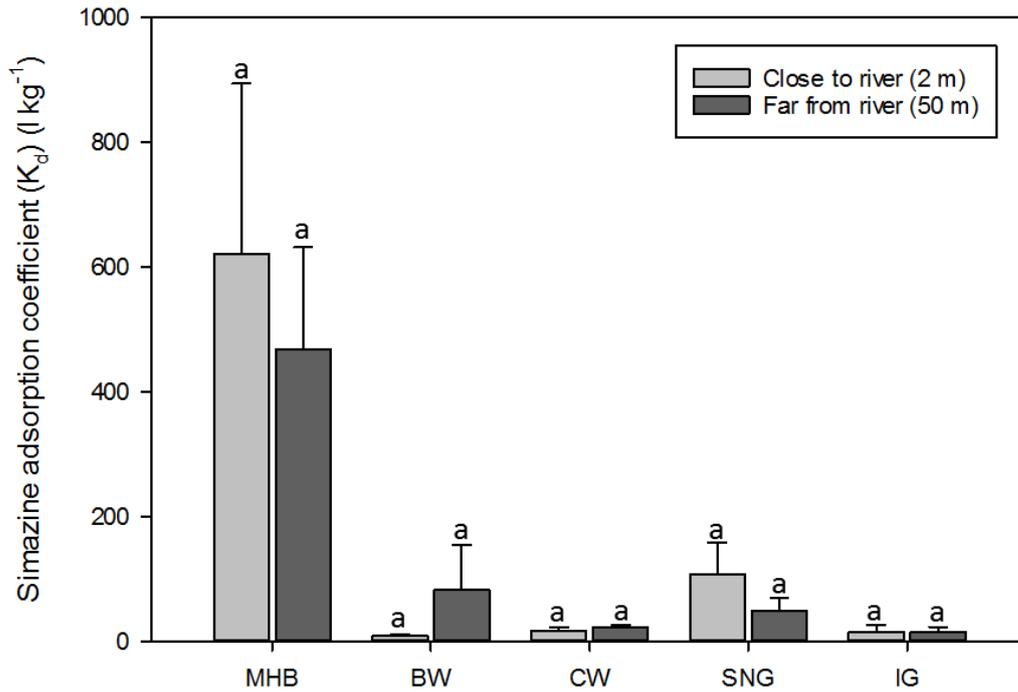
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1143 **Figure 4.** Simazine adsorption coefficient (K_d) across habitat types (MHB: mountain, heath
 1144 and bog; BW: broadleaf woodland; CW: coniferous woodland; SNG: semi-natural grassland;
 1145 IG: improved grassland) with respect to distance from the river. Same lower-case letters
 1146 indicate no significant difference ($P > 0.05$) between distance from the river and simazine
 1147 adsorption coefficient according to independent t -test within each habitat type. Bars represent
 1148 mean values ($n = 5$) \pm standard error of the mean (SEM).

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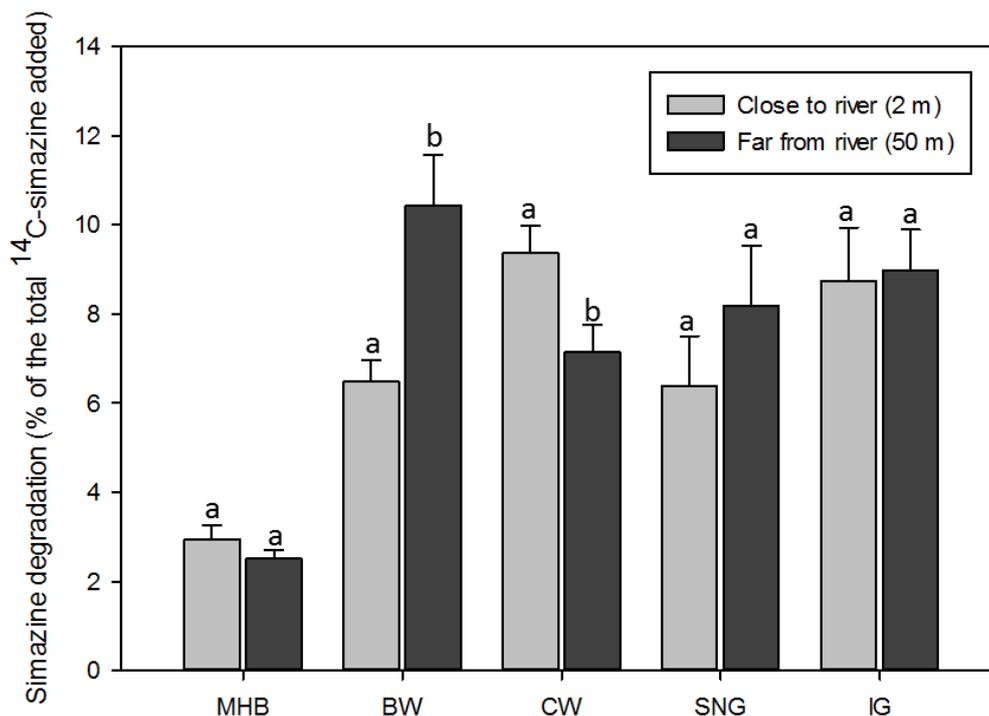
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1156 **Figure 5.** Simazine degradation across habitat types (MHB: mountain, heath and bog; BW:
 1157 broadleaf woodland; CW: coniferous woodland; SNG: semi-natural grassland; IG: improved
 1158 grassland) with respect to distance from the river. Values are expressed as the cumulative
 1159 percentage of the total ¹⁴C-simazine added. Same lower-case letters indicate no significant
 1160 difference ($P > 0.05$) between distance from the river and simazine degradation according to
 1161 independent t -test within each habitat type. Bars represent mean values ($n = 5$) \pm standard error
 1162 of the mean (SEM).

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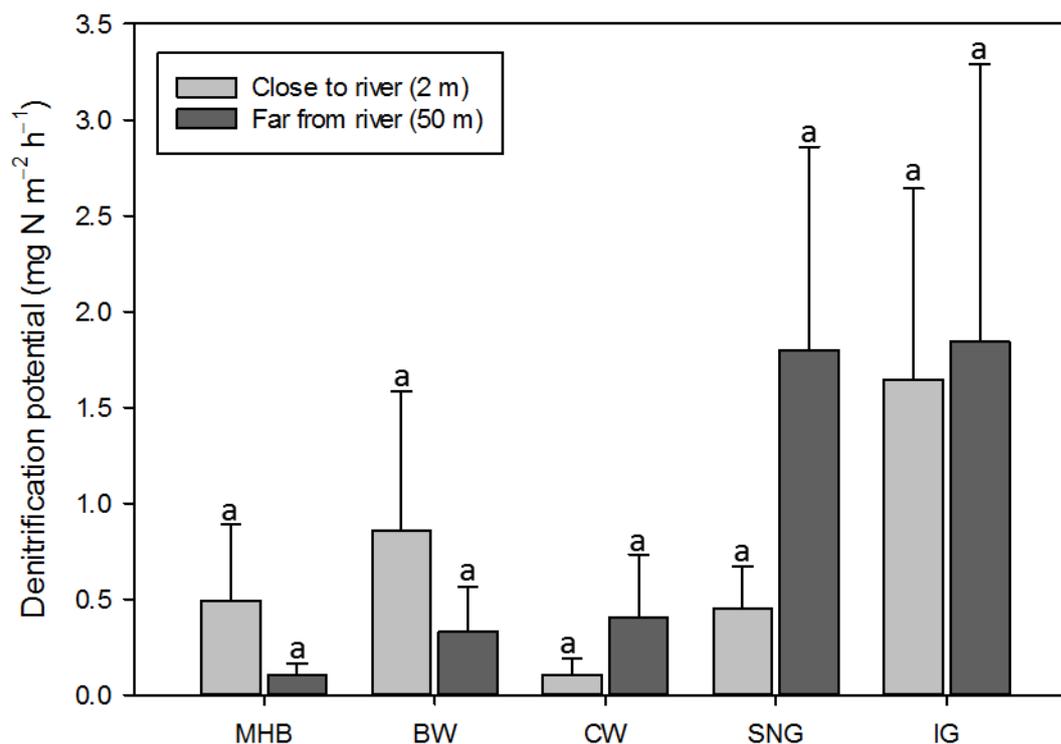
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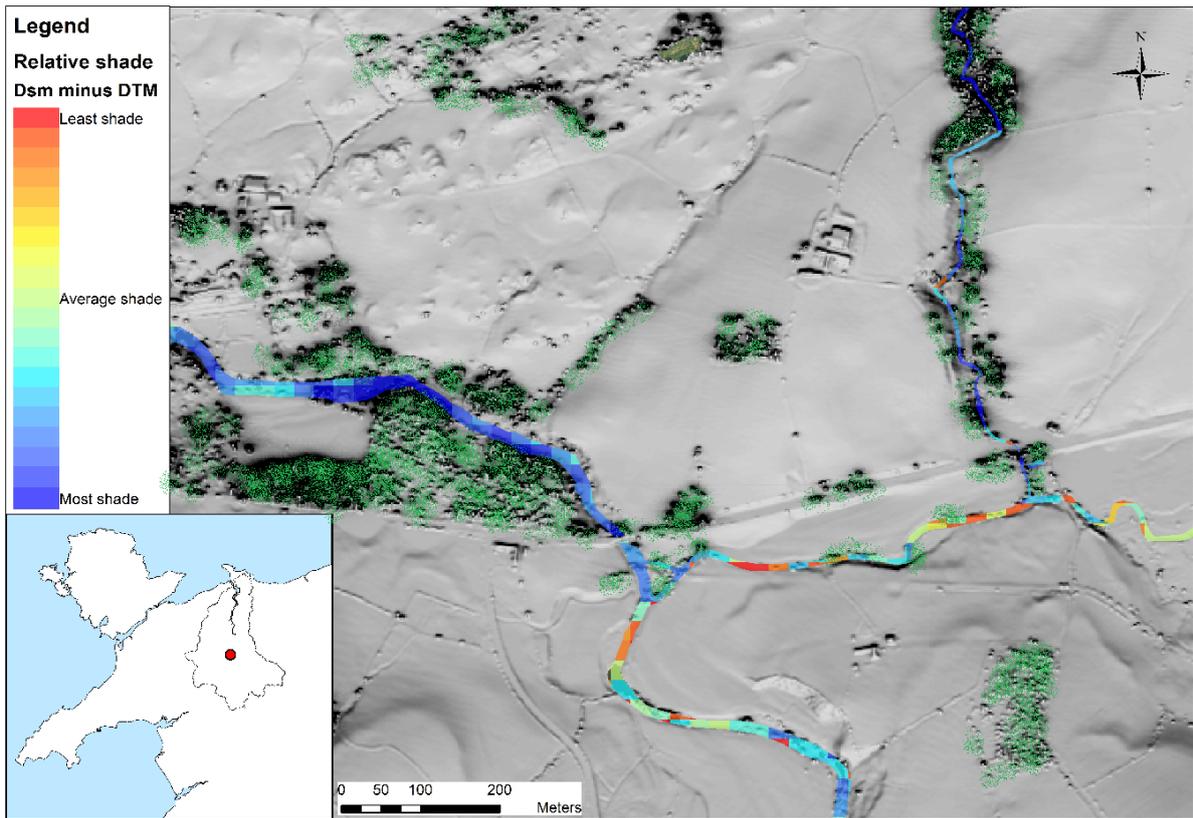
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1179 **Figure 6.** Rate of potential denitrification after 24 h across dominant habitat types (MHB:
 1180 mountain, heath and bog; BW: broadleaf woodland; CW: coniferous woodland; SNG: semi-
 1181 natural grassland; IG: improved grassland) w with respect to distance from the river. Same
 1182 lower case letters indicate no significant differences ($P > 0.05$) respective to distance from the
 1183 river according to the independent t -test. Bars represent mean values ($n = 5$) \pm standard error
 1184 of the mean (SEM).

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1189 **Figure 7.** An example image showing the areas with the least (red) and greatest (blue) amount
 1190 of shade from solar radiation, generated using a Digital Elevation Model (DEM) to represent
 1191 the bare surface without objects (i.e. vegetation and other objects) and the Digital Surface
 1192 Model representing the earth's surface including vegetation and other objects. Areas with dense
 1193 vegetation are coloured in green.

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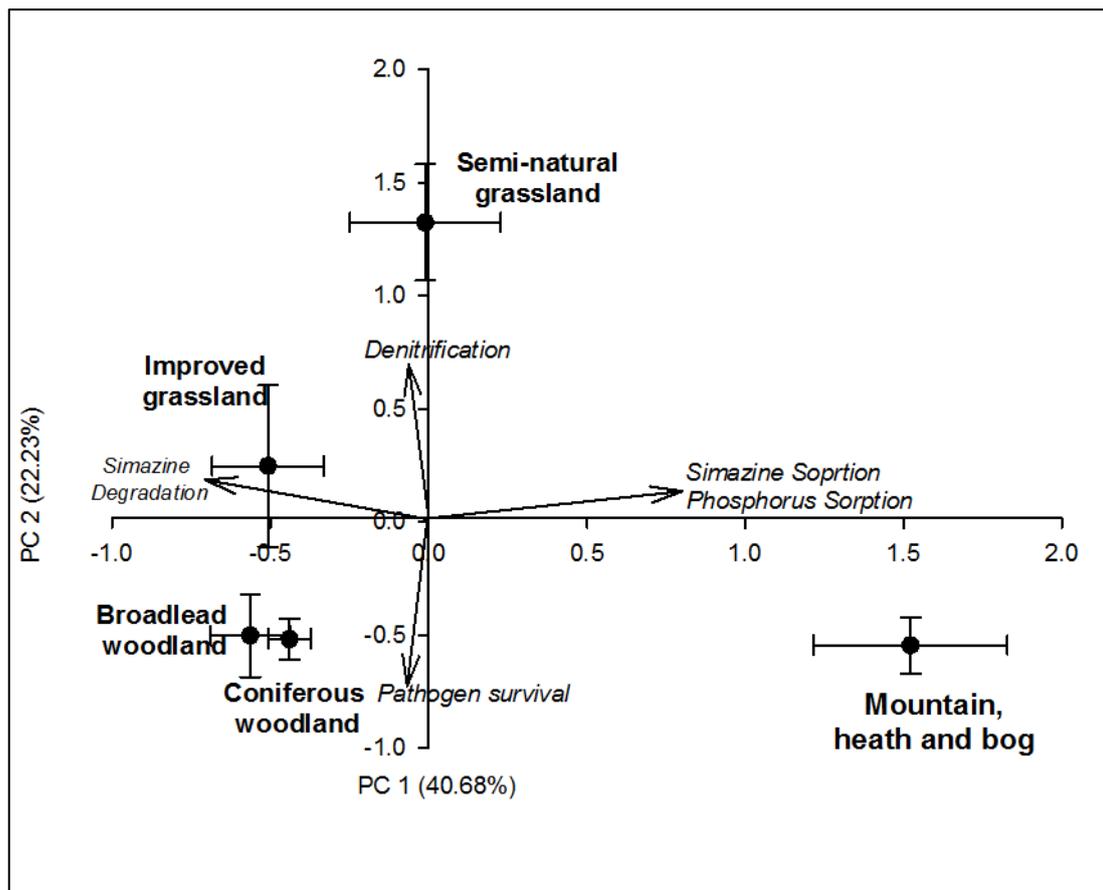
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1210 **Figure 8.** Correlation bi-plot from the principal component analysis (PCA) on ecosystem
1211 services evaluated in this study irrespective of the distance from the river. Correlation of
1212 ecosystem services with the main axes are given by arrows and habitat types by cluster
1213 centroids (average score on each horizontal principal component (PC1) and vertical principal
1214 component (PC2) with standards errors, $n = 10$).

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1216 **Quantifying the contribution of riparian soils to the provision of ecosystem services**

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1232 Funding information

1233 This research was supported by the UK Natural Environment Research Council under the
1234 Macronutrients Programme as part of the ‘Multi-Scale Response of Water Quality,
1235 Biodiversity and Carbon Sequestration to Coupled Macronutrient Cycling from Source to Sea’
1236 project (NE/J011967/1). This research was also supported by a Knowledge Economy Skills
1237 Scholarship (KESS 2) awarded to LDS funded via the European Social Fund (ESF) through
1238 the European Union's Convergence program administered by the Welsh Government.

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1245 Supplementary on-line information

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1247 **Table S1.** Soil physicochemical properties in mountain, heath and bog (MHB) land use type
1248 with respect to the distance from the river and soil depth in the Conwy Catchment. Data are
1249 mean values ($n = 5$) \pm standard error of the mean (SEM). Significant differences are shown
1250 according to two-way ANOVA (One-way ANOVA for bulk density) with distance and depth
1251 as main factors. No interactions between depth and distance were found in the analysis. No
1252 significant differences were found by the interaction of distance with depth.

Riparian distance				P-values	
Close to river (2 m)		Far from river (50 m)		Distance	Depth
0-15 cm	15-30 cm	0-15 cm	15-30 cm		

pH	4.85 ± 0.40	4.92 ± 0.40	4.34 ± 0.20	4.46 ± 0.20	ns	ns
EC (µS cm ⁻¹)	33.2 ± 6.3	26.8 ± 5.4	37.1 ± 4.4	24.0 ± 5.0	ns	ns
Bulk density (g cm ⁻³)	0.07 ± 0.01	ND	0.09 ± 0.02	ND	ns	ND
Moisture content (%)	87.7 ± 0.8	87.4 ± 0.5	87.4 ± 1.7	84.2 ± 1.1	ns	ns
Organic matter (%)	78.7 ± 6.8	86.1 ± 5.6	86.3 ± 3.5	78.6 ± 5.9	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	19.8 ± 1.3	18.4 ± 1.2	20.7 ± 4.0	18.1 ± 1.2	ns	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	51.5 ± 18.7	50.5 ± 19.3	56.8 ± 15.1	42.5 ± 12.1	ns	ns
Available P (mg kg ⁻¹ soil)	10.8 ± 4.04	3.11 ± 1.49	3.42 ± 0.53	2.29 ± 0.72	0.002	ns
Total C (g kg ⁻¹ soil)	453 ± 102	456 ± 147	545 ± 30	524 ± 40	ns	ns
Total N (g kg ⁻¹ soil)	17.8 ± 3.1	21.6 ± 1.8	13.8 ± 4.5	21.1 ± 2.2	ns	ns
Dissolved organic C (g kg ⁻¹ soil)	0.95 ± 0.30	1.00 ± 0.30	1.07 ± 0.20	1.01 ± 0.20	ns	ns
Total dissolved N (g kg ⁻¹ soil)	0.14 ± 0.03	0.16 ± 0.04	0.17 ± 0.04	0.14 ± 0.01	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	3.20 ± 0.89	1.04 ± 0.41	3.81 ± 1.07	1.20 ± 0.19	ns	0.005
Microbial biomass N (g kg ⁻¹ soil)	0.26 ± 0.11	0.28 ± 0.11	0.43 ± 0.24	0.38 ± 0.08	ns	ns

1253 EC, electrical conductivity; ND, not determined.

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1274 **Table S2.** Soil physicochemical properties in broadleaf woodland (BW) land use type with
1275 respect to the distance from the river and depth in the Conwy Catchment. Data are mean values
1276 ($n = 5$) ± standard error of the mean (SEM). Significant differences are shown according to
1277 two-way ANOVA (One-way ANOVA for bulk density) with distance and depth as main
1278 factors. No interactions between depth and distance were found in the analysis. No significant
1279 differences were found by the interaction of distance with depth.

	Riparian distance				P-values	
	Close to river (2 m)		Far from river (50 m)		Distance	Depth
	0-15 cm	15-30 cm	0-15 cm	15-30 cm		
pH	5.14±0.30	5.18±0.20	5.07±0.30	5.24±0.30	ns	ns
EC (µS cm ⁻¹)	26.6±5.0	25.2±4.2	42.9±6.2	31.5±5.4	0.047	ns
Bulk density (g cm ⁻³)	0.74±0.11	ND	0.73±0.06	ND	ns	ND
Moisture content (%)	30.0±3.0	27.2±5.0	41.0±7.8	34.3±2.8	ns	ns
Organic matter (%)	14.3±4.8	8.4±1.9	24.8±12.5	10.1±0.7	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	3.75±0.8	4.25±0.7	6.37±0.5	4.70±0.8	0.042	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	1.99±0.6	1.77±1.1	7.01±1.6	3.49±1.0	0.004	ns
P available (mg kg ⁻¹ soil)	0.31±0.11	0.41±0.20	0.57±0.28	0.19±0.12	ns	ns
Total C (g kg ⁻¹ soil)	57±13	44±10	76±8	42±6	ns	ns
Total N (g kg ⁻¹ soil)	3.38±0.60	4.47±0.30	2.72±0.40	3.21±0.20	0.016	ns
Dissolved organic C (g kg ⁻¹ soil)	0.19±0.05	0.19±0.05	0.26±0.06	0.14±0.02	ns	ns
Total dissolved N (g kg ⁻¹ soil)	0.03±0.01	0.03±0.01	0.04±0.005	0.02±0.002	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	0.26±0.11	0.28±0.11	0.43±0.24	0.38±0.08	ns	ns
Microbial biomass N (g kg ⁻¹ soil)	0.16±0.03	0.18±0.02	0.26±0.03	0.32±0.11	0.024	ns

EC, electrical conductivity; ND, not determined.

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Table S3. Soil physicochemical properties in coniferous woodland (CW) land use type with respect to the distance from the river and depth in the Conwy Catchment. Data are mean values ($n = 5$) ± standard error of the mean (SEM). Significant differences are shown according to two way ANOVA (One way ANOVA for bulk density) with distance and depth as main factors. No interactions between depth and distance were found in the analysis. No significant differences were found by the interaction of distance with depth.

	Riparian distance				P-values	
	Close to river (2 m)		Far from river (50 m)		Distance	Depth
	0-15 cm	15-30 cm	0-15 cm	15-30 cm		
pH	4.75±0.20	4.95±0.10	4.23±0.10	4.52±0.10	0.002	ns
EC (µS cm ⁻¹)	28.9±4.8	27.0±3.2	43.6±7.5	45.0±10.1	ns	ns
Bulk density (g cm ⁻³)	0.45±0.15	ND	0.41±0.16	ND	ns	ND
Moisture content (%)	36.4±9.9	36.2±10.7	39.3±5.8	32.9±7.5	ns	ns
Organic matter (%)	13.5±5.8	12.9±6.6	18.9±3.4	13.3±1.6	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	5.62±0.90	4.79±0.60	5.08±0.90	4.75±0.80	ns	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	4.95±1.2	4.11±1.4	7.54±2.2	4.63±5.9	ns	ns
Available P (mg kg ⁻¹ soil)	0.27±0.08	0.34±0.20	0.40±0.08	0.28±0.03	ns	ns
Total C (g kg ⁻¹ soil)	71±33	56±36	109±13	58±11	ns	ns
Total N (g kg ⁻¹ soil)	4.21±1.40	5.38±0.50	3.32±1.60	3.11±0.40	ns	ns
Dissolved organic C (g kg ⁻¹ soil)	0.22±0.04	0.22±0.04	0.32±0.03	0.33±0.03	0.011	ns
Total dissolved N (g kg ⁻¹ soil)	0.03±0.004	0.03±0.005	0.04±0.004	0.04±0.004	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	1.09±0.38	0.85±0.41	2.15±0.23	1.15±0.28	ns	ns
Microbial biomass N (g kg ⁻¹ soil)	0.20±0.05	0.10±0.02	0.22±0.03	0.13±0.04	ns	0.019

EC, electrical conductivity; ND, not determined.

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1329 **Table S4.** Soil physicochemical properties in semi-natural grassland (SNG) land use type with
1330 respect to the distance from the river and depth in the Conwy Catchment. Data are mean values
1331 ($n = 5$) ± standard error of the mean (SEM). Significant differences are shown according to two
1332 way ANOVA (One way ANOVA for bulk density) with distance and depth as main factors.

1333 No interactions between depth and distance were found in the analysis. No significant
 1334 differences were found by the interaction of distance with depth.

	Riparian distance				P-values	
	Close to river (2 m)		Far from river (50 m)		Distance	Depth
	0-15 cm	15-30 cm	0-15 cm	15-30 cm		
pH	4.95 ± 0.20	5.07 ± 0.10	5.25 ± 0.40	5.27 ± 0.20	ns	ns
EC (µS cm ⁻¹)	35.1 ± 5.3	26.9 ± 4.6	44.4 ± 8.4	28.1 ± 4.6	ns	ns
Bulk density (g cm ⁻³)	0.16 ± 0.05	ND	0.31 ± 0.12	ND	ns	ND
Moisture content (%)	73.0 ± 7.6	68.9 ± 10.1	62.7 ± 9.3	51.7 ± 13.0	ns	ns
Organic matter (%)	41.4 ± 11.6	39.9 ± 12.2	33.9 ± 11.4	25.9 ± 13.2	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	15.5 ± 4.9	14.1 ± 4.4	12.9 ± 5.9	7.40 ± 2.3	ns	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	14.6 ± 5.6	14.7 ± 4.2	13.7 ± 5.1	9.10 ± 1.9	ns	ns
Available P (mg kg ⁻¹ soil)	1.06 ± 0.36	0.64 ± 0.25	0.63 ± 0.21	0.57 ± 0.24	ns	ns
Total C (g kg ⁻¹ soil)	74 ± 35	218 ± 67	101 ± 25	83.3 ± 20	ns	ns
Total N (g kg ⁻¹ soil)	5.47 ± 1.9	7.46 ± 1.5	11.03 ± 3.7	12.28 ± 4.0	ns	ns
Dissolved organic C (g kg ⁻¹ soil)	0.40 ± 0.10	0.41 ± 0.14	0.42 ± 0.10	0.35 ± 0.1	ns	ns
Total dissolved N (g kg ⁻¹ soil)	0.07 ± 0.02	0.07 ± 0.02	0.07 ± 0.01	0.06 ± 0.008	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	6.84 ± 2.40	5.50 ± 2.68	1.05 ± 0.38	0.94 ± 0.30	0.050	ns
Microbial biomass N (g kg ⁻¹ soil)	0.90 ± 0.23	0.29 ± 0.08	0.43 ± 0.11	0.27 ± 0.10	ns	0.014

1335 EC, electrical conductivity; ND, not determined.

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1359 **Table S5.** Soil physicochemical properties in improved grassland (IG) land use type with
 1360 respect to the distance from the river and depth in the Conwy Catchment. Data are mean values
 1361 ($n = 5$) ± standard error of the mean (SEM). Significant differences are shown according to two

1362 way ANOVA (One way ANOVA for bulk density) with distance and depth as main factors.
 1363 No significant differences were found by the interaction of distance with depth.
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	Riparian distance				P-values	
	Close to river (2 m)		Far from river (50 m)		Distance	Depth
	0-15 cm	15-30 cm	0-15 cm	15-30 cm		
pH	5.19±0.30	5.28±0.30	5.39±0.10	5.43±0.20	ns	ns
EC (µS cm ⁻¹)	104±37	34±7	131±55	101±47	ns	ns
Bulk density (g cm ⁻³)	0.60±0.11	ND	0.71±0.10	ND	ns	ND
Moisture content (%)	39.0±6.9	35.4±8.9	44.0±5.3	30.6±2.8	ns	ns
Organic matter (%)	13.3±3.7	12.6±6.3	20.0±4.4	10.0±2.0	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	5.18±1.7	3.42±1.1	5.87±2.1	3.39±1.1	ns	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	9.78±3.4	6.96±1.8	22.7±9.1	21.4±12.1	ns	ns
Available P (mg kg ⁻¹ soil)	2.08±1.06	1.05±0.55	1.84±0.75	0.93±0.48	ns	ns
Total C (g kg ⁻¹ soil)	270±65	87±59	223±65	56±8	ns	0.001
Total N (g kg ⁻¹ soil)	14.8±3.4	14.2±3.3	3.31±0.5	6.10±1.9	0.017	ns
Dissolved organic C (g kg ⁻¹ soil)	0.17±0.02	0.18±0.05	0.20±0.02	0.15±0.02	ns	ns
Total dissolved N (g kg ⁻¹ soil)	0.04±0.01	0.04±0.01	0.07±0.01	0.05±0.02	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	1.90±0.55	1.54±0.77	2.49±0.31	1.19±0.20	ns	ns
Microbial biomass N (g kg ⁻¹ soil)	0.18±0.04	0.30±0.10	0.38±0.06	0.31±0.11	ns	ns

1365 EC, electrical conductivity; ND, not determined.

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1383 **Table S6.** Controlling factors affecting the performance of the ecosystem services selected in
 1384 this study, accompanied by unmeasured factors that mostly likely influence the behaviour of
 1385 riparian areas in accomplishing ecosystem functioning.

Ecosystem service	Habitat physicochemical property found	Process likely to occur in riparian areas affecting the delivery of the ecosystem services
Phosphorus and simazine sorption	Organic matter	Erosion processes
	Moisture content	Rapid uptake by macrophytes
	Bulk density	Fluxes of organic matter from upland and streams creating ‘hot moments’
	Available forms of N and P	Changes in moisture content and pH
	Microbial biomass ¹	controlling pollutant solubility
Simazine degradation	C content	
	Microbial competition and specialisation	Changes in pH and redox potential which control pesticide hydrolysis and bioavailability
	pH	
Denitrification activity	Total carbon	
	High spatial variation	Carbon and nitrogen sources provided by the stream
	Bulk density	Oscillation of anoxic and oxic conditions due to hydrographic regime
Pathogen survival	pH	
	-	More exposure to animal waste events due to livestock attraction to watercourses
Shade provision	Habitat type canopy	Land change use

¹Controlling factor only identified for P adsorption

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1402 **Aerial photographs sample points**

1403 1. Aerial photograph of sample point n° 1 within the broadleaf woodland habitat type.



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1415 2. Aerial photograph of sample point n° 2 within the broadleaf woodland habitat type.



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1428 3. Aerial photograph of sample point n° 3 within the broadleaf woodland habitat type.



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1441 4. Aerial photograph of sample point n° 4 within the broadleaf woodland habitat type.



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1454 5. Aerial photograph of sample point n° 5 within the broadleaf woodland habitat type.



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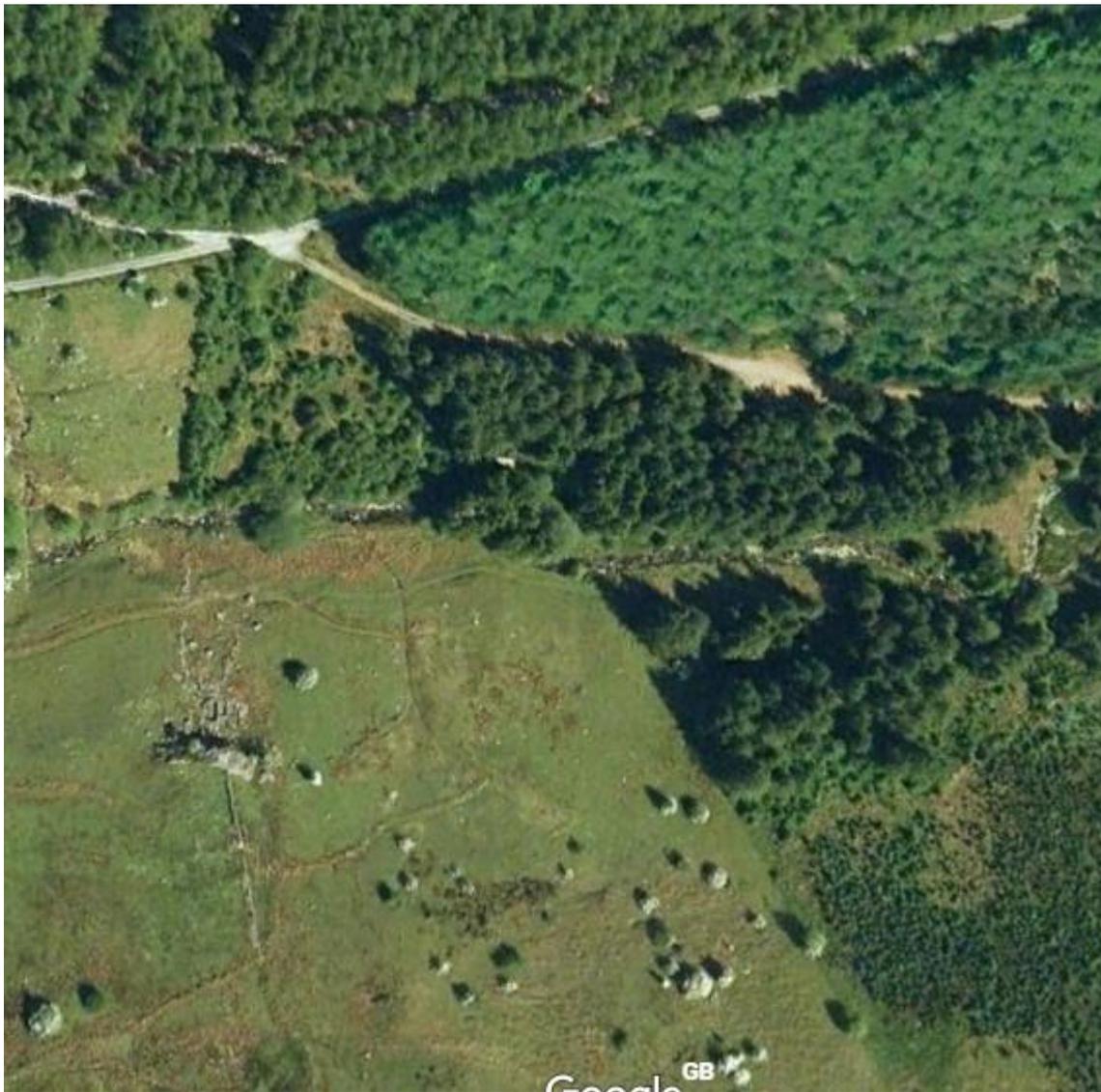
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1467 1. Aerial photograph of sample point n° 1 within the coniferous woodland habitat type.



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1480 2. Aerial photograph of sample point n° 2 within the coniferous woodland habitat type.



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1493 3. Aerial photograph of sample point n° 3 within the coniferous woodland habitat type.



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1507 4. Aerial photograph of sample point n° 4 within the coniferous woodland habitat type.



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1521 5. Aerial photograph of sample point n° 5 within the coniferous woodland habitat type.



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1534 1. Aerial photograph of sample point n° 1 within the improved grassland habitat type.



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1548 2. Aerial photograph of sample point n° 2 within the improved grassland habitat type.



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1561 3. Aerial photograph of sample point n° 3 within the improved grassland habitat type.



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1574 4. Aerial photograph of sample point n° 4 within the improved grassland habitat type.



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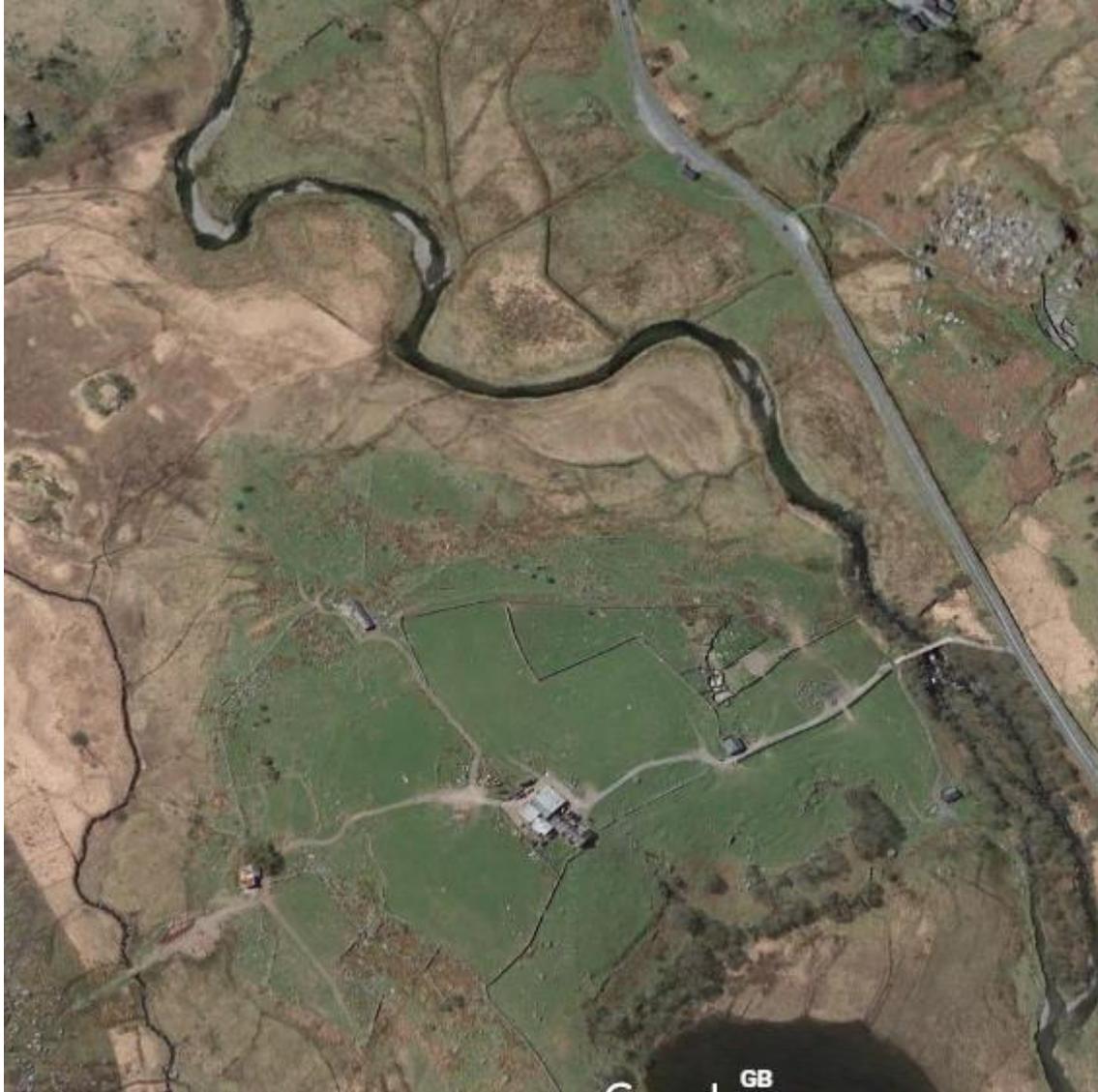
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1587 5. Aerial photograph of sample point n° 5 within the improved grassland habitat type.



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1600 1. Aerial photograph of sample point n° 1 within the mountain, heath and bog habitat type.



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1614 2. Aerial photograph of sample point n° 2 within the mountain, heath and bog habitat type.



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1627 3. Aerial photograph of sample point n° 3 within the mountain, heath and bog habitat type.



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1640 4. Aerial photograph of sample point n° 4 within the mountain, heath and bog habitat type.



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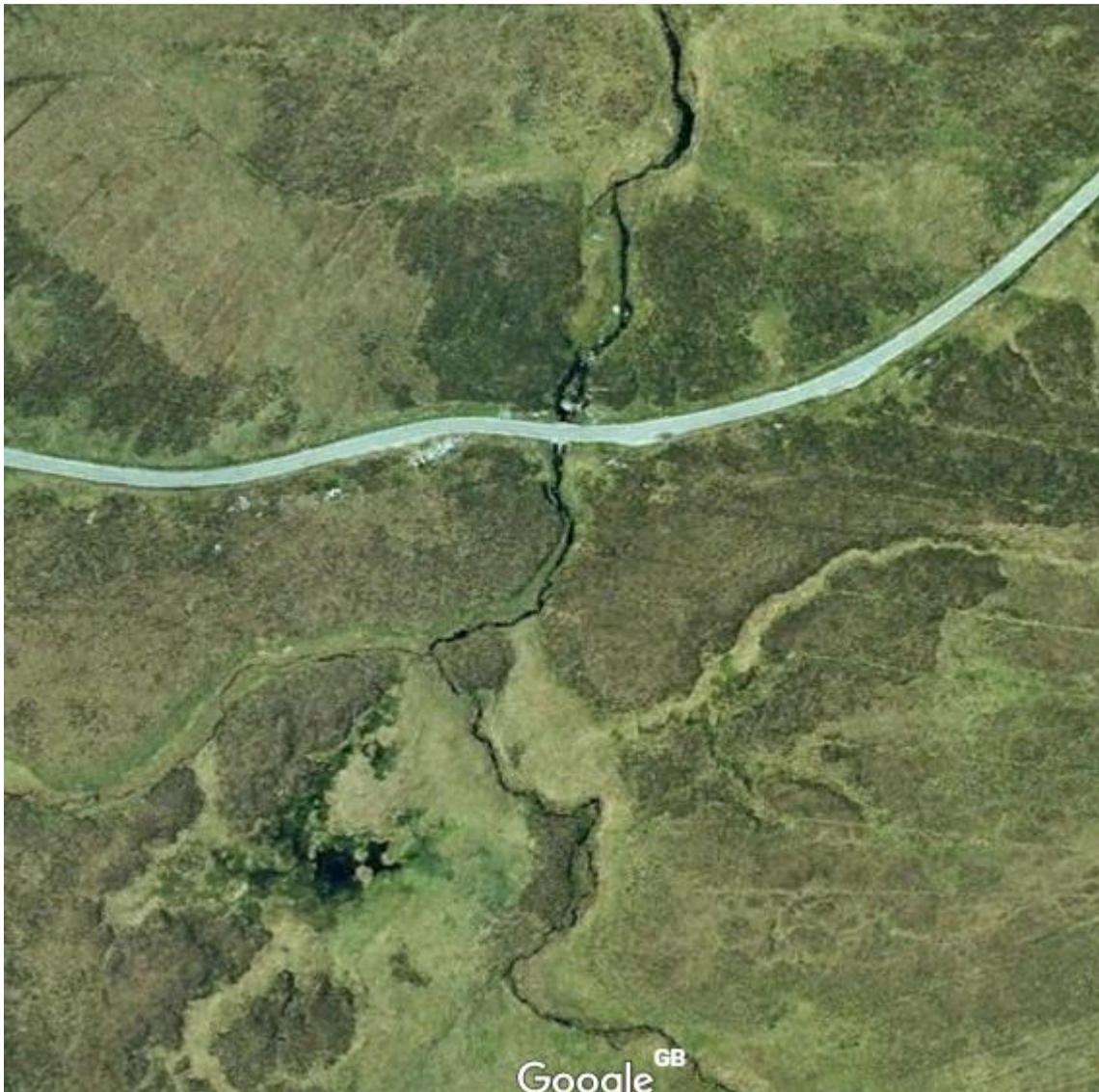
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1653 5. Aerial photograph of sample point n° 5 within the mountain, heath and bog habitat type.



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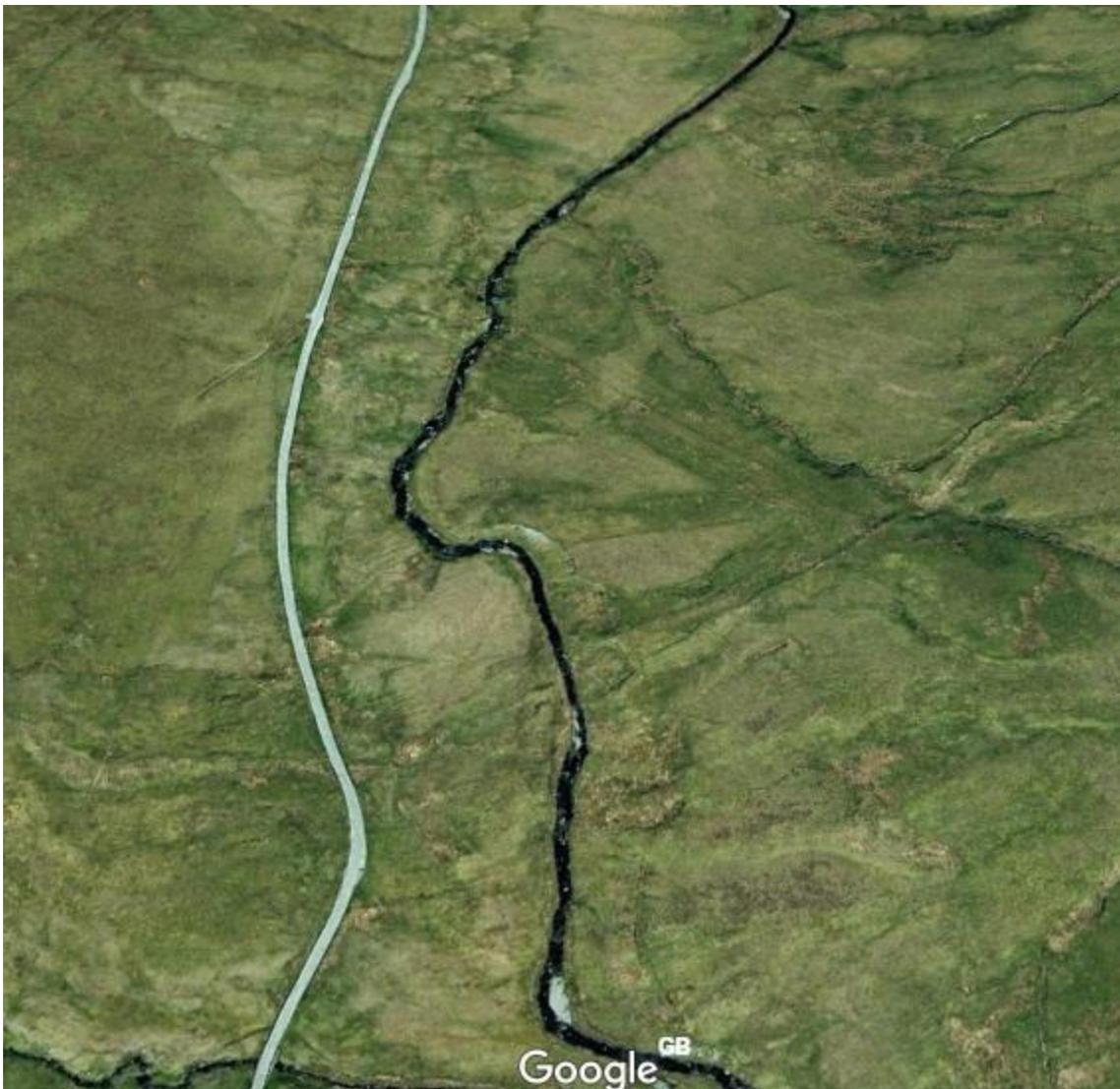
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1666 1. Aerial photograph of sample point n° 1 within the semi-natural grassland habitat type.



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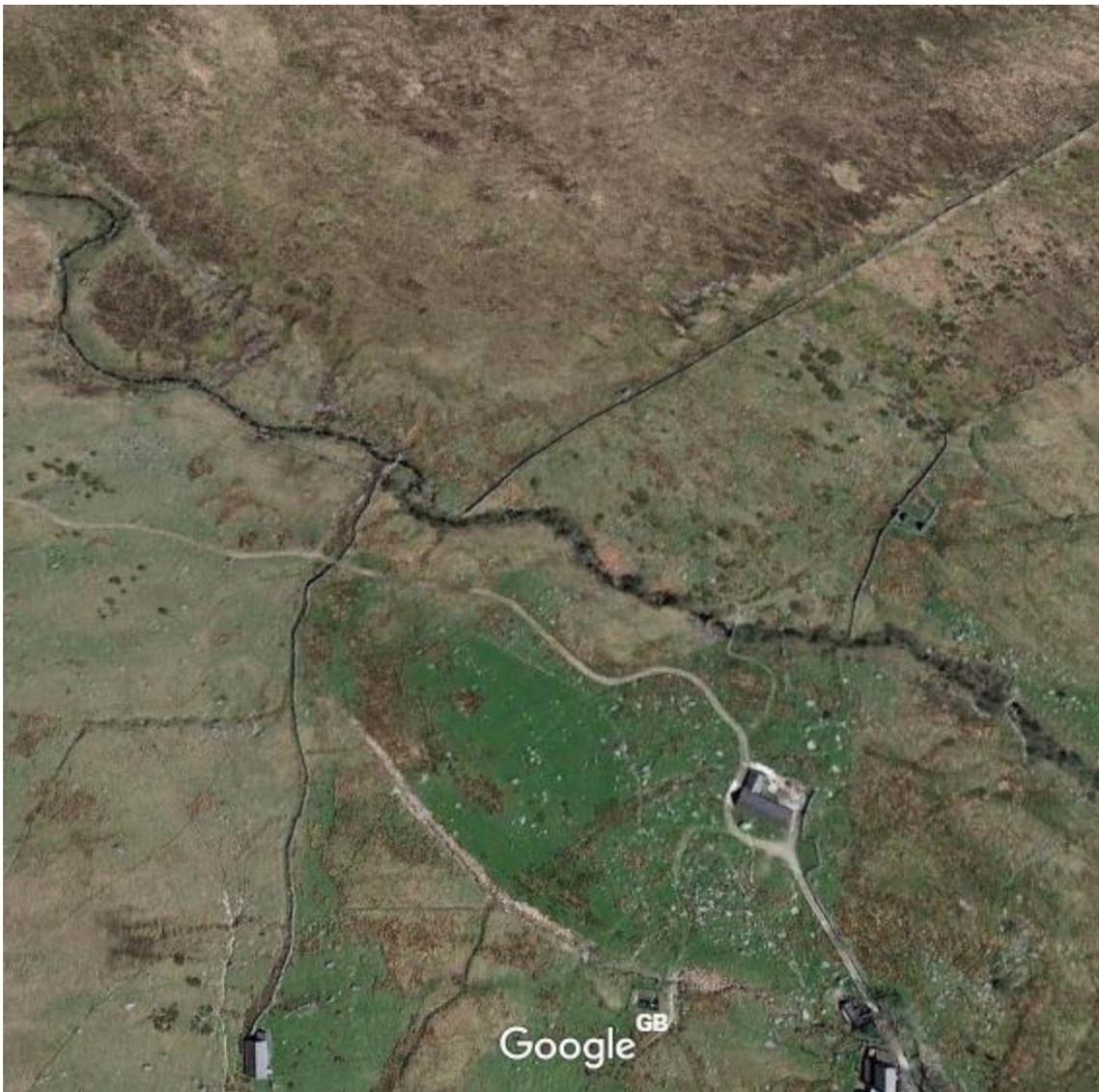
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1680 2. Aerial photograph of sample point n° 2 within the semi-natural grassland habitat type.



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3. Aerial photograph of sample point n° 3 within the semi-natural grassland habitat type.



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1707 4. Aerial photograph of sample point n° 4 within the semi-natural grassland habitat type.



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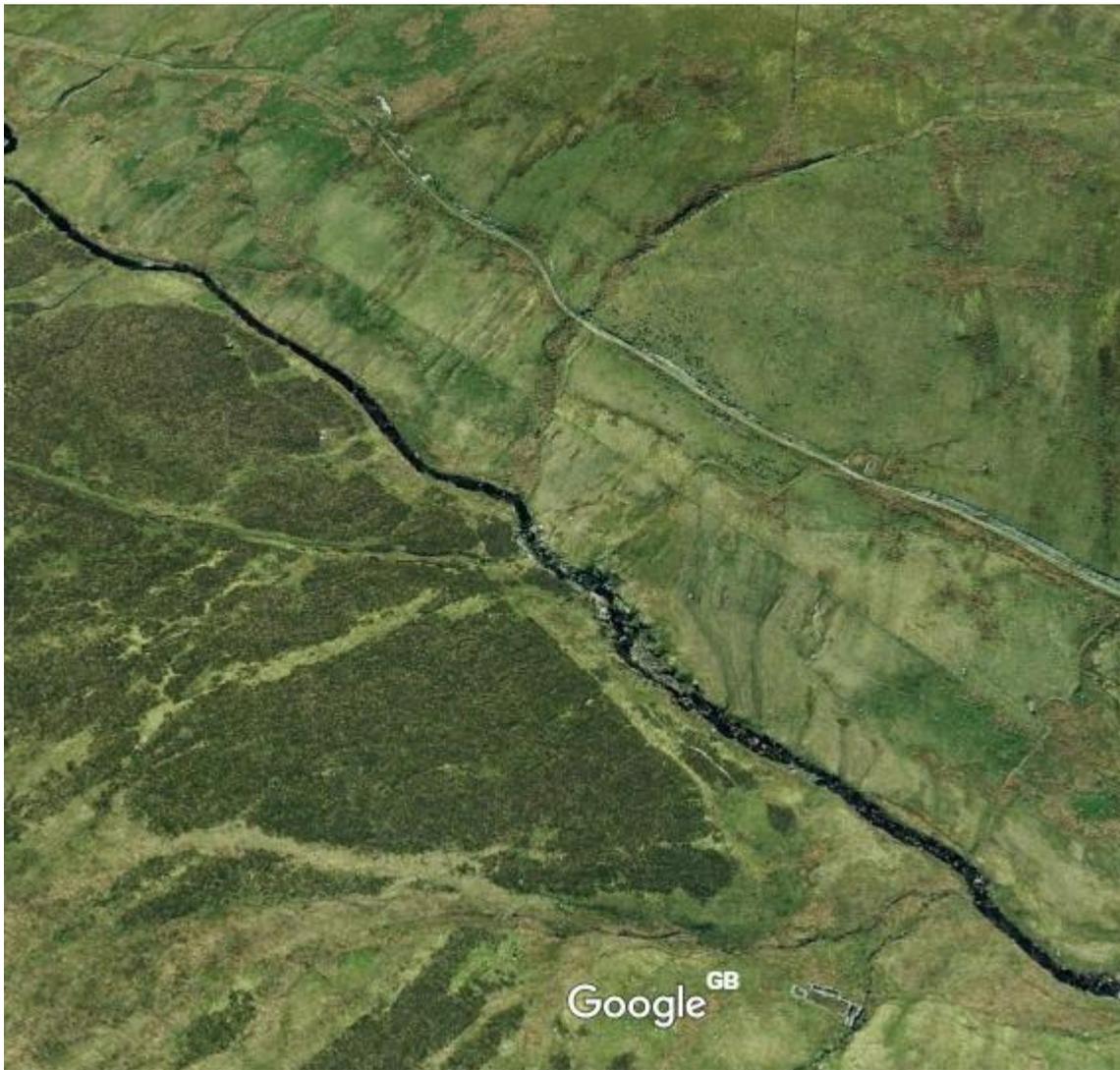
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1720 5. Aerial photograph of sample point n° 5 within the semi-natural grassland habitat type.



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1734 **Table 1**

1735 Summary of riparian soil characteristics and their associated provision of ecosystem services.

Ecosystem services	Causal factor	Resulting soil characteristics
Supporting services Soil formation Nutrient cycling Regulating services Water purification by reducing non-point source pollutants Flood and erosion regulation by slowing and spreading flood water	<ul style="list-style-type: none"> • Periodic sediment deposition together with flushes of organic litter during floods events • Large variation of soil chemical composition mainly due to filtration and nutrient removal from terrestrial upland and aquatic ecosystems 	Heterogeneity (Mikkelsen and Vesho, 2000)
Supporting services Biodiversity Regulating services Carbon sequestration Provisioning services Shading by vegetation	<ul style="list-style-type: none"> • High vegetation density and diversity associated with higher moisture and organic matter content which leads to more microbial activity • Provide (roots, fallen logs) refuge for aquatic and terrestrial fauna 	Biological diversity (Naiman et al., 2010)
Supporting services Soil formation Regulating services Carbon sequestration	<ul style="list-style-type: none"> • New material (organic matter fluxes and sediments) being deposited by flood events and water fluctuation • Regular inundation of soils by river water preventing horizon formation 	Undeveloped soils (Zaimes et al., 2007)
Regulating services Water storage	<ul style="list-style-type: none"> • Their proximity with the river enhances water storage and infiltration 	High moisture content (Lewis et al., 2003)
Regulating services Fast engineering resilience ¹	<ul style="list-style-type: none"> • Anthropogenic activities such as farming, water abstraction, livestock and deforestation • Frequent environmental disturbances such as floods or droughts 	Disturbance driven (Klemaš, 2014)

1736 ¹ Speed with which a system returns to equilibrium after a disturbance (Holling, 1996).

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1748 **Table 2**

Dataset	Scale	Data Type	IPR holder	Description
Digital Terrain Model	2 m	Raster	Natural Resources Wales	This dataset is derived from a combination of all data that is at 2 m resolution or better which has been merged and re-sampled to give the best possible coverage. Available at: https://data.gov.uk/dataset/lidar-terrainand-surfaces-models-wales
Digital Surface Model	2 m	Raster	Natural Resources Wales	This dataset is derived from a combination of all data that is at 2 m resolution or better which has been merged and re-sampled to give the best possible coverage. Available at: https://data.gov.uk/dataset/lidar-terrainand-surfaces-models-wales
OS Open Rivers	1:25,000	Shapefile	Edina Digimap	Water bodies polygons within the catchment.

1749 Data inputs and sources for the computational GIS tool.

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Table 3

Main soil physicochemical characteristics for the five different habitat types. Sampling depth and distance from the river were amalgamated together as there was no significant differences from the result of a factorial analysis with habitat, depth and distance as the main factors (see Tables S1-S5). Data are mean values ($n = 10$) \pm standard error of the mean (SEM).

	Mountain, heath and bog (MHB)	Broadland woodland (BW)	Coniferous woodland (CW)	Semi-natural grassland (SNG)	Improved grassland (IG)
pH	4.5 \pm 0.1	5.2 \pm 0.1	4.6 \pm 0.1	5.1 \pm 0.1	5.3 \pm 0.1
EC ($\mu\text{S cm}^{-1}$)	32.5 \pm 3.3	31.8 \pm 2.9	35.7 \pm 3.6	33.3 \pm 3.0	93.1 \pm 20.5
Bulk density (g cm^{-3})	0.08 \pm 0.01	0.74 \pm 0.06	0.43 \pm 0.1	0.23 \pm 0.06	0.66 \pm 0.07
Moisture content (%)	86.6 \pm 0.6	32.2 \pm 1.5	31.9 \pm 3.0	64.1 \pm 5.0	35.5 \pm 2.7
Organic matter (%)	82.4 \pm 2.6	10.6 \pm 0.8	14.6 \pm 2.2	35.3 \pm 5.7	11.4 \pm 1.4
NH₄⁺-N (mg kg^{-1} soil)	18.0 \pm 0.76	4.77 \pm 0.39	5.06 \pm 0.38	12.48 \pm 2.21	4.47 \pm 0.75
NO₃⁻-N (mg kg^{-1} soil)	50.3 \pm 8.32	3.07 \pm 0.47	5.31 \pm 0.76	10.6 \pm 1.42	12.7 \pm 3.14
P available (mg kg^{-1} soil)	4.92 \pm 1.28	0.31 \pm 0.07	0.32 \pm 0.06	0.78 \pm 0.14	1.27 \pm 0.31
Total C (g kg^{-1} soil)	522 \pm 27	54 \pm 5	73 \pm 12	121 \pm 24	149 \pm 31
Total N (g kg^{-1} soil)	20.5 \pm 1.11	3.45 \pm 0.26	4.01 \pm 0.55	6.86 \pm 1.00	9.10 \pm 1.58
Dissolved organic C (g kg^{-1} soil)	1.01 \pm 0.11	0.19 \pm 0.02	0.27 \pm 0.02	0.39 \pm 0.05	0.17 \pm 0.01
Total dissolved N (g kg^{-1} soil)	0.15 \pm 0.02	0.03 \pm 0.003	0.03 \pm 0.002	0.06 \pm 0.01	0.05 \pm 0.01
Microbial biomass C (g kg^{-1} soil)	2.31 \pm 0.44	0.93 \pm 0.07	1.31 \pm 0.19	3.58 \pm 1.03	1.63 \pm 0.22
Microbial biomass N (g kg^{-1} soil)	0.34 \pm 0.07	0.23 \pm 0.03	0.16 \pm 0.02	0.47 \pm 0.09	0.29 \pm 0.04

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Table 4

Maximum adsorption values (S_{\max}), binding energy constant (k) and correlation coefficients (R^2) as estimated by Langmuir isotherm with respect to distance from the river. Data are mean values ($n = 5$) \pm standard error of the mean (SEM).

	Langmuir model				R^2
	Maximum P sorption S_{\max} (mg kg^{-1})		Binding strength k (l kg^{-1})		
	Close to river	Far from river	Close to river	Far from river	
Mountain, heath and bog (MHB)	379 \pm 74	385 \pm 137	3.6 \pm 2.5	7.3 \pm 5.1	0.90 \pm 0.03
Broadleaf woodland (BW)	88 \pm 10	82 \pm 7	42.2 \pm 8.0	28.7 \pm 9.6	0.87 \pm 0.04
Coniferous woodland (CW)	81 \pm 6	114 \pm 15	31.6 \pm 5.3	25.3 \pm 5.1	0.91 \pm 0.04
Semi-natural grassland (SNG)	246 \pm 62	172 \pm 55	22.8 \pm 8.1	23.7 \pm 6.8	0.95 \pm 0.04
Improved grassland (IG)	148 \pm 68	86 \pm 9	14.6 \pm 5.1	19.9 \pm 3.2	0.97 \pm 0.01

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