

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

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24 **ABSTRACT**

25 Riparian areas, the interface between land and freshwater ecosystems, are considered to play
26 a 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
32 river 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
43 was maximal in forests (ca. 52% shade cover) in comparison to the other habitat types (7-
44 17%). Our data suggest that the functioning of riparian areas in less intensive agricultural
45 areas, such as those studied here, may be broadly predicted from the surrounding land use,
46 however, further 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
60 natural resources and implement better land-management practices with respect to the
61 environment (Van Looy et al., 2017). Riparian areas, the interface between land and
62 freshwater ecosystems, are considered to play a pivotal role in the supply of regulating,
63 provisioning, cultural and supporting services (Jones et al., 2010; Clerici et al., 2011; Aguiar
64 et al., 2015). However, despite the fact that the number of studies referring to ecosystem
65 services has increased by 38% in Europe over the last 20 years (Adhikari and Hartemink,
66 2016), riparian zones have received less attention than other land use types from an
67 ecosystem services perspective. The few publications which have integrated an ecosystem
68 service approach to the assessment of riparian areas have tended to address this from a
69 modelling perspective (Clerici et al., 2014; Tomscha et al., 2017; Sharps et al., 2017).
70 McVittie et al. (2015) proposed a model which aims to outline the fundamental ecological
71 processes that deliver ecosystem services within riparian areas. Models provide a powerful
72 and cost-effective tool to assess and map ecosystem services at the landscape scale, however,

73 they do not always provide a mechanistic process-level understanding. It is therefore
74 important that models are supported and developed with robust underpinning data to correctly
75 identify and describe the main factors affecting ecosystem services delivery within complex
76 landscapes (i.e. those which may contain a diverse array of different riparian typologies).
77 Little is known, however, about how inherent riparian properties and ecosystem functioning
78 vary across different habitats within a catchment area (Burkhard et al., 2009). This
79 uncertainty is largely due to the majority of riparian studies being focused on single sites,
80 typically intensive agricultural systems (i.e. arable and grasslands) as these represent a major
81 source of pollution (e.g. from fertilizers, livestock and pesticides) and because riparian zones
82 associated with agriculture present pollution mitigation potential (Pierson et al., 2001;
83 Rasmussen et al., 2011; Broetto et al., 2017). However, these studies tend to overlook the fact
84 that riparian areas are inter-related systems and therefore changes (both natural and
85 anthropogenic) occurring in headwater riparian zones across different habitat types could also
86 affect riparian processes occurring downstream (Harper and Everard, 1998; Charron et al.,
87 2008).

Field Code Changed

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

water purification (Klapproth and Johnson., 2000; Meador and Goldstein, 2003; Chase et al., 2016). This pollution mitigation potential is often attributed to specific characteristics within riparian soils (Mikkelsen and Vescho, 2000; Naiman et al., 2010). Table 1 summarizes the link between riparian soil properties and the provision of ecosystem services found in the literature. A better understanding of the causal factors for ecosystem services delivery will provide an improved knowledge base on which to make land management decisions and protection policies.

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

The main focus of this study is to assess the link between riparian areas and the regulating service of water purification through a wide range of ecological processes. In particular, we aim to: 1) evaluate the spatial variation in riparian soils properties (i.e. general nutrient status, soil acidity and conductivity, and microbial community size) with respect to distance with the river and soil depth in contrasting habitat types; 2) gain further insights into the underlying mechanisms of pollutant removal (i.e. pesticide sorption/degradation, denitrification, etc) by riparian soils; and 3) quantify and evaluate how riparian vegetation

across different habitat types contribute to the provision of shade. This could help identify areas especially vulnerable to excessive solar radiation and offer a cost-effective way to improve ecosystem service provision (Ghermandi et al., 2009; De Groot et al., 2012). We hypothesized that riparian areas would support a greater delivery of ecosystem services in comparison to the upslope area, but that the balance of these services would be land use specific within a catchment area.

2. Methodology

2.1. Site description

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

2.2. Field sampling

Five dominant habitat types (MHB = mountain, heath and bog; BW = broadleaf woodland; CW = coniferous woodland; SNG = semi-natural grassland; IG = improved grassland) were selected for soil sampling throughout the catchment. Habitat classification was derived from the new Phase 1 National Vegetation Survey (Lucas et al., 2011) and subsequently grouped, for simplicity, into the same broad habitat classes (see Appendix 1 for details of groupings) defined in the UK's Land Cover Map 2007 (Morton et al., 2014).

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

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

2.3. Soil characterisation

Soil samples were sieved (< 2 mm) to remove stones and any visible plant material and to ensure sample homogeneity (Jones and Willett, 2006). Samples were then stored at 4 °C

prior to laboratory analysis. Soil water content was determined gravimetrically (24 h, 105 °C) and soil organic matter (SOM) content was determined by loss-on-ignition (LOI) (450 °C, 16 h). Soil pH and electrical conductivity (EC) were measured using standard electrodes in a 1:2.5 (w/v) soil-to-deionised water mixture. Total available ammonium (NH₄-N) and nitrate (NO₃-N) were determined with 0.5 M K₂SO₄ extracts (Jones and Willett, 2006) with colorimetric analysis following the salicylate-based procedure of Mulvaney (1996) and the VCl₃ method of Miranda et al. (2001), respectively. Available P was quantified with 0.5 M acetic acid extracts (1:5 w/v) following the ascorbic acid-molybdate blue method of Murphy and Riley (1962) and total C (TC) and N (TN) were determined with a TruSpec[®] elemental analyser (Leco Corp., St Joseph, MI). Dissolved organic C (DOC) and total dissolved N (TDN) were quantified in 1:5 (w/v) soil-to-0.5 M K₂SO₄ extracts using a Multi N/C 2100 TOC analyzer (AnalytikJena, Jena, Germany)(Jones and Willett, 2006). Microbial biomass C and N was assayed by chloroform fumigation-extraction after a 72 h incubation using conversion factors of $k_{ec} = 0.45$ and $k_{en} = 0.54$ (Vance et al., 1987).

2.4. Process-level studies to measure ecosystem services

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

2.4.1. Phosphorus sorption to soil

P adsorption isotherms were determined to estimate the soil's capacity for removing dissolved P from solution, and hence assess the potential for soils to reduce the amount of P

entering freshwaters. Sorption of P was determined following an adapted method of Nair et al. (1984). In brief, 2.5 g of field-moist soil was shaken in 0.01 M CaCl₂ (1:5 w/v soil-to-extractant ratio) containing known concentrations of P (0, 0.3, 1, 5, 10, 20 mg P l⁻¹ as KH₂PO₄) spiked with ³³P (PerkinElmer Inc., Walham, MA) (0.2 kBq ml⁻¹). These concentrations were selected due to their likelihood of being encountered in the catchment (DeLuca et al., 2015). Samples were shaken (2 h, 150 rev min⁻¹, 25 °C) on an orbital shaker. This time was chosen to assess intermediate equilibrium conditions (Santos et al., 2011). After 2 h, 1.5 ml of supernatant was removed, centrifuged (10,000 g, 5 min), and subsequently, 1 ml of supernatant was mixed with 4 ml of Optiphase HiSafe 3 liquid scintillation fluid (PerkinElmer Inc.). The amount of ³³P activity remaining in solution measured using a Wallac 1404 liquid scintillation counter (Wallac EG&G, Milton Keynes, UK) and the total amount of P adsorbed was determined as the difference between the initial ³³P activity added and the final amount of ³³P remaining in solution. Any P not recovered in the solution was assumed to be sorbed onto the soil's solid phase.

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

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

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

2.4.2. Bacterial pathogen survival

Soils from different habitat types were inoculated with human-pathogenic *Escherichia coli* O157:H7 to investigate pathogen persistence in soils with respect to proximity to

waterbodies. Faecal samples, collected from a commercial beef farm in North Wales in January 2016, were inoculated with *E. coli* O157:H7 to reproduce the natural vector by which the pathogen is introduced into the environment (Jones, 1999; Williams et al., 2008). Samples were transported to the laboratory and stored at 4.0 ± 0.1 °C prior to use. Both faecal and soil samples were previously screened for the background *E. coli* O157:H7 cells using an enrichment technique (Avery et al., 2008) and absence of *E. coli* O157:H7 was confirmed by latex agglutination (Oxoid DR620; Oxoid Ltd., Basingstoke, UK). Prior to the start of the experiment a basic characterization of the faecal samples was undertaken and moisture content, organic matter, EC, pH, NO₃-N, NH₄-N and P determined as previously described. The bacterial inoculum was prepared from a fresh overnight culture (LB broth; 18 h, 37 °C, 150 rev min⁻¹ on an orbital shaker) of two environmental isolates of *E. coli* O157:H7 (strains #2920 and #3704) (Campbell et al., 2001; Ritchie et al., 2003). A 40 ml aliquot of the *E. coli* O157:H7 was added to 360 g of cow faecal samples and thoroughly mixed to deliver a final concentration of approximately 10⁸ cfu g⁻¹ faeces (to reproduce the highest natural concentration encountered; Besser et al., 2001; Fukushima and Seki, 2004). In brief, 5 g of faeces spiked with *E. coli* O157:H7 was added to 5 g of soil in a sterile 50 ml polypropylene tube and incubated at 10 °C (mean annual temperature for the catchment) for 1, 3, 7 and 14 d. After each incubation time, samples were placed on an orbital shaker (150 rev min⁻¹, 15 min, 37 °C) with 20 ml of sterile quarter-strength Ringers solution (Oxoid Ltd.), followed by 4 × 3 s bursts on a vortex mixer. Serial dilutions were plated in duplicate onto Sorbitol MacConkey agar (SMAC) (Oxoid Ltd.), then incubated (37 °C, 20 h) and colonies enumerated. Presumptive *E. coli* O157:H7 colonies were confirmed via latex agglutination as described previously.

2.4.3. Pesticide sorption and degradation in soil

The s-triazine herbicide, simazine ($C_7H_{12}ClN_5$; Water solubility, 5 mg l⁻¹; K_{ow} , 2.2; pKa, 1.6), was selected to investigate the fate of a common pesticide when applied to soils influenced by different environmental factors.

Simazine sorption followed the procedure of Jones et al. (2011). Briefly, 5 ml of ¹⁴C-labelled simazine (final concentration 0.5 mg l⁻¹; 0.02 kBq ml⁻¹) was added to 2.5 g of soil 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 then centrifuged (10,000 g, 5 min) and the supernatant mixed with Scintisafe 3[®] scintillation cocktail (Fisher Scientific, Leicestershire, UK). The ¹⁴C activity remaining in solution was then determined as described before. The simazine partition coefficient, K_d , was determined as follows:

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

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

To determine how soil influences pesticide degradation, 5 g of soil was placed in individual 50 ml polypropylene tubes and ¹⁴C-labelled simazine was added to the soil at a rate 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 to capture any ¹⁴CO₂ evolved. The tubes were hermetically sealed and placed at room temperature (25 °C). The first NaOH traps were replaced after 24 h and then every 5 d for 30 d. On removal, NaOH traps were immediately mixed with Optiphase HiSafe 3 scintillation fluid (PerkinElmer Inc.) and the amount of ¹⁴CO₂ captured was determined using a Wallac 1404 liquid scintillation counter. Total simazine degradation was calculated as the cumulative percentage of ¹⁴C labelled CO₂ evolved at the end of the incubation period.

2.4.4. Nitrate loss from soil

Loss of nitrate via denitrification represents a major N loss pathway (Sgouridis and Ullah, 2015). Denitrification capacity was estimated using the acetylene inhibition technique (AIT) as described in Abalos and Sanz-Cobena (2013). Although the application of this technique presents limitations (i.e. poor diffusion of C_2H_2 into the soil and inhibition of NO_3^- production via nitrification), it has been widely used to give a qualitative estimate of denitrification activity (Estavillo et al., 2002; Groffman and Altabet, 2006; Tellez-Rio and García-Marco, 2015)).

In brief, 20 g of field-moist soil was placed in 150 ml gas-tight polypropylene containers. Subsequently, KNO_3 (8 ml, 42.9 mM) was added to the soil to remove NO_3^- limitation, the containers sealed and placed under vacuum and filled with O_2 -free N_2 gas to induce anaerobic conditions. Ten percent of the container headspace was then replaced with acetylene to block the conversion of N_2O to N_2 gas. The containers were put on a reciprocating shaker at 25 °C. After 0, 8 and 24 h, gas samples (10 ml) were removed with a syringe and stored in pre-evacuated 20 ml glass vials, refilled with O_2 -free N_2 gas. Nitrous oxide was analysed by gas chromatography (GC) using a Clarus 500 GC equipped with a headspace autoanalyzer Turbomatrix (HS-40) (PerkinElmer Inc.). Emission rates and cumulative fluxes were determined as described by MacKenzie (1998) and Menéndez et al. (2006), respectively.

2.5. Water temperature regulation and riparian shading provision

A GIS-based methodology was used to determine the extent to which vegetation contributes to water channel shading in the different habitats. Based on the UK Environment Agency 'Keeping River Cool' programme (Lenane, 2012), a LiDAR dataset (2 m resolution Natural Resources Wales composite dataset) (Table 2) was used to provide a riparian shade map to quantify how different habitat types and their associated riparian zones contribute to

shade provision. Using the ArcGIS Solar Radiation tool, we calculated the difference in average incoming solar radiation during the summer months (1st May to 30th Sept.) between two different elevation datasets to produce a measure of relative shade for the catchment. A Digital Terrain Model (DTM) provided the 'bare earth elevation' whereas a Digital Surface Model (DSM) provided the earth's surface data including all objects on it. Differences in incoming solar radiation between these datasets indicates the likely amount of shade created by vegetation. Although the relative shade was calculated for the whole catchment, only the parts which overlap with rivers were considered. The Zonal Statistics function (Arc GIS) was used to attach the difference in solar radiation from the DTM and DSM to the water body features (clipped using a 25 × 25 m grid in order to make small but similar sized units to attach results) extracted from the OS Open Rivers dataset (Ordnance Survey, Southampton, UK). The resultant shapefile was exported to Excel where shading differences were ranked (1-20, with 1 being the least shaded and 20 the most shaded). The term "relative shading" was used to refer to those areas that appear to have more or less than others due to the effect of the vegetation. Finally, those areas which scored >10 on the ranking scale (higher provision of shade) were then analysed to assess the influence of the habitat type on shade provision. A 2 m margin was applied to each river, to ensure accurate intersection with the adjacent Phase 1 habitat classification (Lucas et al., 2011) to estimate the percentage occurrence of each habitat in relation to provision of shade.

2.6. Statistical analyses

For physicochemical soil properties, principal component analysis (PCA) was used to explore the spatial relationships of selected soil properties for the different habitat types. A two-way ANOVA was used to evaluate the interactions between physicochemical properties with distance from river and soil depth within each habitat type. For each ecosystem process,

an independent t-test was performed to assess the influence of proximity to the river in terms of ecosystem service provision. Pearson correlations were used to explore the relationships between physicochemical properties and the results from the processing studies. All data were analysed for normality and homogeneity of variance with Shapiro Wilk's tests and Levene's statistics, respectively. Transformations to accomplish normality were done when necessary. For all statistical tests, $P < 0.05$ was selected as the significance cut-off value. Statistical analyses were performed with SPSS version 22 for Windows (IBM Corp., Armonk, NY).

3. Results

3.1. Soil properties

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

Results of the PCA showed that habitat type (represented by cluster centroids, average score on each PC1 and PC2 with standard errors) was an important predictor of soil physicochemical variables. In terms of soil properties, BW and CW, and IG were closely associated to each other in the Conwy catchment, although IG displayed overall higher total C and N content (Table 3). At the other end of the spectrum (positive axis of PC1), the MHB habitat was driven by moisture content (2.5 times more compared to woodlands and IG and

1.5 times greater than SNG) and total C (ranging between 3.5 times greater than IG and 9.5 for BW) (Table 3). The SNG habitat resembled MHB in the sense that it had a greater moisture content, total C and N compared to woodlands and IG habitats. However, they were more influenced by microbial biomass showing larger variability in their vertical component. The sites IG, SNG and BW were characterized by more alkaline pH values (ca. 5.2), whilst MHB and CW displayed a more acidic pH (ca. 4.5) (Table 3).

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

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

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

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

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

3.2. Ecosystem service provisioning

3.2.1. Phosphorus sorption to soil

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

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

3.2.2. Human bacterial pathogen survival in soil

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

3.2.3. Pesticide sorption to soil

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

3.2.4. Pesticide degradation in soil

After 30 d of incubation, the total percentage of simazine degradation ranged from 2.7 to 8.8% of the total ¹⁴C-simazine activity added across habitat types irrespective of distance from the river. The amount of simazine mineralized was noticeably less in the MHB sites

compared with the rest of the habitats. Across all habitats and distances, the rate of simazine mineralization was maximal in the first week of incubation and then progressively decreased over the 30 d incubation period. No significant differences were noted for MHB and IG with respect to distance from the river. In contrast, significant differences with distance from the river were observed in the two woodland habitats (Fig. 5; $P = 0.041$ for BW and $P = 0.035$ for CW). However, while the final percentage of simazine mineralized tended to be higher close to the river in CW, the opposite trend was seen for BW. Across habitat types, the most striking relationships between simazine degradation and soil physicochemical properties were a positive correlation with pH ($P < 0.01$) and negative correlation with DOC ($P < 0.001$). Simazine degradation also correlated negatively with N inorganic forms ($\text{NH}_4\text{-N}$, $P = 0.002$, $\text{NO}_3\text{-N}$, $P = 0.003$) and available P ($P = 0.008$).

3.2.5. Denitrification potential in soil

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

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

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

3.2.6. Provision of riparian shade

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

4. Discussion

4.1. General approach

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

4.2. Riparian soil physicochemical properties

Many studies have linked the provision of riparian ecosystem services to their unique intrinsic characteristics (Vought et al., 1994; Natta and Sinsin, 2002; Groffman and Crawford, 2003). Riparian soils may have higher organic C contents (Figueiredo et al., 2016; Graf-Rosenfellner, 2016), greater amounts of nutrients and fine-grained sediments (Lee et al., 2000; Mayer et al., 2007), increased moisture contents (Lewis et al., 2003; Zaines et al., 2007) and microbial biomass (Naiman et al., 2010) than adjacent non-riparian areas. Contrary to expectations, our findings contradict the frequently held assumption of riparian area ‘uniqueness’. We observed little or no effect of the proximity to the river on the soil physicochemical properties measured, despite major differences in vegetation community composition and exposure to different hydrological regimes. General soil physicochemical properties across habitat types followed the same trends as previous studies undertaken in the catchment (Ullah and Faulkner, 2006; Sgouridis and Ullah, 2014; ;2015) and the inherent habitat characteristics proved to be the main drivers explaining soil physicochemical variability in riparian areas. In support of our findings, Richardson et al. (2005) also noticed little difference in soil properties between riparian and upslope areas along small streams in temperate forested areas of the Pacific Northwest. In addition, riparian studies have commonly focussed on agriculturally-managed grasslands and more specifically on riparian buffer strips as management tools (Pierson et al., 2001; Hefting and Bobbink, 2003; Hickey and Doran, 2004), even though this habitat type has shown less value in terms of ecosystem service provision (Maes et al., 2011; 2012). Stutter et al. (2012) and Smith et al. (2012) found significant differences when comparing soil physicochemical properties of riparian buffers versus adjacent fields. However, the comparison was undertaken between areas which possessed vastly different management regimes and in which the vegetation cover changed dramatically. Similarly, Burger et al. (2010) also showed differences in soil properties between agriculturally impacted riparian areas and ones conserved in pristine natural

conditions. Most of the habitats assessed in our study have little or no management intervention so natural or semi-natural habitat conditions remained consistent across the upslope and riparian area. This was true even for the areas subject to agricultural practices (improved and to a lesser extent semi-natural grassland), although it should be stated that these agricultural areas generally have good soil quality (unlike those under arable cropping; Emmett et al., 2016). It is possibly for this reason that we did not identify any significant change in soil physicochemical properties as reported by others. Further studies are therefore needed to take into account management intensity and to include seasonal patterns as they may also represent an important component in riparian dynamics (Dhondt et al., 2002; Greet et al., 2011).

4.3. Ecosystem service provision

In comparison to the surrounding region, riparian areas are usually considered to have extra functionality in terms of ecosystem service provision through enhanced flood control, water purification or biodiversity (Salo and Theobald, 2016; Sutfin et al., 2016; Xiang et al., 2016). However, in our study there was no evidence that fundamental differences exist between riparian zones and the adjacent land. This is supported by the clear segregation of results according to habitat types and not by riparian areas (Fig. 8). Main habitat characteristics and not distance from the river was the driving factor in all cases. In this respect, Table S6 summarizes the soil habitat physicochemical properties which are most likely to be driving the ecosystem service delivery in this study. Together with that, we also include other factors that, despite not being measured, should be considered in future riparian studies to predict the spatial and temporal variation in ecosystem service delivery. These processes could be responsible for creating ‘hot spots and moments’ within riparian zones (McClain et al., 2003; Vidon et al., 2010). For example, erosion is more prevalent in riparian

areas due to the exposure to a more dynamic water regime (McCloskey, 2010). This can cause a large release of N, P and C into the water column producing similar loads to those induced by fertilizer application (Quinton et al., 2010). Likewise, water table fluctuations that modifies oxygen levels and nutrient availability, and the presence of macrophytes are also good examples that could potentially alter ecosystem service delivery dynamics in riparian areas (Naiman and Decamps, 1997; Hill, 2000; Lewis et al., 2003; Ng and Chan, 2017).

4.3.1 Pollutant removal via sorption

Values of S_{\max} (P sorption) and K_d (simazine sorption) resulted in good agreement with other values found in the literature across habitat types (Dunne et al., 2005; Flores et al., 2009). Analysis suggested that simazine and P sorption was driven by high organic matter content as has been highlighted in previous studies (Li et al., 2003; Hogan et al., 2004; Kang and Hesterberg, 2009; Alister and Kogan, 2010). Particularly for P sorption, some authors attribute this affinity of P for organic matter to the co-occurrence of Al and Fe oxides, which can sorb high amounts of P (Pant et al., 2001; Kang and Hesterberg, 2009). We had expected that the riparian areas would be wetter, have a lower redox status and would contain a lesser amount of oxidised forms of Fe and thus a lower P retention capacity, however, this was not apparent in our soils. Barrow (2017) illustrated different pathways for P sorption according to soil pH but due to the relatively small shifts in pH relative to the distance to the river, no such effect was found in this study.

Comparing the results obtained in this study is challenging as most studies within riparian areas try to identify the most cost-effective buffer width depending on the pollutant load in agricultural systems or constructed wetlands. This is motivated by the fact that land managers do not want to sacrifice more productive land than they have to (Wenger, 1999; Shearer and Xiang, 2007). Consequently, the centre of attention has been on comparing

inputs versus outputs of pollutants in runoff through vegetative buffer strips (Schultz et al., 2000; Maillard and Imfeld, 2014). Results found in the literature about the long-term effectiveness of riparian buffers in trapping pollutants are contradictory as riparian areas can vary from being sources to sinks depending mostly on physicochemical soil properties and hydrology (Hickey and Doran 2004; Fisher and Acreman, 2004; Stutter et al., 2009; Maillard and Imfeld, 2014). Some studies (e.g. Miller et al., 2016) reported different P retention capacities with distance from the river. However, it was only true for samples included inside a concentrated flow path that was visually identified prior to sampling. In contrast, samples outside this concentrated flow path did not reveal any differences in P retention across the transect.

The similar pollutant sorption capacities relative to distance from the river found in this study, combined with fact that simazine and P retention by soil can only occur when they are in direct contact with the adsorbent suggest that the soil potential data alone is not very useful in predicting the pollutant retention capacity (Reddy and Kadlec, 1999). Thus, the study of transport pathways, potential sources of pollutant loads, ease of degradation, desorption potential from the soil, shifts in temperature that controls simazine solubility or pH that controls P precipitation may contribute more efficiently to understanding riparian pollutant attenuation.

4.3.2 Pollutant removal through degradation

Degradation, together with sorption, is one of the main processes determining the fate of pollutants within the environment (Gunasekara et al., 2007; Maillard and Imfeld, 2014). In our study, we investigated the degradation of a pesticide and loss of the biological contaminant, *E. coli* O157, which are of concern in terms of their impact on human health (Holden et al., 2017). Sorption and transport of pollutants, and the extension of buffer strips

on agricultural and wetland systems has often been the focus of attention (Vellidis et al., 2002; Hickey and Doran 2004; Rasmussen et al., 2011), but processes influencing pollutant degradation in riparian areas are much less well understood (Vidon et al., 2010). Microbial activity has long been identified as a critical factor determining the fate of pesticides in the environment (Kaufman and Kearney, 1976; Anderson, 1984), and it is suggested that microbial populations within riparian areas are able to degrade pesticides due to their continuous exposure to such chemicals through runoff from agricultural lands (Vidon et al., 2010). Overall, simazine degradation in this study showed a similar percentage decrease (of the total of ^{14}C -simazine added) to other studies (Laabs et al., 2002; Gunasekara et al., 2007; Jones et al., 2011). Laabs et al. (2002) and Cox et al. (2001) found a negative correlation between simazine degradation rates and organic matter content due to the residue binding to organic matter reducing herbicide movement in the soil. This fact could explain the minimal amount of simazine degraded in MHB sites in this study. Previous studies have demonstrated enhanced pesticide degradation within riparian areas (Mudd et al., 1995; Staddon et al., 2001). However, the riparian buffer strips in these previous studies differed considerably from the adjacent habitat (i.e. bare or highly modified fields versus vegetated buffer strips). In our study, only the woodlands showed a different pattern in terms of pesticide degradation when comparing sites close and distal to the river. However, we hypothesized that the negative correlation between simazine degradation and N and P inorganic forms content could explain this spatial variability as the use of pesticides as a source of energy in areas with low nutrient status has been identified (Błaszak et al., 2011). In addition, it has been shown that some organisms (e.g. *Pseudomonas*) are able to mineralise simazine more rapidly (Regitano, 2006; Błaszak et al., 2011) and therefore a more diverse microbial population associated with a higher above-ground plant diversity could be involved in different ecosystems. Our results may therefore reflect the spatial heterogeneity of microbial

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populations within these habitat types rather than a specialization of microbial population in riparian areas. This fact is endorsed by studies like Widenfalk et al. (2008) where an effect on microbial composition due to pesticide exposure could not be identified. Our results reveal that there is a need for linking functional soil biota groups with the maintenance of ecosystem services to better explain the inherent spatial heterogeneity (Brussaard, 1997; Graham et al., 2016).

Along with pesticides, biological contaminants, in particular faecal coliform bacteria (FCB), have become an important source of water contamination from human and animal wastes applied to land (Bai et al., 2016). Although the use of riparian buffer strips for reducing FCB transport into streams has been explored (Coyne et al., 1995; Parkyn et al., 2003; Sullivan et al., 2007), bacterial survival and behaviour in terrestrial systems has received less attention than in water ecosystems (Jones, 1999). Our results corroborate previous studies that show *E. coli* O157 can survive for long periods (more than 120 d) in a diverse range of soils and under a wide range of environmental conditions (Bogosian et al., 1996; Kauppi and Tatini, 1998; Jones, 1999). Some studies have suggested that moisture status and organic matter are the principal factors controlling *E. coli* survival (Jamieson et al., 2002). However, the lack of correlation between soil properties and pathogen survival in this study suggest that other factors, such as predation or the presence of elements highlighted in other studies (Al, Zn; Avery et al., 2008), might better explain the lower survival rate found in semi-natural grassland sites.

4.3.3 Pollutant removal through denitrification

Denitrification, as a mechanism for permanent removal of NO_3^- from ecosystems, has important implications for both water quality and greenhouse emissions (Groffman et al., 2009). It has been extensively studied in riparian areas due to the frequency of locally anoxic

conditions and labile organic C which trigger denitrification (Bettez and Groffman, 2012). In our study, rates of N₂O emissions across habitat types followed similar trends to those described in Sgouridis and Ullah (2014). However, we could not find any clear evidence that leads us to identify more efficient patterns of NO₃⁻ removal by denitrification with proximity to the river. We also observed a high degree of spatial variability in denitrification with some extremely high rates as has been observed in other studies and described as ‘hot spots or moments’ controlled by oxygen, NO₃⁻ and C availability (Parkin, 1987; McClain et al., 2003; Groffman et al., 2009; Vidon et al., 2010). Previous riparian studies have also reported no clear spatial patterns in denitrification rates (Martin et al., 1999). In our study, it was clear that the addition of NO₃⁻ was not sufficient to trigger large amounts of N₂O production, indicating that factors other than NO₃⁻ limitation were playing a key role. Sgouridis and Ullah (2015) describe significant relationships between denitrification rates and pH and bulk density, and the same pattern was found in our study. However, those factors do not explain the high variability encountered within habitat types, and it was not possible to demonstrate significantly increased N₂O production rates within riparian areas as demonstrated in previous studies (Hanson et al., 1994; Groffman et al., 2000; Groffman and Crawford, 2003). Further research is therefore required to better understand why denitrification is so spatially variable and the spatial/temporal existence of ‘hot spots or moments’.

4.3.4 Riparian shading

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

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

As expected, in our study the effects of shading were more significant in woodlands than in any other habitat type. Woodland riparian zones are likely to offer the greatest influence on water temperature within a catchment. Any assessment, however, should also consider excessive shading, mostly caused by abandoned woodlands (Suzuki, 2013) which can be detrimental to aquatic ecosystems by excessively reducing water temperature. This can have a direct impact on aquatic fauna and result in a loss of shade-intolerant plants (Forestry Commission, 2004; Hédal et al., 2010). Shading may also reduce the UV radiation-induced photooxidation of many pesticides within the water column.

5. Conclusions

Recommendations and guidance about riparian zone management are frequently undertaken without an accurate evaluation of their status and the ecosystem services that they actually provide. Consequently, many previous environmental protection measures involving riparian management remain too general and untargeted and may offer little environmental

benefit. Through a series of laboratory experiments and GIS-based mapping, this study has shown that across a diverse range of habitats, riparian soils diverge from their capacity to deliver the specific ecosystem service of water purification. However, contrary to expectation, riparian soils did not differ greatly in their ability to provide this service in comparison to neighbouring upslope (non-riparian) soils. We ascribe this to our habitats being in a close to natural or semi-natural state rather than the more frequently studied riparian areas in degraded agricultural systems. Further work should focus on validating our findings using an even greater range of ecosystem services (e.g. inclusion of CH₄/CO₂ emissions, metal attenuation, biodiversity), using in situ measurements, encompassing inter-annual variation and over a wider range of ecosystem types.

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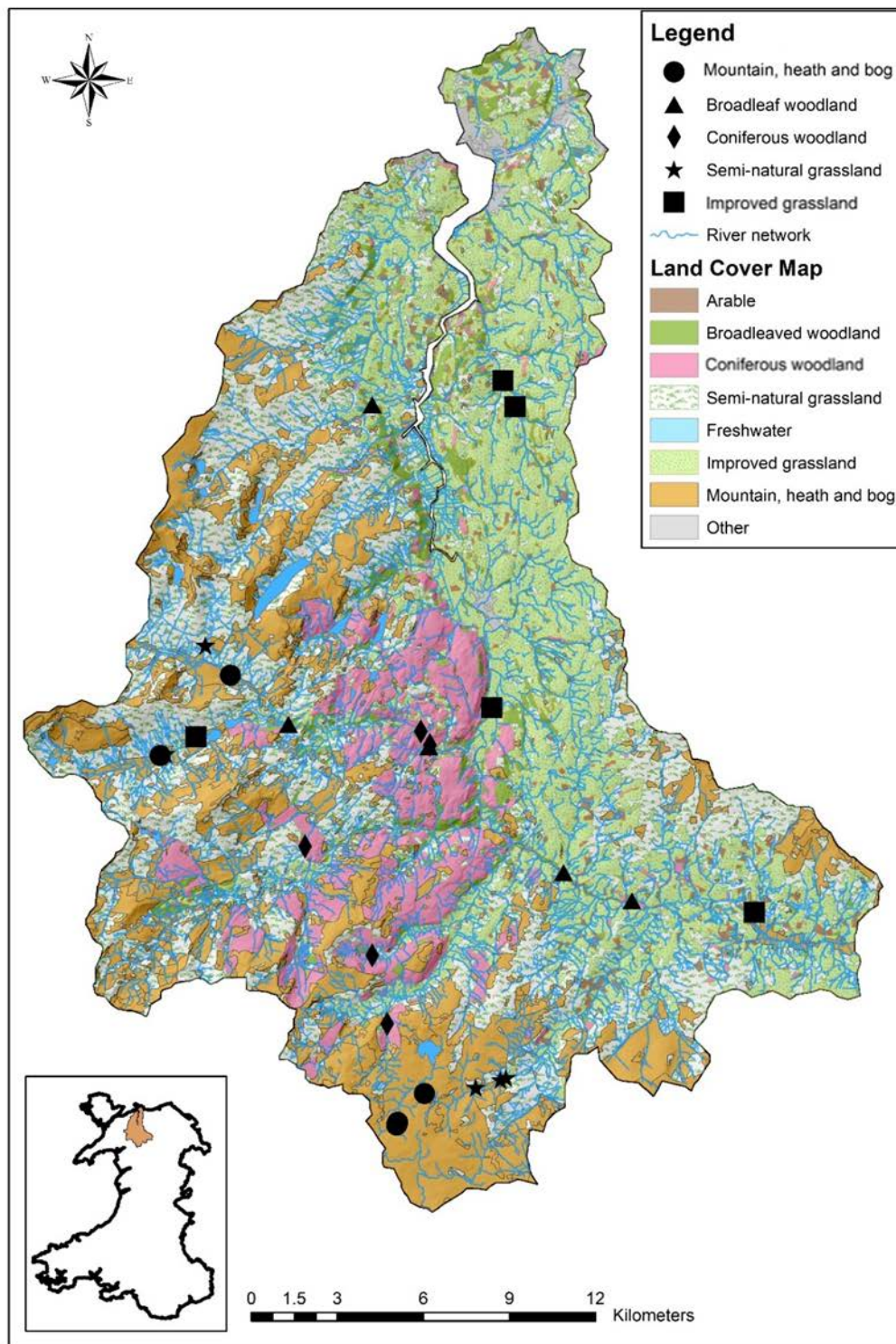


Figure 1. The Conwy catchment, North Wales, UK showing location of sample points, land cover classes (Lucas et al., 2011) and river network. Samples sites were distributed within the five dominant habitat types in the Conwy catchment (mountain, heath and bog, broadleaf and coniferous woodlands, semi-natural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

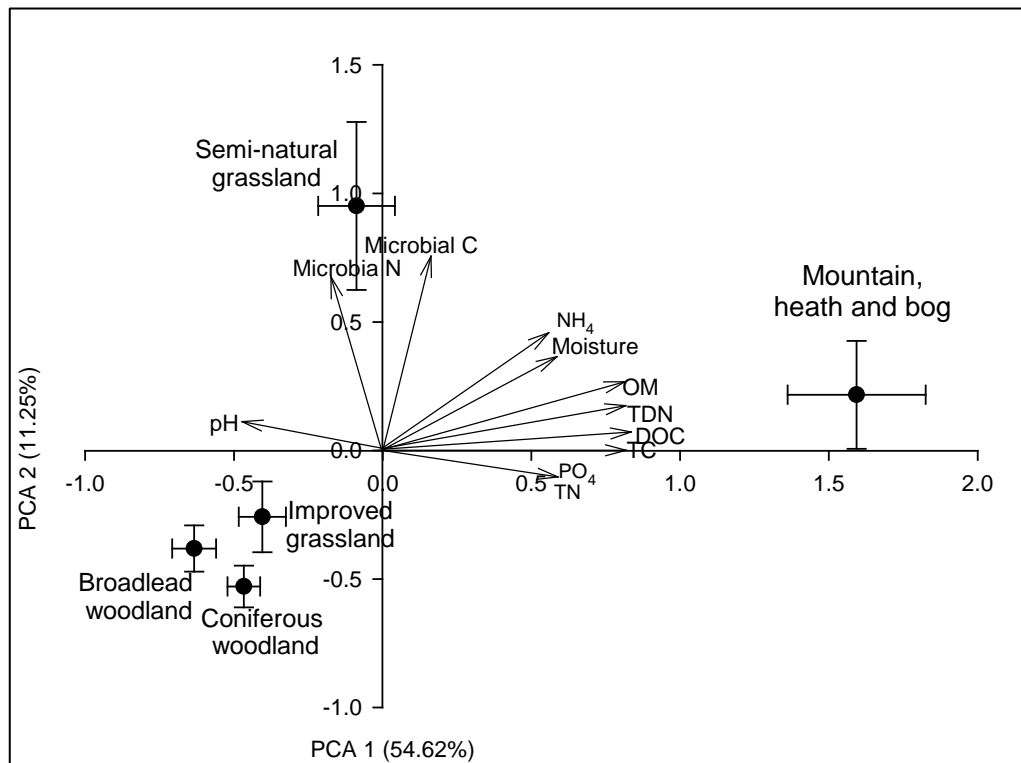


Figure 2. Correlation bi-plot from the principal component analysis (PCA) on soil physicochemical variables according to their dominant habitat type and irrespective of distance and depth ($n = 100$). Correlation of soil properties with the main axes are given by arrows and habitat types by cluster centroids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

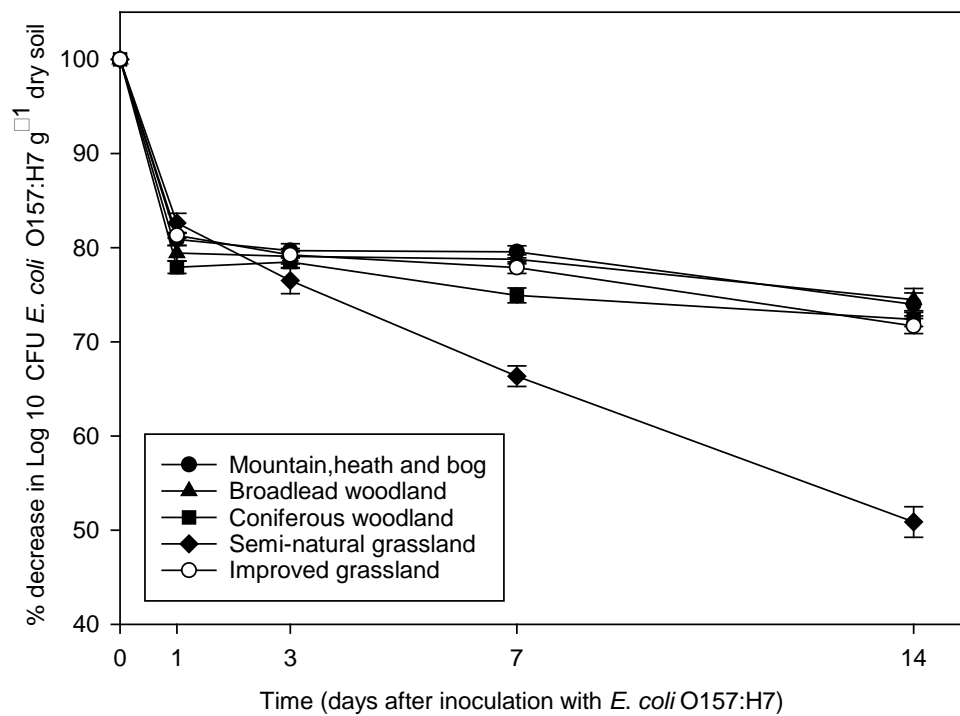


Figure 3. Survival of *Escherichia coli* O157:H7 following the application of pathogen-contaminated cattle slurry to the soil from different habitat types amalgamating distance from the river. Data points represent mean values ($n = 10$) \pm standard error of the mean (SEM).

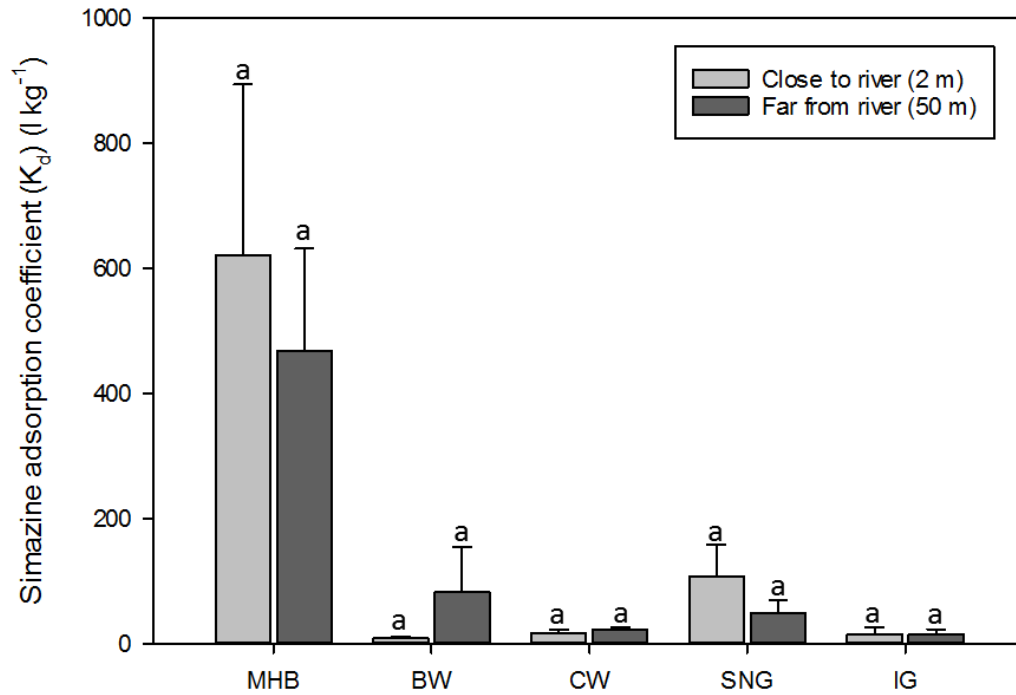


Figure 4. Simazine adsorption coefficient (K_d) across habitat types (MHB: mountain, heath and bog; BW: broadleaf woodland; CW: coniferous woodland; SNG: semi-natural grassland; IG: improved grassland) with respect to distance from the river. Same lower-case letters indicate no significant difference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

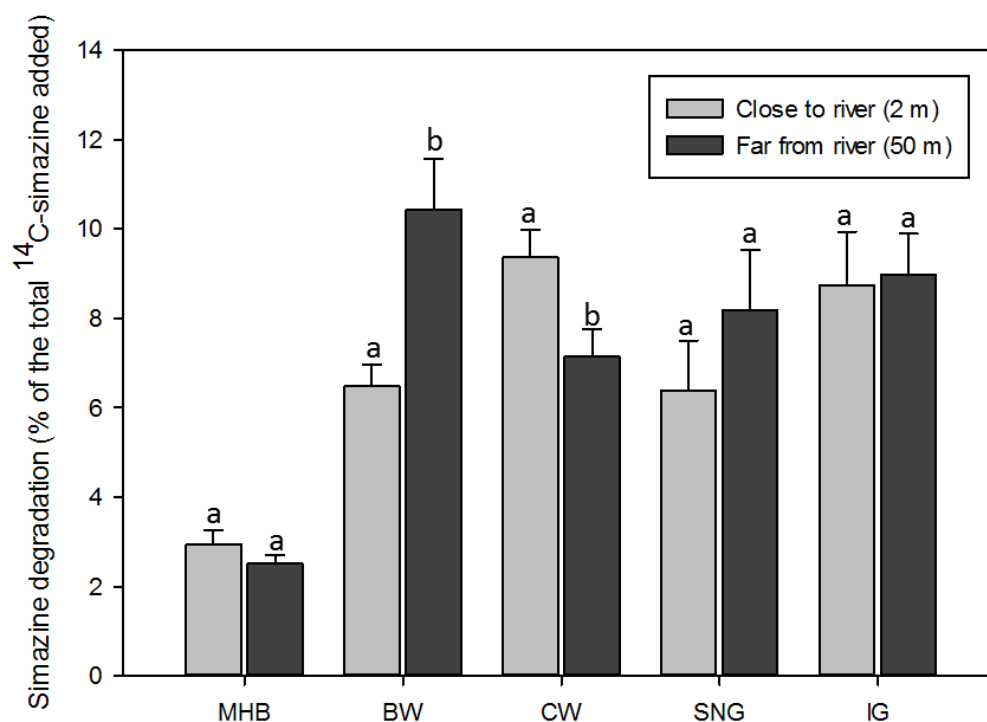


Figure 5. Simazine degradation across habitat types (MHB: mountain, heath and bog; BW: broadleaf woodland; CW: coniferous woodland; SNG: semi-natural grassland; IG: improved grassland) with respect to distance from the river. Values are expressed as the cumulative percentage of the total ^{14}C -simazine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

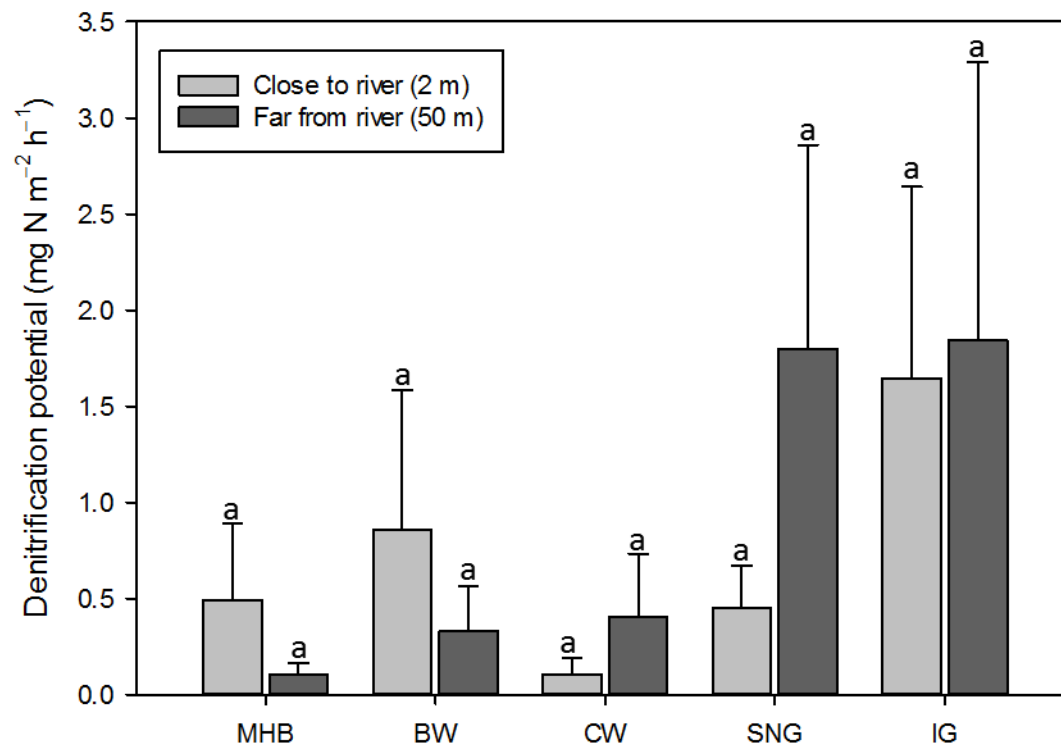


Figure 6. Rate of potential denitrification after 24 h across dominant habitat types (MHB: mountain, heath and bog; BW: broadleaf woodland; CW: coniferous woodland; SNG: semi-natural grassland; IG: improved grassland) with respect to distance from the river. Same lower case letters indicate no significant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

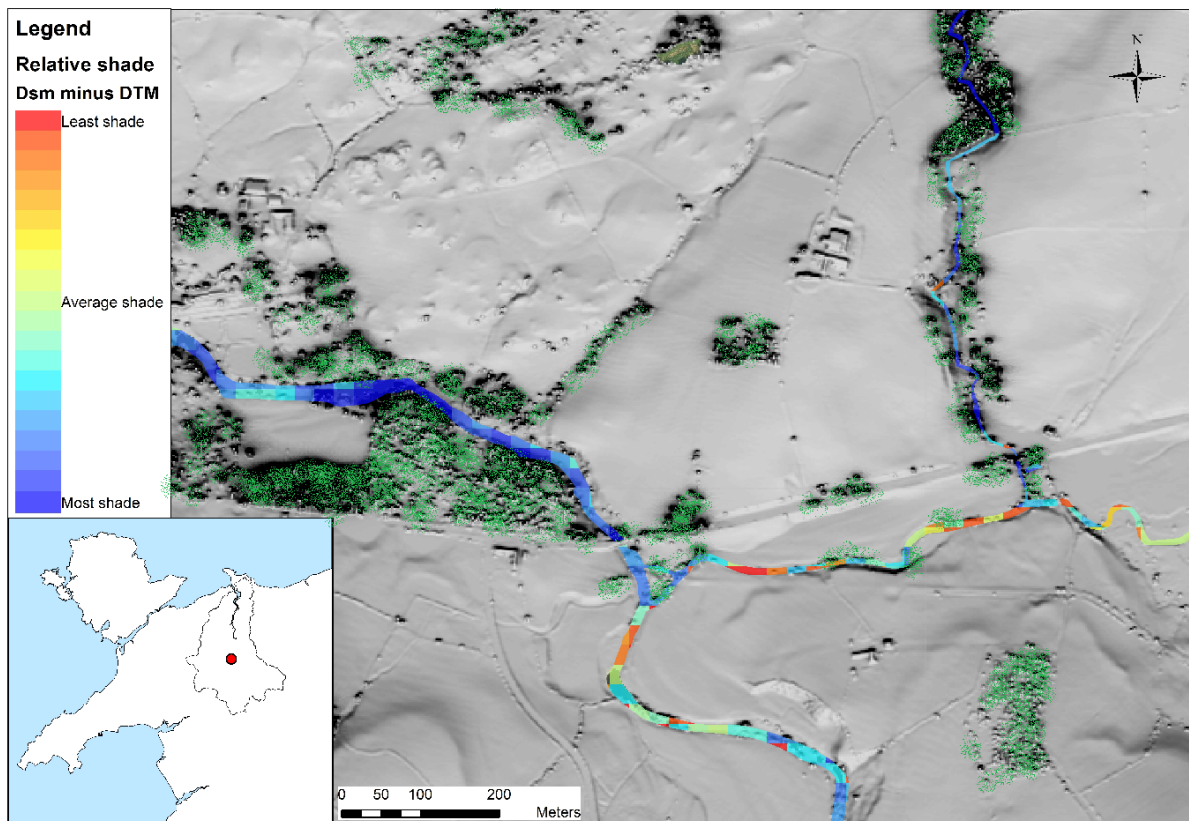


Figure 7. An example image showing the areas with the least (red) and greatest (blue) amount of shade from solar radiation, generated using a Digital Elevation Model (DEM) to represent the bare surface without objects (i.e. vegetation and other objects) and the Digital Surface Model representing the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

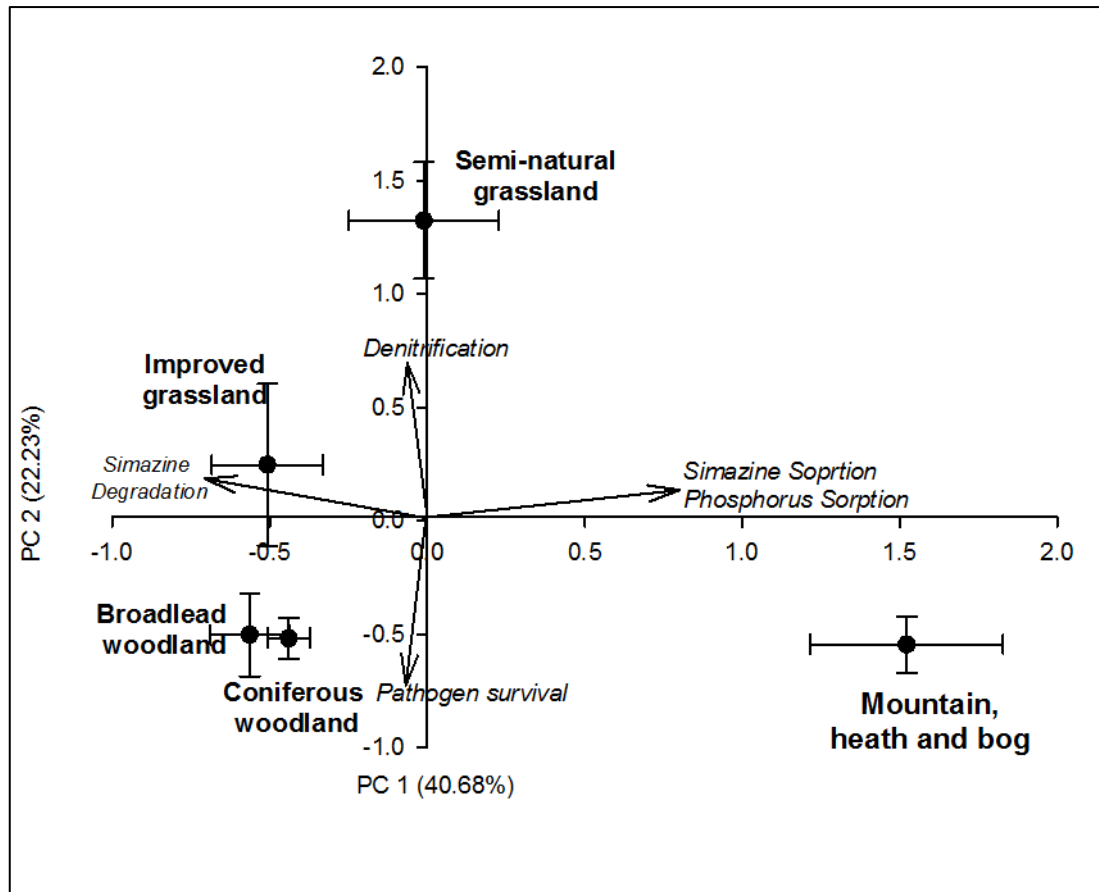


Figure 8. Correlation bi-plot from the principal component analysis (PCA) on ecosystem services evaluated in this study irrespective of the distance from the river. Correlation of ecosystem services with the main axes are given by arrows and habitat types by cluster centroids (average score on each horizontal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

Table 1

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 Veshtoh, 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)

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

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.

Data inputs and sources for the computational GIS tool.

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
NH ₄ ⁺ -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
NO ₃ ⁻ -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

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				
	Maximum P sorption S_{\max} (mg kg ⁻¹)		Binding strength k (l kg ⁻¹)		R^2
	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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Supplementary on-line information

Table S1. Soil physicochemical properties in mountain, heath and bog (MHB) land use type with respect to the distance from the river and soil depth in the Conwy Catchment. Data are mean values ($n = 5$) \pm 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	4.85 \pm 0.40	4.92 \pm 0.40	4.34 \pm 0.20	4.46 \pm 0.20	ns	ns
EC ($\mu\text{S cm}^{-1}$)	33.2 \pm 6.3	26.8 \pm 5.4	37.1 \pm 4.4	24.0 \pm 5.0	ns	ns
Bulk density (g cm^{-3})	0.07 \pm 0.01	ND	0.09 \pm 0.02	ND	ns	ND
Moisture content (%)	87.7 \pm 0.8	87.4 \pm 0.5	87.4 \pm 1.7	84.2 \pm 1.1	ns	ns
Organic matter (%)	78.7 \pm 6.8	86.1 \pm 5.6	86.3 \pm 3.5	78.6 \pm 5.9	ns	ns
NH ₄ ⁺ -N (mg kg^{-1} soil)	19.8 \pm 1.3	18.4 \pm 1.2	20.7 \pm 4.0	18.1 \pm 1.2	ns	ns
NO ₃ ⁻ -N (mg kg^{-1} soil)	51.5 \pm 18.7	50.5 \pm 19.3	56.8 \pm 15.1	42.5 \pm 12.1	ns	ns
Available P (mg kg^{-1} soil)	10.8 \pm 4.04	3.11 \pm 1.49	3.42 \pm 0.53	2.29 \pm 0.72	0.002	ns
Total C (g kg^{-1} soil)	453 \pm 102	456 \pm 147	545 \pm 30	524 \pm 40	ns	ns
Total N (g kg^{-1} soil)	17.8 \pm 3.1	21.6 \pm 1.8	13.8 \pm 4.5	21.1 \pm 2.2	ns	ns
Dissolved organic C (g kg^{-1} soil)	0.95 \pm 0.30	1.00 \pm 0.30	1.07 \pm 0.20	1.01 \pm 0.20	ns	ns
Total dissolved N (g kg^{-1} soil)	0.14 \pm 0.03	0.16 \pm 0.04	0.17 \pm 0.04	0.14 \pm 0.01	ns	ns
Microbial biomass C (g kg^{-1} soil)	3.20 \pm 0.89	1.04 \pm 0.41	3.81 \pm 1.07	1.20 \pm 0.19	ns	0.005
Microbial biomass N (g kg^{-1} soil)	0.26 \pm 0.11	0.28 \pm 0.11	0.43 \pm 0.24	0.38 \pm 0.08	ns	ns

EC, electrical conductivity; ND, not determined.

Table S2. Soil physicochemical properties in broadleaf woodland (BW) land use type with respect to the distance from the river and depth in the Conwy Catchment. Data are mean values ($n = 5$) \pm 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

	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 \pm 0.30	5.18 \pm 0.20	5.07 \pm 0.30	5.24 \pm 0.30	ns	ns
EC ($\mu\text{S cm}^{-1}$)	26.6 \pm 5.0	25.2 \pm 4.2	42.9 \pm 6.2	31.5 \pm 5.4	0.047	ns
Bulk density (g cm^{-3})	0.74 \pm 0.11	ND	0.73 \pm 0.06	ND	ns	ND
Moisture content (%)	30.0 \pm 3.0	27.2 \pm 5.0	41.0 \pm 7.8	34.3 \pm 2.8	ns	ns
Organic matter (%)	14.3 \pm 4.8	8.4 \pm 1.9	24.8 \pm 12.5	10.1 \pm 0.7	ns	ns
$\text{NH}_4^+\text{-N}$ (mg kg^{-1} soil)	3.75 \pm 0.8	4.25 \pm 0.7	6.37 \pm 0.5	4.70 \pm 0.8	0.042	ns
NO_3^-N (mg kg^{-1} soil)	1.99 \pm 0.6	1.77 \pm 1.1	7.01 \pm 1.6	3.49 \pm 1.0	0.004	ns
P available (mg kg^{-1} soil)	0.31 \pm 0.11	0.41 \pm 0.20	0.57 \pm 0.28	0.19 \pm 0.12	ns	ns
Total C (g kg^{-1} soil)	57 \pm 13	44 \pm 10	76 \pm 8	42 \pm 6	ns	ns
Total N (g kg^{-1} soil)	3.38 \pm 0.60	4.47 \pm 0.30	2.72 \pm 0.40	3.21 \pm 0.20	0.016	ns
Dissolved organic C (g kg^{-1} soil)	0.19 \pm 0.05	0.19 \pm 0.05	0.26 \pm 0.06	0.14 \pm 0.02	ns	ns
Total dissolved N (g kg^{-1} soil)	0.03 \pm 0.01	0.03 \pm 0.01	0.04 \pm 0.005	0.02 \pm 0.002	ns	ns
Microbial biomass C (g kg^{-1} soil)	0.26 \pm 0.11	0.28 \pm 0.11	0.43 \pm 0.24	0.38 \pm 0.08	ns	ns
Microbial biomass N (g kg^{-1} soil)	0.16 \pm 0.03	0.18 \pm 0.02	0.26 \pm 0.03	0.32 \pm 0.11	0.024	ns

significant differences were found by the interaction of distance with depth.

EC, electrical conductivity; ND, not determined.

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 ($n = 5$) \pm 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				<i>P</i> -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 \pm 0.20	4.95 \pm 0.10	4.23 \pm 0.10	4.52 \pm 0.10	0.002	ns
EC ($\mu\text{S cm}^{-1}$)	28.9 \pm 4.8	27.0 \pm 3.2	43.6 \pm 7.5	45.0 \pm 10.1	ns	ns
Bulk density (g cm^{-3})	0.45 \pm 0.15	ND	0.41 \pm 0.16	ND	ns	ND
Moisture content (%)	36.4 \pm 9.9	36.2 \pm 10.7	39.3 \pm 5.8	32.9 \pm 7.5	ns	ns
Organic matter (%)	13.5 \pm 5.8	12.9 \pm 6.6	18.9 \pm 3.4	13.3 \pm 1.6	ns	ns
NH ₄ ⁺ -N (mg kg^{-1} soil)	5.62 \pm 0.90	4.79 \pm 0.60	5.08 \pm 0.90	4.75 \pm 0.80	ns	ns
NO ₃ ⁻ -N (mg kg^{-1} soil)	4.95 \pm 1.2	4.11 \pm 1.4	7.54 \pm 2.2	4.63 \pm 5.9	ns	ns
Available P (mg kg^{-1} soil)	0.27 \pm 0.08	0.34 \pm 0.20	0.40 \pm 0.08	0.28 \pm 0.03	ns	ns
Total C (g kg^{-1} soil)	71 \pm 33	56 \pm 36	109 \pm 13	58 \pm 11	ns	ns
Total N (g kg^{-1} soil)	4.21 \pm 1.40	5.38 \pm 0.50	3.32 \pm 1.60	3.11 \pm 0.40	ns	ns
Dissolved organic C (g kg^{-1} soil)	0.22 \pm 0.04	0.22 \pm 0.04	0.32 \pm 0.03	0.33 \pm 0.03	0.011	ns
Total dissolved N (g kg^{-1} soil)	0.03 \pm 0.004	0.03 \pm 0.005	0.04 \pm 0.004	0.04 \pm 0.004	ns	ns
Microbial biomass C (g kg^{-1} soil)	1.09 \pm 0.38	0.85 \pm 0.41	2.15 \pm 0.23	1.15 \pm 0.28	ns	ns
Microbial biomass N (g kg^{-1} soil)	0.20 \pm 0.05	0.10 \pm 0.02	0.22 \pm 0.03	0.13 \pm 0.04	ns	0.019

EC, electrical conductivity; ND, not determined.

Table S4. Soil physicochemical properties in semi-natural grassland (SNG) land use type with respect to the distance from the river and depth in the Conwy Catchment. Data are mean values ($n = 5$) \pm 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				<i>P</i> -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 \pm 0.20	5.07 \pm 0.10	5.25 \pm 0.40	5.27 \pm 0.20	ns	ns
EC ($\mu\text{S cm}^{-1}$)	35.1 \pm 5.3	26.9 \pm 4.6	44.4 \pm 8.4	28.1 \pm 4.6	ns	ns
Bulk density (g cm^{-3})	0.16 \pm 0.05	ND	0.31 \pm 0.12	ND	ns	ND
Moisture content (%)	73.0 \pm 7.6	68.9 \pm 10.1	62.7 \pm 9.3	51.7 \pm 13.0	ns	ns
Organic matter (%)	41.4 \pm 11.6	39.9 \pm 12.2	33.9 \pm 11.4	25.9 \pm 13.2	ns	ns
NH ₄ ⁺ -N (mg kg^{-1} soil)	15.5 \pm 4.9	14.1 \pm 4.4	12.9 \pm 5.9	7.40 \pm 2.3	ns	ns
NO ₃ ⁻ -N (mg kg^{-1} soil)	14.6 \pm 5.6	14.7 \pm 4.2	13.7 \pm 5.1	9.10 \pm 1.9	ns	ns
Available P (mg kg^{-1} soil)	1.06 \pm 0.36	0.64 \pm 0.25	0.63 \pm 0.21	0.57 \pm 0.24	ns	ns
Total C (g kg^{-1} soil)	74 \pm 35	218 \pm 67	101 \pm 25	83.3 \pm 20	ns	ns
Total N (g kg^{-1} soil)	5.47 \pm 1.9	7.46 \pm 1.5	11.03 \pm 3.7	12.28 \pm 4.0	ns	ns
Dissolved organic C (g kg^{-1} soil)	0.40 \pm 0.10	0.41 \pm 0.14	0.42 \pm 0.10	0.35 \pm 0.1	ns	ns
Total dissolved N (g kg^{-1} soil)	0.07 \pm 0.02	0.07 \pm 0.02	0.07 \pm 0.01	0.06 \pm 0.008	ns	ns
Microbial biomass C (g kg^{-1} soil)	6.84 \pm 2.40	5.50 \pm 2.68	1.05 \pm 0.38	0.94 \pm 0.30	0.050	ns
Microbial biomass N (g kg^{-1} soil)	0.90 \pm 0.23	0.29 \pm 0.08	0.43 \pm 0.11	0.27 \pm 0.10	ns	0.014

EC, electrical conductivity; ND, not determined.

Table S5. Soil physicochemical properties in improved grassland (IG) land use type with respect to the distance from the river and depth in the Conwy Catchment. Data are mean values ($n = 5$) \pm 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 significant differences were found by the interaction of distance with depth.

	Riparian distance				<i>P</i> -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 \pm 0.30	5.28 \pm 0.30	5.39 \pm 0.10	5.43 \pm 0.20	ns	ns
EC (μ S cm ⁻¹)	104 \pm 37	34 \pm 7	131 \pm 55	101 \pm 47	ns	ns
Bulk density (g cm ⁻³)	0.60 \pm 0.11	ND	0.71 \pm 0.10	ND	ns	ND
Moisture content (%)	39.0 \pm 6.9	35.4 \pm 8.9	44.0 \pm 5.3	30.6 \pm 2.8	ns	ns
Organic matter (%)	13.3 \pm 3.7	12.6 \pm 6.3	20.0 \pm 4.4	10.0 \pm 2.0	ns	ns
NH ₄ ⁺ -N (mg kg ⁻¹ soil)	5.18 \pm 1.7	3.42 \pm 1.1	5.87 \pm 2.1	3.39 \pm 1.1	ns	ns
NO ₃ ⁻ -N (mg kg ⁻¹ soil)	9.78 \pm 3.4	6.96 \pm 1.8	22.7 \pm 9.1	21.4 \pm 12.1	ns	ns
Available P (mg kg ⁻¹ soil)	2.08 \pm 1.06	1.05 \pm 0.55	1.84 \pm 0.75	0.93 \pm 0.48	ns	ns
Total C (g kg ⁻¹ soil)	270 \pm 65	87 \pm 59	223 \pm 65	56 \pm 8	ns	0.001
Total N (g kg ⁻¹ soil)	14.8 \pm 3.4	14.2 \pm 3.3	3.31 \pm 0.5	6.10 \pm 1.9	0.017	ns
Dissolved organic C (g kg ⁻¹ soil)	0.17 \pm 0.02	0.18 \pm 0.05	0.20 \pm 0.02	0.15 \pm 0.02	ns	ns
Total dissolved N (g kg ⁻¹ soil)	0.04 \pm 0.01	0.04 \pm 0.01	0.07 \pm 0.01	0.05 \pm 0.02	ns	ns
Microbial biomass C (g kg ⁻¹ soil)	1.90 \pm 0.55	1.54 \pm 0.77	2.49 \pm 0.31	1.19 \pm 0.20	ns	ns
Microbial biomass N (g kg ⁻¹ soil)	0.18 \pm 0.04	0.30 \pm 0.10	0.38 \pm 0.06	0.31 \pm 0.11	ns	ns

EC, electrical conductivity; ND, not determined.

Table S6. Controlling factors affecting the performance of the ecosystem services selected in this study, accompanied by unmeasured factors that mostly likely influence the behaviour of 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

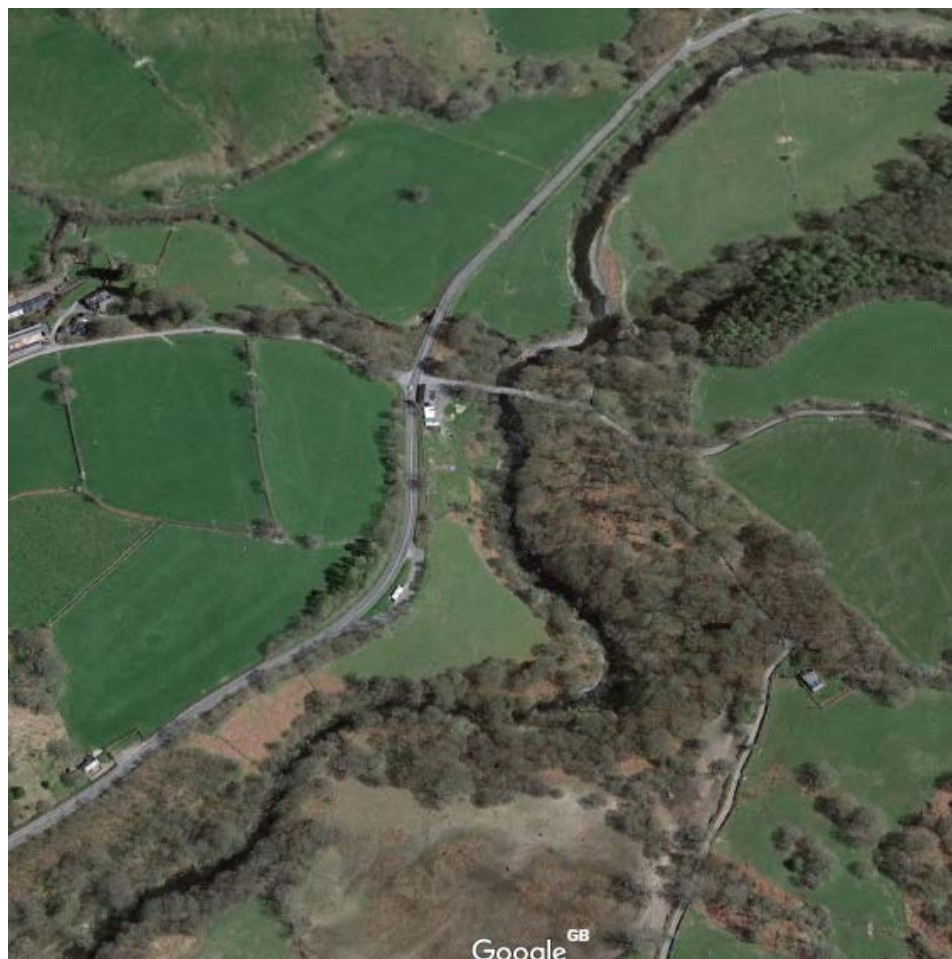
¹Controlling factor only identified for P adsorption

Aerial photographs sample points

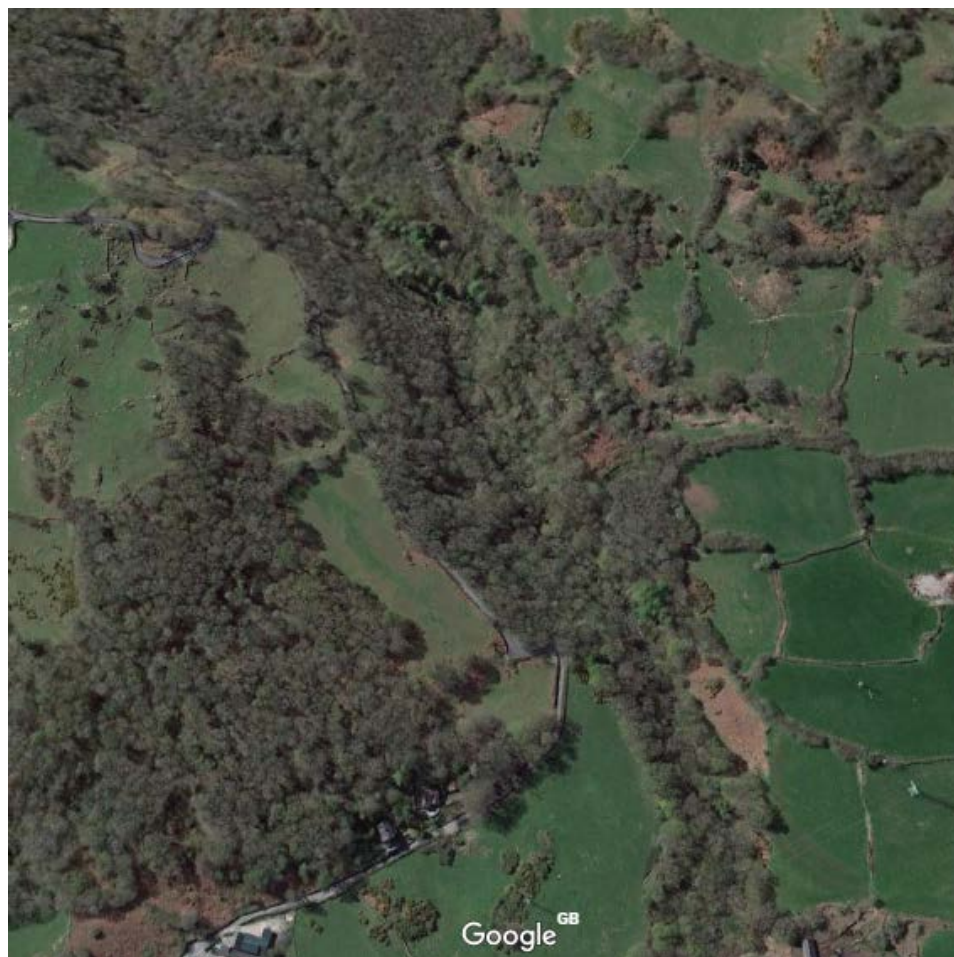
1. Aerial photograph of sample point n° 1 within the broadleaf woodland habitat type.



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



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



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



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



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



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



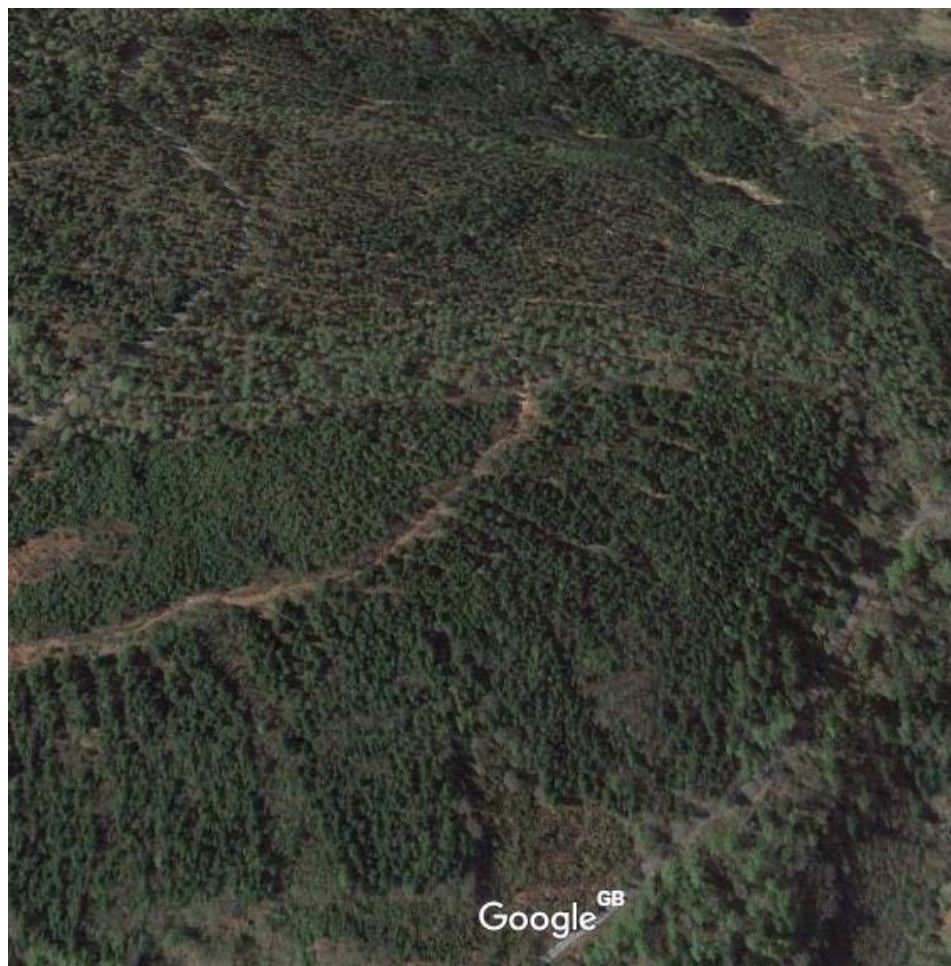
3. Aerial photograph of sample point n° 3 within the coniferous woodland habitat type.



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



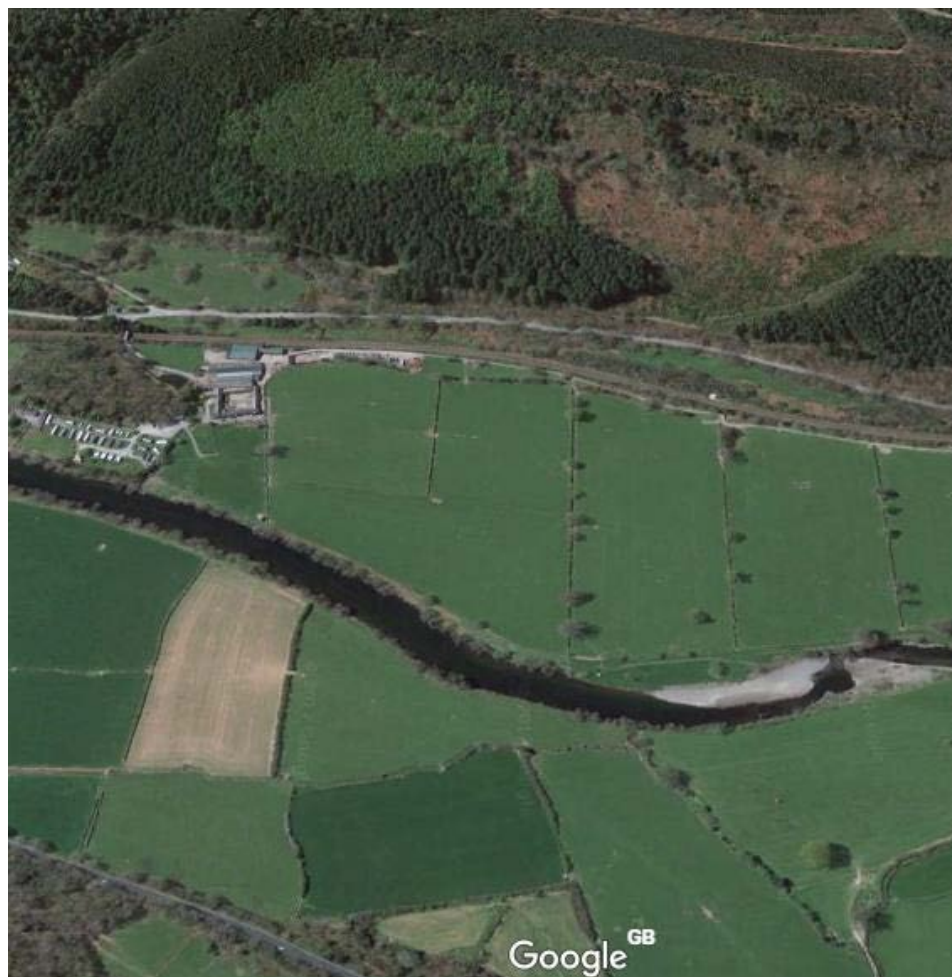
5. Aerial photograph of sample point n° 5 within the coniferous woodland habitat type.



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



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



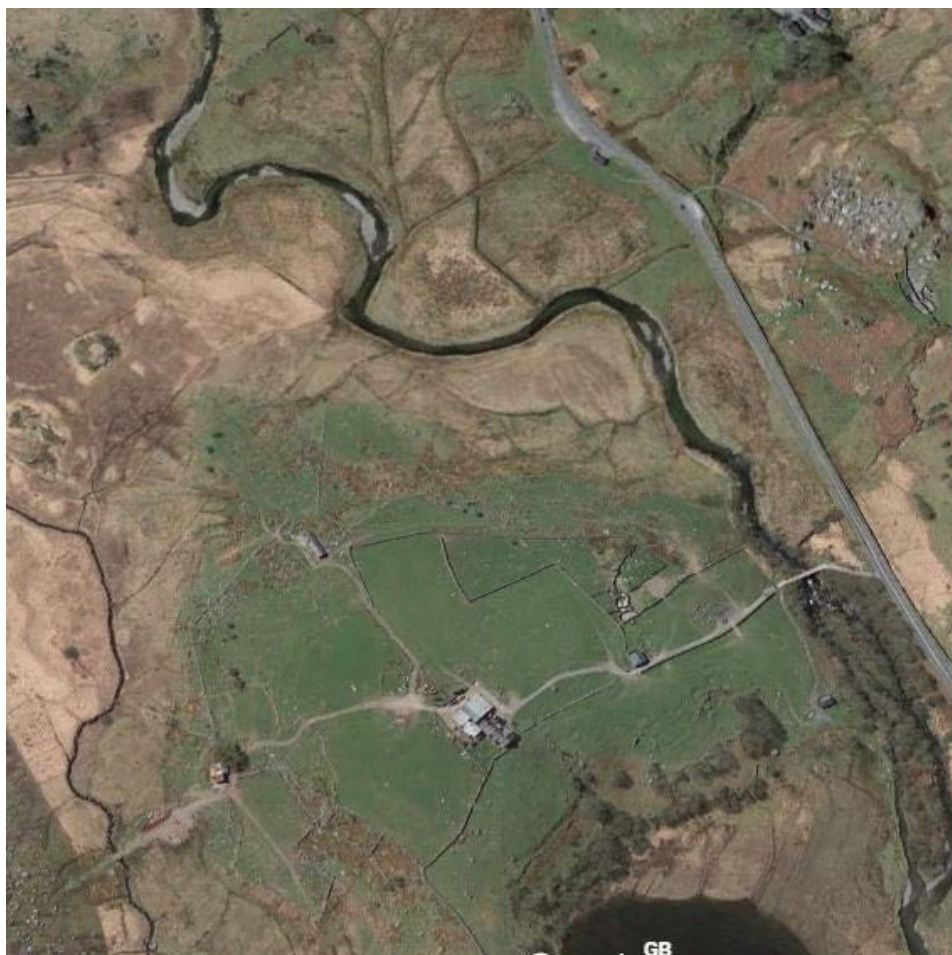
3. Aerial photograph of sample point n° 3 within the improved grassland habitat type.



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



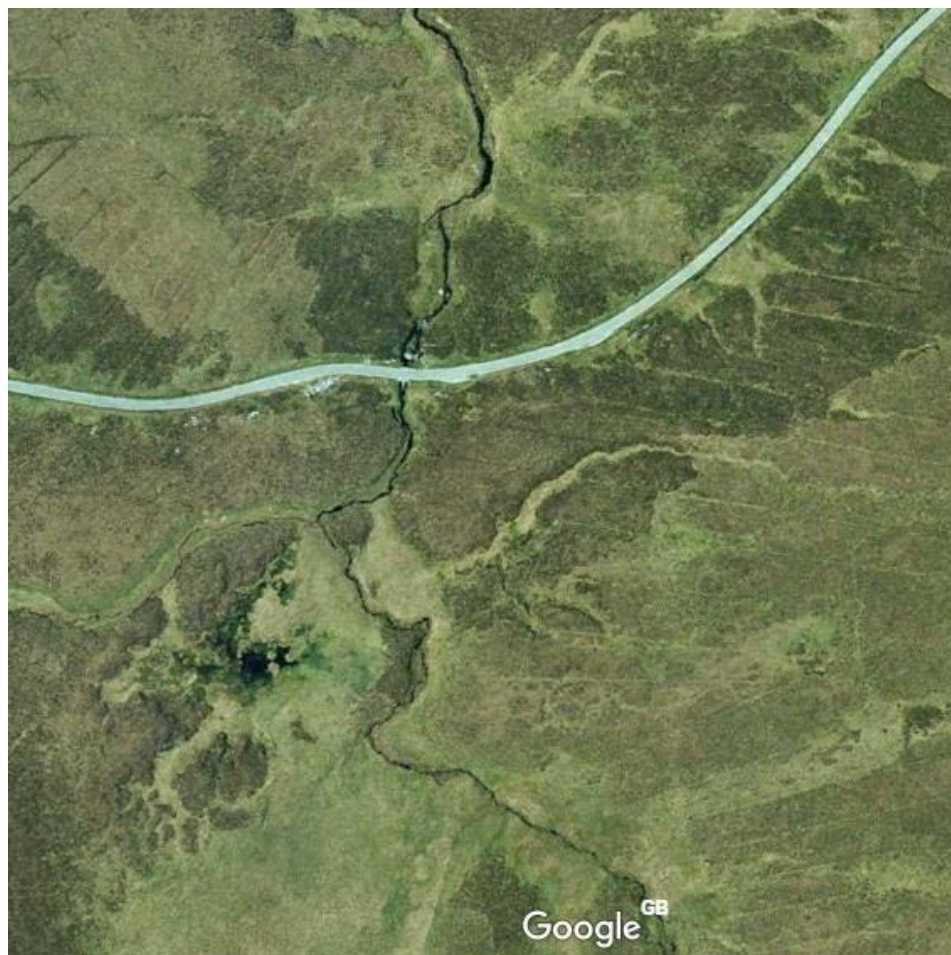
5. Aerial photograph of sample point n° 5 within the improved grassland habitat type.



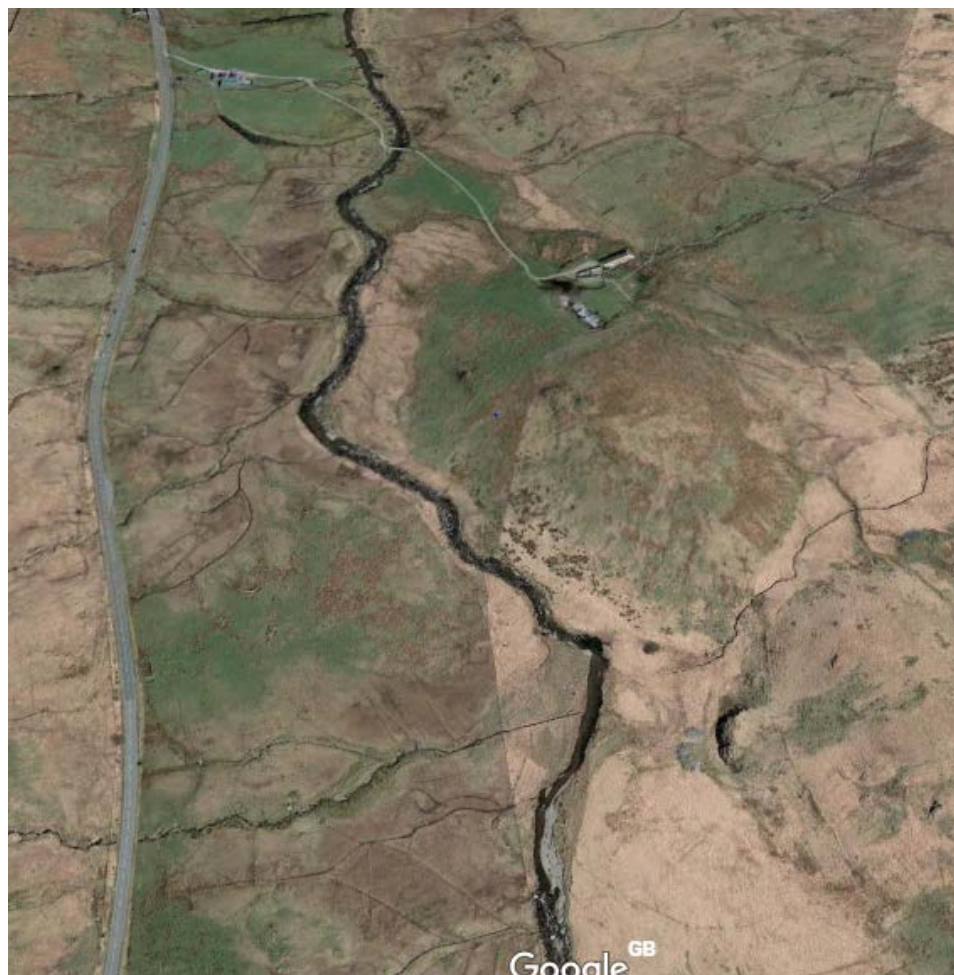
1. Aerial photograph of sample point n° 1 within the mountain, heath and bog habitat type.



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



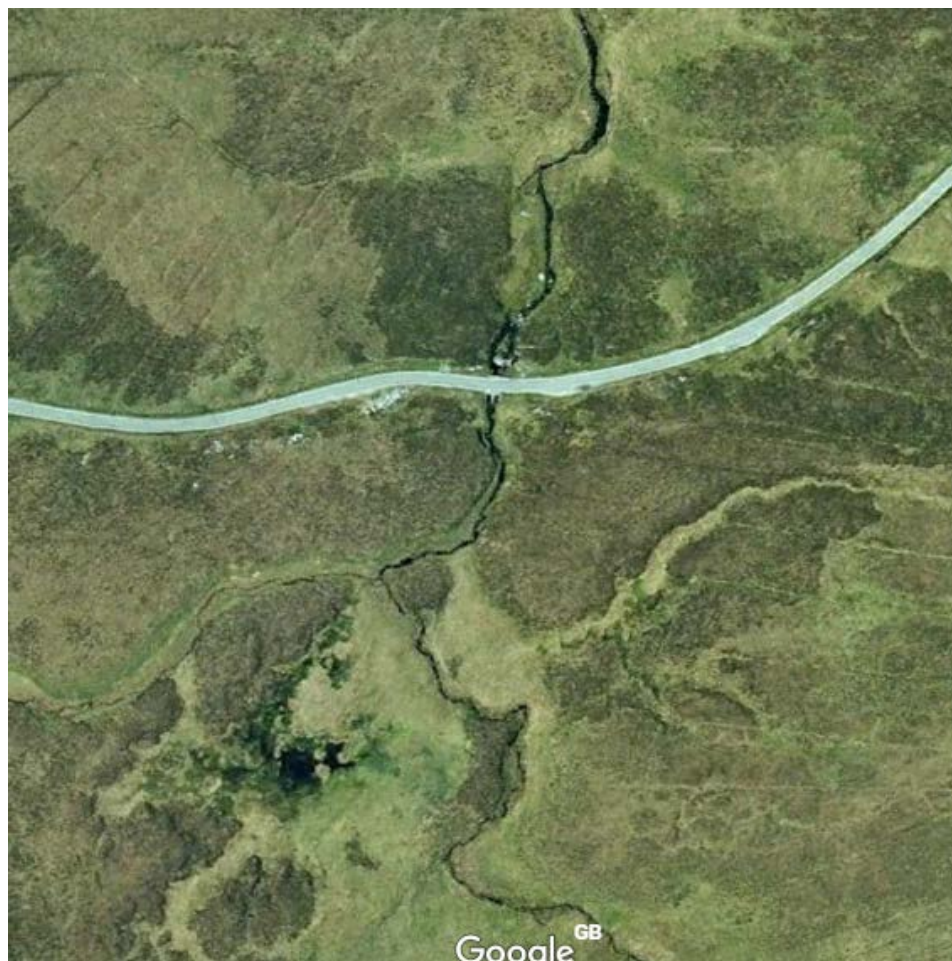
3. Aerial photograph of sample point n° 3 within the mountain, heath and bog habitat type.



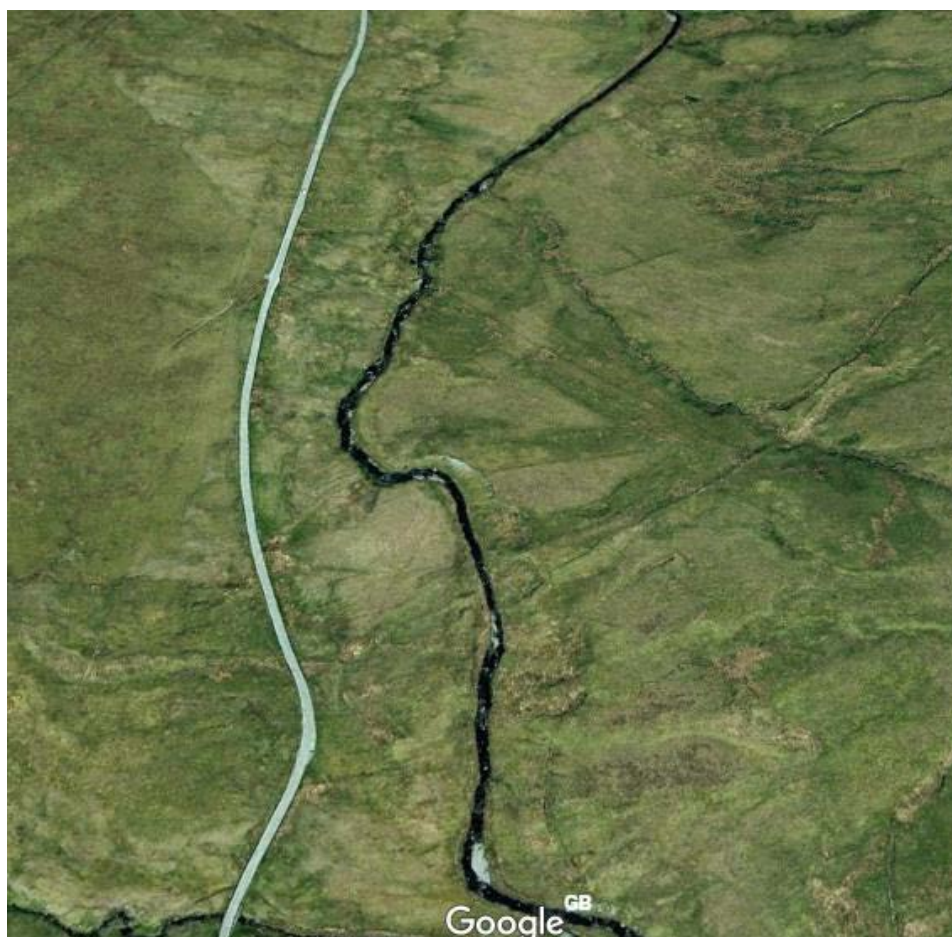
4. Aerial photograph of sample point n° 4 within the mountain, heath and bog habitat type.



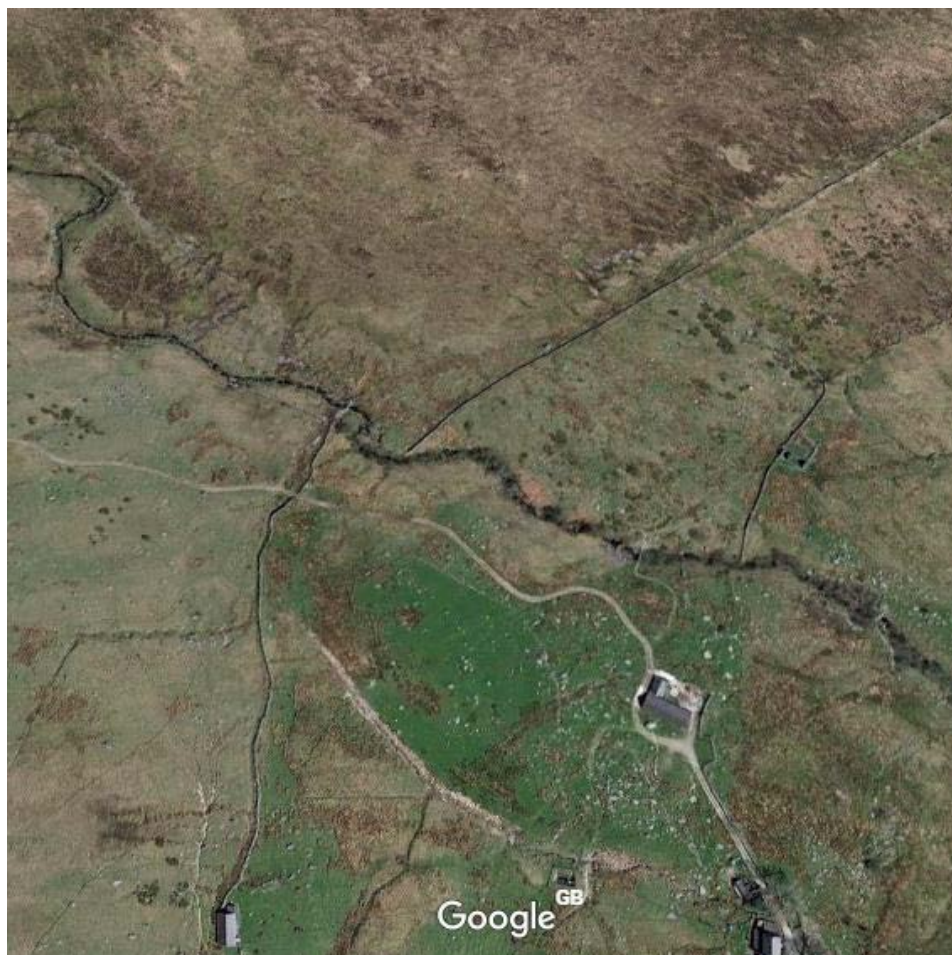
5. Aerial photograph of sample point n° 5 within the mountain, heath and bog habitat type.



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



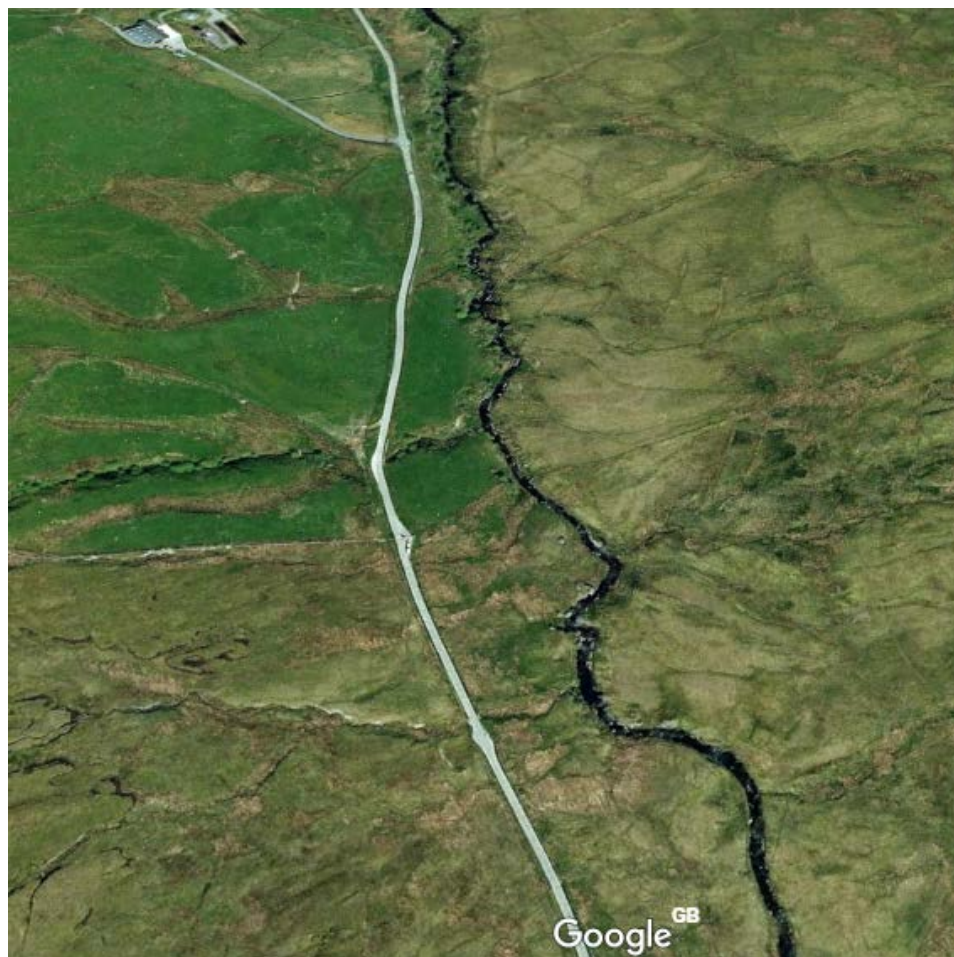
2. Aerial photograph of sample point n° 2 within the semi-natural grassland habitat type.



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



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



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



