

# *Balancing macronutrient stoichiometry to alleviate eutrophication*

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# 1 **Balancing macronutrient stoichiometry to alleviate eutrophication**

2 \*M.I. Stutter<sup>1</sup>, D. Graeber<sup>2</sup>, C.D Evans<sup>3</sup>, A. J. Wade<sup>4</sup>, P. J. A. Withers<sup>5</sup>

3 <sup>1</sup>The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, UK; <sup>2</sup>Aquatic Ecosystem Analysis, Helmholtz Centre for  
4 Environmental Research, Magdeburg, Germany; <sup>3</sup>Centre for Ecology and Hydrology, Environment Centre Wales, Bangor  
5 LL57 2UW, UK; <sup>4</sup>Dept. of Archaeology, Geography and Environmental Science, University of Reading, Reading RG6 6AB,  
6 UK; <sup>5</sup>School of Environment, Natural Resources and Geography, Bangor University, Bangor LL57 2UW, UK.

7 \*corresponding author: m.stutter@hutton.ac.uk

## 8 **Abstract**

9 Reactive nitrogen (N) and phosphorus (P) inputs to surface waters modify aquatic environments and  
10 affect public health and recreation. Until now, source control is the dominating measure of  
11 eutrophication management, and biological regulation of nutrients is largely neglected, although  
12 aquatic microbial organisms have huge potential to process nutrients. The stoichiometric ratio of  
13 organic carbon (OC) to N to P atoms should modulate heterotrophic pathways of aquatic nutrient  
14 processing, as high OC availability favours aquatic microbial processing. Such microbial processing  
15 removes N by denitrification and captures N and P as organically-complexed, less eutrophying forms.  
16 With a global data synthesis, we show that the atomic ratios of bioavailable dissolved OC to either N  
17 or P in rivers with urban and agricultural land use are often distant from a 'microbial optimum'. This  
18 OC-deficiency relative to high availabilities of N and P likely overwhelms within-river heterotrophic  
19 processing and we propose that the capability of streams and rivers to retain N and P may be  
20 improved by active stoichiometric rebalancing. This rebalancing should be done by reconnecting  
21 appropriate OC sources such as wetlands and riparian forests, many of which have become  
22 disconnected from rivers concurrent to the progress of agriculture and urbanization. However, key  
23 knowledge gaps leave questions in the safe implementation of this approach in management:  
24 Mechanistic research is required to (i) evaluate system responses to catchment inputs of dissolved  
25 OC forms and amounts relative to internal-cycling controls of dissolved OC from aquatic production

26 and particulate OC from aquatic and terrestrial sources and (ii) evaluate risk factors in anoxia-  
27 mediated P desorption with elevated OC scenarios. Still, we find this to be an approach with high  
28 potential for river management and we recommend to evaluate this stoichiometric approach for  
29 alleviating eutrophication, improving water quality and aquatic ecosystem health.

30 Keywords: Organic carbon; Nitrogen; Phosphorus; Water pollution; Stoichiometry; Microbial cycling

31

## 32 1.1. Introduction

33 Nutrient pollution is a primary cause of degraded water quality (Rockstrom et al., 2009; Dodds et al.,  
34 2009; Strockal et al., 2016). This pollution of fresh and coastal waters has large societal costs, from  
35 2.2 Billion Dollars in the US (Dodds et al. 2009) to 5-8 Billion Euros for nine OECD countries (OECD,  
36 2012), whilst the level water pollution associated with rapid agricultural and urban development in  
37 China is alarming (Cui et al., 2014; Strockal et al., 2016). Across Europe, many of the 107,000  
38 freshwater monitoring sites continuously fail to achieve regulatory targets for good ecological  
39 condition (EU, 2009). Pollution source control is usually used to improve the situation (Conley et al.,  
40 2009), but its success is hampered by many site-specific, contributory factors associated with  
41 transport time-lags, and ecological responses (Withers et al., 2014). This varying, often unknown,  
42 sensitivity of aquatic ecosystems to pollution source control reveals a lack of data and knowledge on  
43 integrative functional measures of river ecosystem health (Pinto and Maheshwari, 2011), and limits  
44 our ability to set restorative targets for ecological functions in river management.

45 The microbial nitrogen (N) removal and release as N<sub>2</sub> gas into the atmosphere (denitrification) and  
46 assimilation and incorporation of N and phosphorus (P) into organic matter are key river ecosystem  
47 services, which can regulate nutrients through biological 'self-cleansing' (von Schiller et al., 2017).  
48 The potential for microbial processes is becoming realised; in rivers, huge substrate surface areas,  
49 hyporheic exchanges (Boano et al., 2014) and biofilm structures (Battin et al., 2016), impart large  
50 potential for microbes to modify river solutes. In fact, significant inorganic N and P recycling and  
51 cumulative uptake through headwater streams to downstream river reaches has been shown for  
52 many streams (Mulholland, 2004; Ensign and Doyle, 2006; Rode et al. 2016). Significant biological  
53 uptake has also been shown for organic C in running waters, especially in the form of dissolved  
54 organic carbon (DOC) (Mineau et al., 2016). The burial and outgassing of C makes running waters  
55 essential components to consider in the global C cycle (e.g. Cole et al., 2007, Regnier et al., 2013,  
56 Marx et al., 2017).

57 Alongside studies of single element cycling rates in rivers a body of literature considers the ratios  
58 (termed stoichiometry) of key macronutrients (N and P) relative to organic carbon (OC) at landscape  
59 scales, how this relates to ecosystem processes and requirements at cellular level and how ratios  
60 may modify nutrient uptake in streams and rivers (Sinsabaugh et al. 2009; Dodds et al., 2004; Xu et  
61 al., 2015; Wymore et al. 2016). For streams and rivers with nutrient pollution, the deficiency in OC to  
62 counter N and P inputs needs to be considered, since the relative availability of substrate may  
63 control uptake of N and P into basal and higher trophic levels (Li et al., 2014; Tanetzap et al., 2014).  
64 For example, C:N in relation to organisms' requirements, highlights thresholds where growth  
65 limitation switches from one element to another (Frost et al, 2006). For example at low C:N ratios  
66 (molar C:N 1 to 5), OC-deficiency limits N sequestration, increasing downstream nitrate delivery (Xu  
67 et al., 2015; Taylor and Townsend, 2010), whereas above the C:N ratio range of most bacteria (C:N >  
68 3 - 20), only minor effects of changes in the C:N ratio on nitrate delivery are likely. Such  
69 stoichiometric control has been shown to act on stream biogeochemistry. For example, simple, labile  
70 DOC compounds have been shown to affect the processing of N (Johnson et al., 2012) and P (Oviedo-  
71 Vargas et al., 2013).

72 To assess whether the uptake and release of these elements in a given stream is limited by  
73 elemental stoichiometry for a large number streams worldwide, the described stoichiometric  
74 constraints of microbial uptake need to be combined with data on OC, N and P concentrations in  
75 streams and rivers. With this, it could be assessed whether there is potential for improving water  
76 quality in streams by altering C:N:P atomic ratios. We conceptualise the relationship between  
77 macronutrient stoichiometry and nutrient uptake as an 'elastic' capability for biota to sequester  
78 nutrients (and provide 'self-cleansing' of waters) until excessive loadings overwhelm internal  
79 processing (Fig. 1). Our conceptual illustration also refers to important interactions of altered river  
80 physical condition and biogeochemical status (Kupilas et al., 2017) that accompany nutrient  
81 stoichiometry changes. These may further reduce the ability of aquatic biota to process and retain  
82 nutrients (Fig. 1).

83 We explore existing literature to test the hypothesis that, globally, stoichiometric ratios of dissolved  
84 OC, N, P for catchment nutrient sources (soils, runoff and effluents) and receiving river waters  
85 deviate from those of biota and near-natural catchments to become 'swamped' by inputs of  
86 available N, P relative to OC, as agriculture and urbanisation intensifies. Furthermore, we consider  
87 not only total or inorganic forms, but a variable portion of inorganic and organically-complexed  
88 bioavailable forms to get a more realistic C:N:P stoichiometry in terms of biologically available  
89 molecular moieties. We focus on the dissolved fractions of OC, N and P due to a scarcity of OC, N  
90 and P concentrations and bioavailability data for the particulate fractions. However, we investigate  
91 the potential impact of leaving particulate matter out of our stoichiometric analysis in the  
92 discussion. Finally, we use the existing literature to evaluate whether bringing C:N, and C:P ratios  
93 towards the proposed microbial optimum could sufficiently stimulate an internal 'self-cleansing'  
94 regulation of N and P, governed by relative organic C availability to microbes and identify key  
95 knowledge gaps requiring to be addressed before using this approach in river management. When  
96 we refer to ratios of C:N and C:P (or C:N:P) this concerns organic C forms only.

## 97 **2. Materials and Methods**

98 We used existing literature to assess stoichiometric boundaries, within which microbial 'self-  
99 cleansing' can regulate river N and P. Firstly a database of OC, N and P forms, concentrations and  
100 ratios was assembled from global catchment nutrient sources and rivers, categorised by climate and  
101 land use (Supplementary Table S1). A second quantitative review assembled global evidence for the  
102 bioavailability of dissolved organic C, N and P (DOC, DON, DOP) (Supplementary Table S2). The  
103 methods for deriving these are summarised below and given in full in the Supplementary Materials  
104 (as Supplementary Methods).

### 105 **2.1. Catchment nutrient data sources**

106 Data from literature, available databases and primary data from the authors were gathered from  
107 soil, water and biological studies for OC, N, P compositions enabling C:N and C:P molar ratios for  
108 terrestrial and urban sources, biota and freshwater dissolved constituents. For aquatic solutes these  
109 were included where OC, N and P concentrations included basic nutrient speciation was reported to  
110 enable separation of inorganic and organic dissolved N and P for subsequent bioavailability scaling  
111 procedures (e.g. Berggren et al., 2015). Biota were included on the basis of total elemental ratios of  
112 their tissue. Data were compiled into Supplementary Table S1, where references are given. We  
113 focussed on studies reporting concentrations of dissolved OC, N and P forms in streams and rivers,  
114 since data on river particulate (or sediment composition) OC, N and P and their bioavailability were  
115 severely restricted. However, limited data from a few studies that have reported simultaneously  
116 particulate OC, N and P are briefly examined for comparison with dissolved nutrients  
117 (Supplementary Table S3 and Figure S3).

118 Dissolved OC, N, P mean concentrations were determined over multiple time point data for nine  
119 English River sites between 1997-2009, for thirty Welsh rivers 2013-14 and for sixty-five Scottish  
120 rivers in 2014. Additional sites satisfying data requirements were taken from literature: thirteen sites  
121 of the River Dee (NE Scotland; Stutter et al. 2007), twenty-eight sites from studies in Sweden and  
122 Finland (Stepanauskas et al. 2002; Berggren et al. 2007; Autio et al. 2016) and twenty-three from  
123 Peru and Brazil (Bott and Newbold, 2013; Gücker et al., 2016). To check data compatibility, we  
124 compared analytical methods for freshwater dissolved constituents (Supplementary methods).

125 For soil runoff water from subsurface drains at seventeen and eleven arable and intensive grassland  
126 fields soil water extracts (1:100 w/v) of one pasture and one riparian forest soils and effluents from  
127 two small wastewater treatment works, unpublished data from Scotland were used. Further data for  
128 OC, N and P sources came from published data in ten lowland wetlands (fens and marshes) in North  
129 America and Europe (Fellman et al. 2008; Wiegner and Seitzinger, 2004; Graeber et al. 2012).



130 Sites were categorised by major categories of climate zone and by dominant (ie >50%) land cover.  
131 World climate zones were those of the Koeppen-Geiger system ([http://koeppen-geiger.vu-](http://koeppen-geiger.vu-wien.ac.at/present.htm)  
132 [wien.ac.at/present.htm](http://koeppen-geiger.vu-wien.ac.at/present.htm)) classified by latitude and longitude. Land cover was on a catchment area  
133 basis using literature data and stated classifications or GIS data for authors' primary studies. Land  
134 cover category rules comprised: (i) agricultural catchments were classified on the basis of >50% crop  
135 + intensive grassland land cover, (ii) since urbanisation affects water chemistry disproportionately  
136 urban catchments were classified at >20% urban area, (iii) due to a large spread of data in moorland  
137 and forest land cover categories it became evident there was a need to split pristine from  
138 agriculturally-influenced moorland and forested catchments and for this a pragmatic value of >10%  
139 agriculture in the catchment for agriculturally-influenced catchments (crop + intensive grassland)  
140 was used. We gathered a total of 171 data points for river data, with 120, 28 and 33 data points  
141 from warm temperate (WT), snow (Sn) and equatorial (Eq) climate zones. For the different  
142 categories, we gathered the following sample sizes: agriculture (58WT > 11Eq > 3 Sn), forest <10%  
143 agriculture (15Sn > 7Eq > 5WT), forest >10% agriculture (5WT), moorland and mire <10% agriculture  
144 (25WT > 4Sn), moorland and mire >10% agriculture (19WT > 6Sn) and urbanized (8WT > 5Eq). The  
145 number of samples for sources comprised: agricultural soils (n = 3), agricultural source waters (13),  
146 moorland soils (3), moorland source waters (5), forest source waters (1), lowland fens (10) and  
147 effluents (9). These were compared to aquatic (10) and terrestrial biota (5).

## 148 **2.2. Nutrient bioavailability studies**

149 Metadata from 47 literature studies were used to explore evidence of the bioavailability of  
150 organically-complexed macronutrients. Studies with information on bioavailable DOC, DON and/or  
151 DOP (termed BDOC, BDON, BDOP) were recorded together with method and site metadata (for  
152 example land use, catchment size, location). Data covered aquatic ecosystems and catchment  
153 nutrient sources (soil and wetland waters, leaf litter, urban runoff and effluents), which allowed  
154 exploration of land cover as a grouping factor. We thoroughly reviewed the bioavailability data and

155 metadata described in the supplementary methods and presented in Supplementary Table 2. The  
156 data comprise 131 rows of our database, each row summarising 1-113 sites depending on whether  
157 these were separated within studies and to maximise the division of results across land cover  
158 categories.

159 Initially we tried to generate models to predict BDOC, BDON and BDOP as a function of the % of each  
160 of the land cover data in the reported catchments. This was attempted using REML mixed-model  
161 approaches within Genstat (v.8.1) building progressive factors of the study covariates of  
162 experimental method (e.g. temperature, duration and nature of inocula as variables) and landscape  
163 covariates (catchment size, land use proportions) and study and climate zone as random effects. This  
164 was desired to model the bioavailability of the OC, N and P from the wider catchment source and  
165 water quality datasets. However, none of these models were successful and instead the scaling of  
166 BDOC, BDON, BDOP for the catchment sources was done by land cover categories (as opposed to as  
167 a continuous variable of % catchment land cover). For this the groupings of dominant land cover  
168 shown in Supplementary Data Table 2 were used and weighted means and variance calculated using  
169 spatial sample number weightings. This metadata analysis facilitated incorporation of reactive forms  
170 of dissolved OC, N and P into our stoichiometric plots, but was limited to the good evidence for  
171 BDOC, but comparatively poorer evidence for BDON and BDOP, when using studies of microbial  
172 uptake associated with dark-only assays. Few studies reported simultaneous measurements of  
173 multiple dissolved macronutrients and none reported all three. Evaluation of the literature  
174 confirmed extremely limited reporting of the bioavailability of particulate OC, N, P in rivers.

### 175 **3. Calculations**

176 We calculated the *available* solute resource C:P vs C:N stoichiometry of river and catchment source  
177 waters across the globally distributed dataset. To include the realistic roles of these wider nutrient  
178 forms, we incorporated scaling factors for the bioavailability of complexed nutrient forms drawn  
179 from the reviewed microbial bioavailability studies (see for example the concept outlined first by

180 Berggren et al., 2015). The two stages of extensive quantitative metadata reviews were required for  
181 this synthesis. Firstly the global database of OC, N and P forms, concentrations and ratios  
182 (Supplementary Table S1) was used as the basis for plots with total stoichiometric ratios.  
183 Subsequently, the BDOC, BDON, BDOP data from the second quantitative review (Supplementary  
184 Table S2) were summarised according to source and river water categories. However, where data  
185 were limited (particularly for BDOP and BDON), estimated values were drawn using literature  
186 knowledge derived from the review process. Here, we chose a bioavailability scaling factor of 20%  
187 for DON for peaty soil water and leaf litter leachate, 30% for agricultural and forest soil water and  
188 40% for urban rivers and sewage effluent. For DOP, we chose scaling factors of 15% for lowland  
189 wetland waters, 30% for forest and peat soil waters and peatland rivers and 50% for sewage. The  
190 measured and estimated bioavailability scaling factors were applied to the database of  
191 concentrations of chemical forms of OC, N, P such that inorganic reactive N (nitrate, ammonium) and  
192 P (orthophosphate) were considered 100% bioavailable and dissolved organically-complexed forms  
193 were scaled according to source type or river categories. The sum of the inorganic reactive N  
194 concentrations + BDON concentrations, the sum of the inorganic reactive P concentration + BDOP  
195 concentration was then used together with the BDOC concentration to derive bioavailable  
196 stoichiometric ratios on a molar basis.

197 Within our microbial 'self-cleansing' concept (Fig. 1), we incorporate evidence of stoichiometric  
198 flexibility, whereby microbial populations regulate their elemental compositions relative to greater  
199 ranges in external freshwater resource environments. To assess the potential bacterial  
200 stoichiometric flexibility, we defined zones of stoichiometric balance or imbalance between bacteria  
201 and their food and energy sources. Recent work has shown a zone of flexibility for C:P for different  
202 strains of freshwater bacteria (Godwin and Cotner, 2015). For this Godwin & Cotner (2015) grew  
203 bacteria on substrates at C:P of  $10^2$  to  $10^5$  and C:N fixed at 3.0. They then reported the resulting  
204 cellular C:P and C:N for multiple species that we use to define our ideal stoichiometric zone (zone A,  
205 Table 1). Although the C:N range they report results from manipulation of C:P at fixed C:N in the

206 growth media the C:N response of these manipulated bacteria matched other reported ranges (Xu et  
207 al., 2015). We interpret this zone of flexibility to represent a microbial 'comfort zone' (Zone A; Table  
208 1), whereby ecosystem available resource ratios are optimal for microbial assimilation. We further  
209 defined an N-enriched zone (Zone B) and a zone where N and P are enriched relative to OC (Zone C).  
210 We consider these zones as representing river waters and catchment sources that have a strong  
211 stoichiometric imbalance presently. Finally, we defined a zone which represents OC-rich resources  
212 with N and P-deficiency (Zone D) that we see could provide opportunities for rebalancing  
213 stoichiometry by restoration of habitats of these contributing sources. Zone D represents OC-rich  
214 resources with N and P-deficiency could provide opportunities for rebalancing stoichiometry by  
215 restoration of habitats of these contributing sources.

216

## 217 **4. Results**

### 218 ***4.1. Total resource stoichiometry of catchment dissolved nutrient sources and river waters***

219 For C:N<sub>total</sub> ratios of the sources (Fig. 2a), the order followed forest source waters (40.3) > lowland  
220 fen pore waters (21.7±4.1) > moorland soils (15.6±0.5) > agricultural soils (12.7±0.9) > moorland  
221 source waters (11.3±1.3) > agricultural source waters (3.6±1.3) > effluents (0.6±0.1). These can be  
222 compared to aquatic (16.4±3.2) and terrestrial biota (32.4±11.0). For C:P<sub>total</sub> ratios the order differed  
223 with forest source waters (1343) > lowland fen pore waters (1275±521) > moorland source waters  
224 (785±181) > moorland soils (775±152) > agricultural source waters (167±41) > agricultural soils  
225 (147±31) > effluents (18±3). These can be compared to aquatic (372±108) and terrestrial biota  
226 (891±553). Agricultural and moorland soils, agricultural and moorland source waters and aquatic  
227 biota plot within or close to the microbial 'comfort-zone' (zone A, Table 1). Conversely, forest source  
228 waters, fen waters and terrestrial biota show OC enrichment relative to N, P (positioning in zone D)  
229 and effluents plot at an extreme low C:N<sub>total</sub> and C:P<sub>total</sub> ratios (zone C).

230 Total resource ratios for  $C:N_{total}$  of river waters followed the order forested ( $36.9 \pm 4.9$  1SE) >  
231 moorland ( $20.9 \pm 3.4$ ) > moorland with >10% agriculture ( $15.5 \pm 2.1$ ) > forest with >10% agriculture  
232 ( $7.3 \pm 2.0$ ) > urbanized ( $5.4 \pm 1.7$ ) > agricultural ( $4.9 \pm 0.7$ ) (Fig. 2b). The same order was found for  $C:P_{total}$   
233 with forested ( $2123 \pm 364$ ) > moorland ( $1234 \pm 205$ ) > moorland with >10% agriculture ( $1041 \pm 133$ ) >  
234 forest with >10% agriculture ( $567 \pm 192$ ) > urbanized ( $343 \pm 49$ ) > agricultural ( $267 \pm 32$ ). These were  
235 related to our four conceptual eutrophication zones (Table 1). None of the stoichiometric ratios for  
236 total resources plot in the N- and N, P- enriched eutrophication zones B or C (Fig. 2a). In snow  
237 climates C dominance was increased relative to N or P. Conversely warm temperate sites plot  
238 towards N, P enriched total ratios, but for agriculture warm temperate sites enrich N relative to OC  
239 but equatorial sites enrich P relative to C (Fig. 2a).

#### 240 **4.2 Bioavailability of DOC, DON and DOP**

241 The bioavailability of DOC (Fig. 3 and 4) may be summarised as being high in sewage effluents  
242 ( $44.8 \pm 9.8\%$  1SE) > agricultural source water ( $34.9 \pm 0.9\%$ ) > lowland fens ( $30.7 \pm 4.0\%$ ), moderate  
243 bioavailability in forest soil water ( $22.4 \pm 3.4\%$ ) > agricultural rivers ( $18.5 \pm 4.2\%$ ) > urban runoff  
244 (streams and drains;  $17.1 \pm 2.3\%$ ) > leaf litter extract ( $14.3 \pm 6.5$ ) and limited bioavailability in forested  
245 rivers ( $9.5 \pm 1.4$ ) > moorland rivers ( $4.0 \pm 0.4\%$ ) > moorland source waters ( $2.4 \pm 1.3\%$ ). For BDON data  
246 were more limited but were available showed that forested rivers ( $33.1 \pm 1.0\%$ ) > urban runoff  
247 ( $28.8 \pm 1.9\%$ ) > lowland fens ( $24.9 \pm 0.4\%$ ) > agricultural rivers ( $21.5 \pm 0.5\%$ ) > moorland rivers  
248 ( $20.8 \pm 4.5\%$ ). FOR BDOP this became limited only to agricultural rivers ( $66.0 \pm 11.0$ ) > forested rivers  
249 ( $33.1 \pm 1.0\%$ ). The numbers of samples and raw data can be seen in Supplementary Table S2. These  
250 values and the those estimated for missing values of BDON and BDOP (Fig. 3) were used to scale the  
251 bioavailable resource stoichiometry.

#### 252 **4.3. Bioavailable resource stoichiometry of catchment nutrient sources and river waters**

253 Bioavailable catchment nutrient sources (Fig. 2c) where characterized by higher N, P enrichment  
254 relative to bioavailable organic C for (effluents =  $C:N_{avail} 0.3\pm 0.1$ ;  $C:P_{avail} 10\pm 2$ ; moorland source  
255 waters =  $C:N_{avail} 0.4\pm 0.1$ ;  $C:P_{avail} 23\pm 7$ ) relative to the total C:N and C:P ratios (Fig. 2b). However, they  
256 still occupied zone C. Agricultural and moorland soils, agricultural source waters, aquatic and  
257 terrestrial biota plotted within the microbial 'comfort-zone' (respectively,  $C:N_{avail} 11.7\pm 0.3$ ,  $6.8\pm 4.3$ ,  
258  $2.4\pm 1.3$ ,  $8.8\pm 1.2$  and  $10.1\pm 1.8$  and  $C:P_{avail} 50\pm 24$ ,  $205\pm 93$ ,  $74\pm 17$ ,  $82\pm 29$  and  $70\pm 12$ ). Only forest  
259 source waters ( $C:N_{avail} 27.4$ ;  $C:P_{avail} 381$ ) and lowland fen source waters ( $C:N_{avail} 18.3\pm 4.8$ ;  $C:P_{avail}$   
260  $780\pm 357$ ) plotted in zone D, indicative of enrichment in bioavailable OC relative to N and P and a  
261 potential to rebalance stoichiometry of river waters in zone B.

262 For river water bioavailable resources (Fig. 2d)  $C:N_{avail}$  followed the order forested ( $9.0\pm 1.4$  1SE) >  
263 moorland ( $1.7\pm 0.4$ ) > urbanized ( $1.5\pm 0.4$ ) > agricultural ( $1.2\pm 0.2$ ) > moorland with >10% agriculture  
264 ( $1.0\pm 0.2$ ) > forest with >10% agriculture ( $0.9\pm 0.3$ ). For  $C:P_{avail}$  the order differed with forested  
265 ( $258\pm 44$ ) > moorland ( $85\pm 14$ ) > urbanized ( $79\pm 13$ ) > forest with >10% agriculture ( $70\pm 24$ ) > moorland  
266 with >10% agriculture ( $68\pm 9$ ) > agricultural ( $54\pm 6$ ). The pristine and agriculturally-impacted  
267 moorland, agriculturally-impacted forest, agricultural and urbanized rivers plotted closely in a zone  
268 depleted in bioavailable OC relative to P and particularly to N (zone B). Only pristine forest sites  
269 plotted within the microbial 'comfort-zone'. Pristine moorland and agricultural sites in the snow  
270 climate plotted into the microbial zone. Conversely, pristine forests in warm temperate climate were  
271 relatively enriched in N, P compared to global forests and plotted outside of the microbial zone in  
272 equatorial systems. Agriculture in equatorial, tropical climate was characterized by lowered  $C:P_{avail}$   
273 but increased  $C:N_{avail}$ .

274 Only isolated available resource compositions plotted outside of the zones (see full data depicted in  
275 Supplementary Fig. S1), being enriched in P but at microbially-favourable C:N; namely two equatorial  
276 forested rivers, temperate arable soils and aquatic macrophytes.

## 277 5. Discussion

278 Considering dissolved OC, N and P, we found many river waters and catchment sources that have a  
279 strong stoichiometric imbalance for bacteria presently (Table 1, Fig. 2). Increasing agriculture and  
280 urbanization manifests in an increasing imbalance in global freshwater macronutrient resources, as  
281 bioavailable N and P from fertilisers, sewage and urban runoff dominate over OC inputs (Zones A to  
282 B, or C; Fig. 2c,d). Due to that, river water and soil runoff data from agricultural and urbanized  
283 catchments plot in the zones of depleted OC relative to bioavailable N and P in all climate regions  
284 (Zones B and C). Concentrations of N and P are then likely exacerbated by declining microbial growth  
285 rates due to a lack of OC and river metabolisms become insufficient to cope with increasing N and P  
286 loadings. This development may eventually reach critical thresholds such as altered microbial  
287 communities (Zeglin, 2008).

288 The inclusion of nutrient bioavailability (ie Fig. 2c,d vs Fig. 2a,b) shifts stoichiometries towards lower  
289 ratios, stretches the range of C:N and particularly shifts snow climate and temperate moorland-  
290 dominated rivers to lower available ratios, than when total resource ratios are considered. The latter  
291 arises from the low C availability of humic substances that dominate OC forms in peatland rivers.  
292 Available C:N and C:P ratios varied across four orders of magnitude (Fig. 2b). At the lowest available  
293 C:N and C:P are the highly N- and P-enriched temperate agricultural rivers and the sewage source  
294 waters. Temperate moorlands and temperate and equatorial urban-influenced rivers have moderate  
295 available C:N and C:P. Soil and runoff source waters from forest and moorland systems, together  
296 with fens and marshes, have the highest available C:N and C:P, matching that of boreal and some  
297 temperate forests, where anthropogenic influences are small. However the exact position of the  
298 microbial optimum can be subject to further work and is likely related to physical constraints (see  
299 Fig. 1). The main importance is the concept behind this point and to use it as an anchor for  
300 restoration targets and to show potential ecosystem imbalances. Further work is needed to find and  
301 validate the ideal C:N:P zone for microbial nutrient uptake and retention.

302 Our consideration of the wider body of literature on dissolved OC, N, P cannot fully factor in the role  
303 of particulate nutrient processing in metabolic 'hot-spots' such as biofilm surfaces and the river bed.  
304 Biofilms represent the close coupling of heterotrophic with autotrophic systems such that the  
305 former may become independent of catchment C inputs (Graeber et al. 2018), although the bacterial  
306 utilisation of nutrients demands a dissolved state so dissolved stoichiometry remains closest to  
307 bacterial requirements. Downwelling waters will introduce dissolved and particulate OC, N, P into  
308 hyporheic zones where both DOC and POC will be influential to microbial metabolism. These are  
309 seldom separated in the literature, however, Thomas et al. (2005) indicate that ultra-fine particle  
310 POC + DOC was more bioavailable than fine particle (52-1000  $\mu\text{m}$ ) OC.

311 A limited number of studies were found where particulate C, N and P were simultaneously  
312 determined and data in Supplementary Table S3, plotted in Figure S3 (Li et al. 2005; Stutter et al.  
313 2007; Frost et al. 2009), provides a preliminary look particulate stoichiometry using the same  
314 graphical format and catchment classifications as the main paper (Fig. 2). River seston showed  
315 decreasing C:N and C:P as agriculture and urbanisation increased but remain within the microbial  
316 optimal zone when total resources are considered, similarly to total dissolved resources from the  
317 wider dataset. However, limited data exist to scale particulate resources for bioavailability. Generally  
318 OC availability may be limited as with dissolved resources; the percentage of river sediment OC  
319 respired in 24 hour microplate batch tests (Stutter et al. 2017) was 0.7 to 3.8% across a strong  
320 pollution gradient of 16 sites (no relationships with land cover). In contrast, Frost et al. (2009) and  
321 Lambert et al. (2017) suggest that catchment disturbance increases the availability of N and P  
322 associated with river particulates. Hence, stoichiometric ratios of bioavailable particulate C, N and P  
323 would likely tend towards being OC-limited relative to the microbial optimum, similar to what we  
324 have shown for dissolved nutrients. In the absence of wider datasets we propose that particulates  
325 comprise a strong signal of within-river nutrient (re)cycling, where both catchment inputs and  
326 recycled nutrients appear to shift available resource stoichiometry towards increasing relative OC



327 bioavailability compared to N and P. There remains substantial need for further simultaneous data  
328 on OC, N and P to confirm our assumed impact of river particulates on the rebalancing concept.

329 The loss and disconnection of wetlands, floodplains and riparian forest features has occurred  
330 simultaneously with agricultural intensification and urbanization across the globe (Gardner et al.,  
331 2015; Moreno-Mateos et al., 2012), hence disturbance of OC delivery has accompanied  
332 anthropogenic N, P enrichment in many catchments (Stanley et al. 2012). This consequence of land-  
333 use change is rarely considered in freshwater eutrophication (Kupilas et al., 2017), and is entirely  
334 absent from most regulatory efforts to address problems when they arise. Losing natural  
335 bioavailable C sources has amplified the impact of increased N and P loadings to freshwaters. The  
336 literature strongly suggests that adding OC to increase the low C:N and C:P ratios of the streams in  
337 zone B and C (Fig. 2) should stimulate longer-term microbial N and P sequestration (Dodds et al.,  
338 2004; Sinsabaugh et al. 2009; Taylor and Townsend, 2010; Stanley et al., 2012; Xu et al., 2015;  
339 Robbins et al., 2017; Wymore et al., 2016). Such a rebalancing of the stoichiometry could be reached  
340 by reconnecting resources rich in OC (Zone D; Fig. 2d) and may be considered especially in  
341 catchments where attempts to reduce N and P inputs have failed. Based on dissolved OC, N and P,  
342 the reconnection to catchment OC sources (e.g. riparian forest and wetland areas) (Stanley et al.,  
343 2012; Tanentzap et al., 2014) would be the ideal way to rebalance the stoichiometry. We find  
344 limited separation amongst the literature between the roles of DOC vs POC in fuelling river microbial  
345 metabolism and hence whether additional OC loading into rivers should most usefully comprise  
346 particulate or dissolved forms. Beneficial OC inputs (ie increasing available OC relative to N, P) from  
347 buried catchment-derived POC should remain small compared with catchment DOC inputs. Sources  
348 such as lowland wetlands have an optimum composition of moderately bioavailable DOC, low N and  
349 P, with the potential to promote in-stream microbial nutrient uptake (Hansen et al., 2016) (Fig. 4).  
350 Such wetlands may structurally provide good dissolved OC sources, but also particulate organic  
351 matter repositories in floodplain deposition zones (Kupilas et al., 2017), necessary for long-term

352 incorporation of assimilated N and P into buried organic matter (Kandasamy and Nagendar Nath,  
353 2016).

354 When adding catchment DOC to improve C:N:P stoichiometry, secondary effects must be kept in  
355 mind such as changing water coloration and light regimes, any impacts on public water supply, as  
356 well as transport and bioavailability of toxic substances (Stanley et al. 2012). The added OC must be  
357 in an appropriate form and amount to guard against depleting water-column oxygen, or pollutant  
358 swapping (e.g. incomplete denitrification). For example, bioavailable effluent OC would not be a  
359 good option as its input is accompanied with a large associated available N and P loads. Furthermore,  
360 we cannot turn rivers into bioreactors beyond their inherent reoxygenation constraints, which would  
361 damage their ecosystem health. Before such concepts can be developed into management  
362 recommendations appropriate risk factors should be identified for biogeochemical interactions of  
363 added bioavailable OC. One potential effect concerns P bound to redox-sensitive surfaces becoming  
364 solubilised by anoxia associated with microbial OC processing. This is likely to be location-specific  
365 and defined by risk factors such as P/Fe ratios, water velocity and sediment particle size. These  
366 would need to be derived and further work should be done to evaluate conditions where this may  
367 outweigh benefits of assimilatory P uptake on net water column P. However, generally stream  
368 waters are oxygenated and downwelling waters maintain hyporheic oxic status. If anoxia dominated  
369 in bed sediments then denitrification would be the main pathway for N removal whereas  
370 Mullholland et al. (2008) found a median nitrate loss of 16% for 72 streams across different biomes.  
371 Furthermore, if burial rates for seston particulate organic matter are driven by the presence of high  
372 concentrations of water column nutrients and algal growth then stoichiometric rebalancing via  
373 catchment DOC sources may reduce this pathway. Such processes should be subject to further  
374 investigations to identify situation-specific factors.

375 Studies of DOC uptake often use simple DOC substances (sugars, acetate, glutamic acid) due to  
376 difficulties in adding sufficiently large masses of recovered natural DOC to streams. There remains a

377 lack of inclusion of OC composition and cycling research integrated with nutrient cycling studies  
378 (Newcomer Johnson et al., 2016). Where it has been considered, OC is shown as a strong influence  
379 on N cycling (Xu et al., 2015; Taylor and Townsend, 2010; Wymore et al., 2016). Study of river C:P  
380 coupling is considerably less developed, but crucial to represent C:N:P. The hotspots - for example  
381 the stream bed, water column or hyporheic zone - of DOC uptake remain largely unknown, as in-  
382 stream compartmental uptake studies are scarce (Graeber et al. 2018). Furthermore, the importance  
383 of the different stream compartments is debated for N uptake (e.g. Johnson et al. 2015) and largely  
384 unknown for P uptake. Further works should link physico-chemical and biological aspects of linked  
385 OC, N, P cycling in rivers and question the extent of in-river processing, the dominant controls, which  
386 biotic communities are the main players and where (the river bed vs water column) and interactions  
387 with autotrophs that may decouple a reliance on catchment OC sources. Potentially, new high  
388 resolution in-situ monitoring can open up new evidence for in-river processes.

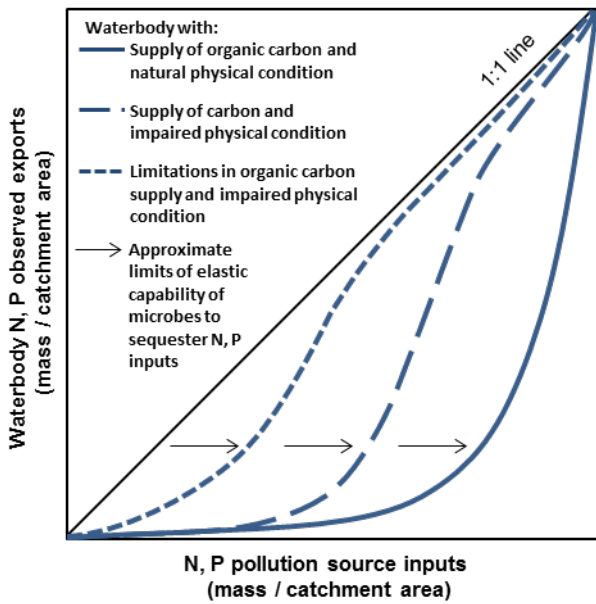
## 389 **6. Conclusions**

390 Globally, natural OC sources and their connectivity have been, and continue to be, degraded  
391 concurrent to N and P delivery. These trajectories must be reversed, and, alongside source pollution  
392 control, our approach to re-balance nutrient stoichiometry by restoring natural landscape OC-  
393 sources would be a vital concept to achieve this. Hence, addressing global eutrophication requires  
394 new concepts of river resilience involving key biotic players, integrated land management, linked  
395 element cycles, alongside source controls.

396 Our stoichiometric approach for improving aquatic ecosystem health by rebalancing OC, N, P from  
397 catchment inputs highlights the need to improve data, knowledge and practical management in  
398 areas of coupled macronutrient processing. We were able to collate dissolved nutrient data that  
399 showed globally that agricultural, urbanized and even forests and moorland with a minimal  
400 agricultural influence (<10% area) had lower C:N and C:P ratios than reference sites. When  
401 stoichiometric ratios of OC, N and P were considered in terms of bioavailable resources these

402 differed from the proposed microbial optimum and other components of biota in catchments across  
403 different global climate zones for all but pristine forests. The strongest stoichiometric imbalances  
404 were associated with urban factors (e.g. effluents) and agricultural runoff, but also highlighted the  
405 importance of bioavailability of DOC. Hence, humic waters were less able to contribute to  
406 stoichiometric rebalancing than key source waters such as riparian wetlands and forests that had a  
407 beneficial combination of DOC availability and low associated N, P load. Although supported here by  
408 literature evidence rather than direct new experimental data there is a growing, but fragmented  
409 body of literature that agrees with our concept of variable river resilience to N and P inputs and a  
410 mechanistic microbial coupling to inputs of catchment-derived bioavailable OC. We hope that the  
411 concepts we have united here will promote experimental evidence of the magnitude and controls on  
412 in-river processing and how we may manage it for benefits. However, many important aspects  
413 related to manipulations of river OC, N, P stoichiometry are still understudied and especially the lack  
414 of information on particulate forms exemplifies this. Still, we feel that our approach generates a  
415 strong incentive for the collection of data on all key macronutrients OC, N and P, including  
416 particulate and dissolved forms, their bioavailability and key river compartments for their  
417 processing.

418 By disregarding this holistic view of coupled macro-nutrients and the optimum resource  
419 stoichiometries for heterotrophs, we would leave a powerful natural regulatory process unused, a  
420 service that can help controlling nutrient leakage from agricultural and urban areas to the aquatic  
421 environment. Our study recognises and promotes the new knowledge required to better understand  
422 the applicability, including identifying risks of interactions with other biogeochemical processes such  
423 as P desorption. The proposed approaches need to be tested at the catchment scale to confirm ways  
424 to implement this in practice.

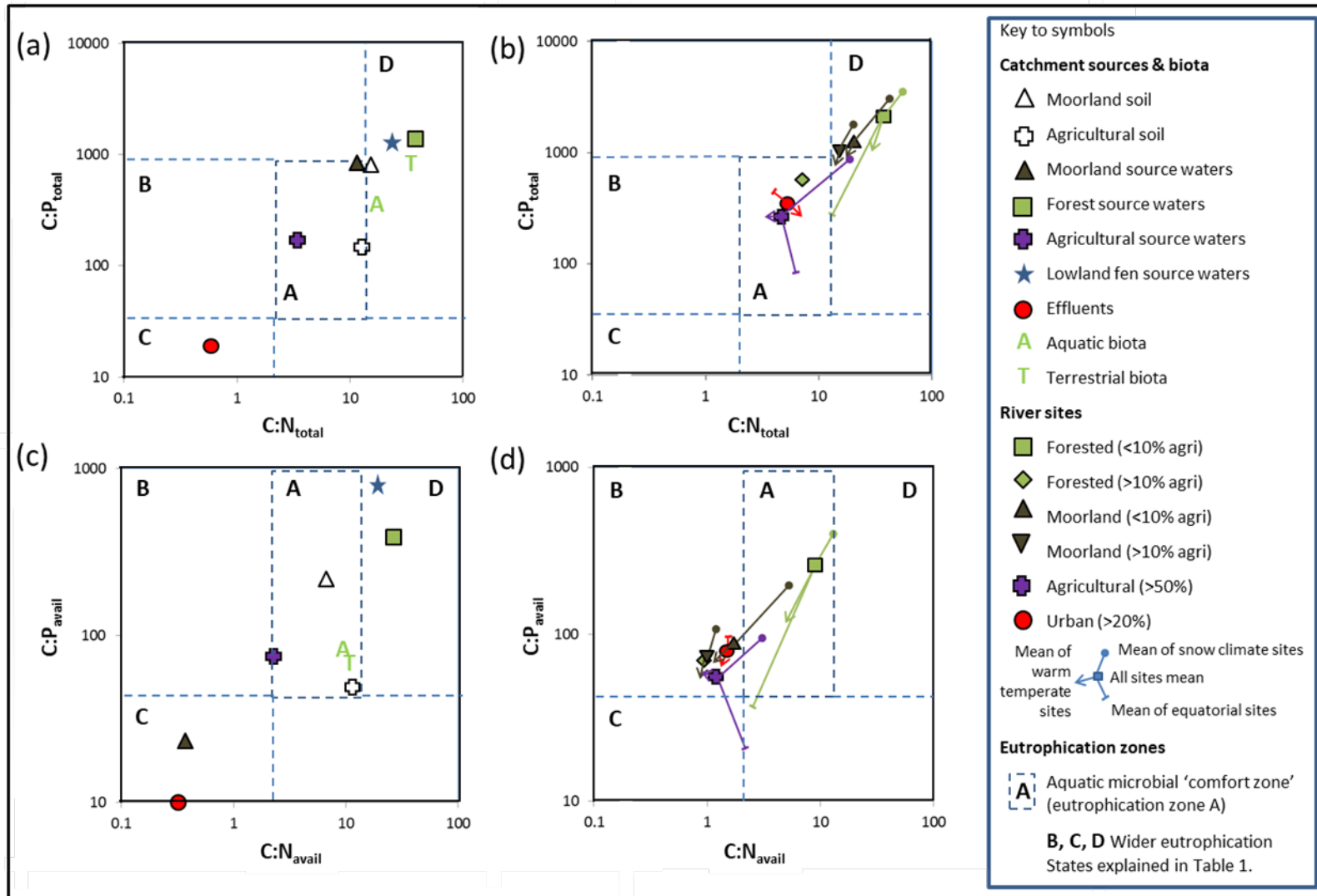


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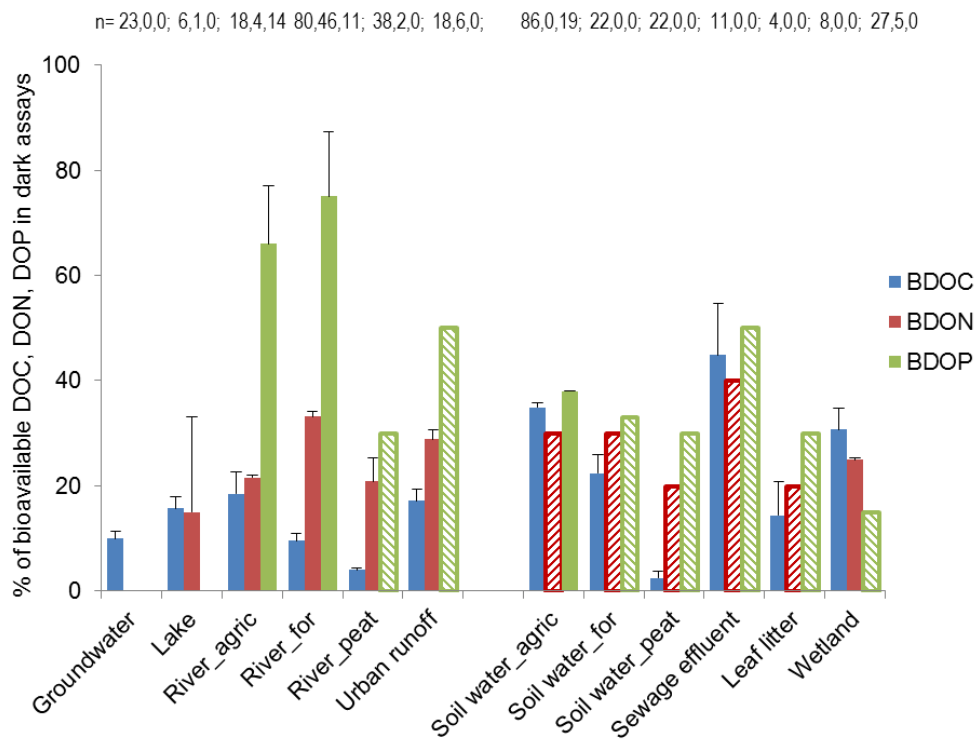
427 **Figure 1.** Conceptual model of resilience to nitrogen and phosphorus source inputs provided by river  
 428 microbial nutrient processing mediated by organic carbon. In rivers, resilience to rising nutrient  
 429 inputs is provided by physical and biochemical factors, crucially by microbial assimilation and longer-  
 430 term incorporation in organic matter or higher food-webs. Here, an adequate supply of reactive  
 431 organic C regulates the microbial assimilation of high N and P source loadings. However, continuing  
 432 microbial functioning also benefits from increased water residence time and good physical condition  
 433 which define longer term nutrient incorporation into organic matter. For example, river  
 434 straightening and the loss of floodplain features and connectivity induces earlier nutrient saturation.  
 435 The simultaneous degradation of organic C sources and physical condition leads to severely  
 436 compromised processing and retention, so that even moderate N and P inputs can directly translate  
 437 to elevated river nutrient concentrations and loads.

438

Fig. 2

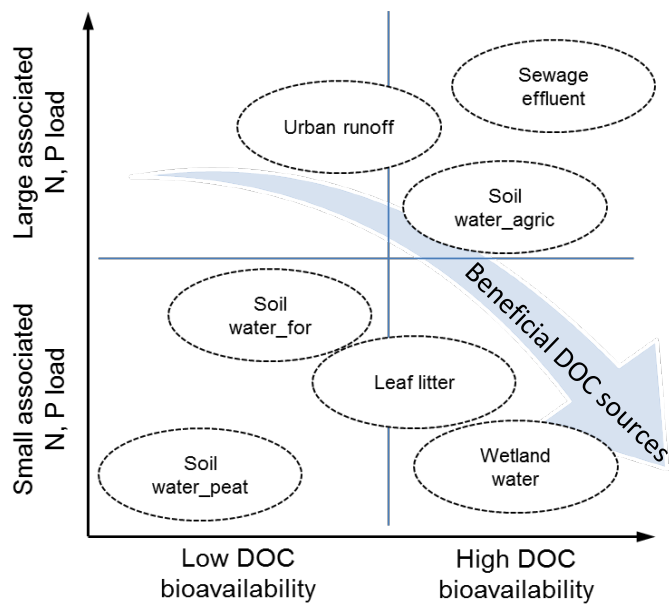


**Figure 2.** Stoichiometric plot of molar C:P against C:N shown firstly for total resources for (a) catchment nutrient sources and (b) river waters, then scaled to 'available' resources for (c) sources and (d) river waters depicting mean values according to land-cover and climate zone categories. The four eutrophication zones (A – D) are explained in Table 1. Mean data of land cover categories are represented by a central point and the means for the separated climate zones are represented by the radiating arms. A graphical representation of the raw data is given in Supplementary Figure S1. Ratios of C:N and C:P refer to organic C forms only.



**Figure 3.** Summary of weighted means and variance for bioavailable proportions of dissolved organic C, N and P taken from literature metadata evidence and used for scaling available resources. Mean values are weighted by sample number ( $\pm 1$  weighted standard error, with stated n numbers indicating total spatial sites; see Supplementary data Table 2) and developed for bioavailable DOC, DON and DOP (BDOC, BDON and BDOP) using the literature evidence in Supplementary Table 2, according to aquatic ecosystem and catchment source waters categories. Bars with hatched fill indicate an absence of data for BDON and BDOP where best-estimate values have been applied (see methods).





**Figure 4.** A conceptual matrix of catchment OC, N, P sources based on quadrants of low vs high available N, P load and low vs high DOC bioavailability (<20% and >20%, respectively) to demonstrate more and less appropriate forms of carbon for rebalancing. Wetland water and leaf litter provide optimum catchment OC inputs without additional N and P loading. Conversely peatland soil runoff has recalcitrant OC despite being low in N and P, whereas effluent has high N and P loading with concentrated available OC that may cause water column oxygen depletion.

**Table 1.** The proposed four zones of freshwater eutrophication according to the degree of stoichiometric imbalance in available C:P and C:N resources relative to a zone of microbial cellular stoichiometry optimising nutrient sequestration. These descriptions of zones relate to the plotted stoichiometric data presented in Figure 2. Ratios of C:N and C:P refer to organic C forms only.

<b>Zone</b>	<b>Available resource ratios</b>	<b>River nutrient conditions</b>	<b>Microbial nutrient processing</b>
<b>A</b>	C:N 2-11 C:P 47-994	Carbon resources balance N and P availability. Microbes adapt to utilise what is available.	Microbial flexibility zone. Nutrients added are sequestered in microbial biomass.
<b>B</b>	C:N 0.01-11 C:P 47-994	Enrichment with available N, but P deficient side of microbial flexible zone relative to available C. Biota such as algae respond to P additions.	Microbes maintain ability over some spatial/temporal scales to sequester P inputs, whilst N inputs passed down-river
<b>C</b>	C:N 0.01-11 C:P 1-47	Outside of microbial flexible zone, P and N become saturated and decoupled from C cycling.	Virtually all nutrient pollution inputs appear as elevated concentrations and N, P loads exported down-river.
<b>D</b>	C:N 2-100 C:P 994-10000, and C:N 11-100 C:P 47-10000	Abundant C-rich resources, relative to N and P, e.g. wetland or leaf litter available carbon.	Whilst microbial biomass is limited locally by lack of N, P, the beneficial C inputs drive microbial N and P sequestration potential down-river.

## References

- EU 2009. Commission Report (COM(2009) 156 final): "Report from the Commission to the European Parliament and the Council in accordance with Article 18.3 of the Water Framework Directive 2000/60/EC on programmes for monitoring of water status". [http://ec.europa.eu/environment/archives/water/implrep2007/index\\_en.htm#second](http://ec.europa.eu/environment/archives/water/implrep2007/index_en.htm#second)
- Autio I, Soenne H, Helin J, Asmala E, Hoikkala L. Effect of catchment land use and soil type on the concentration, quality, and bacterial degradation of riverine dissolved organic matter. *Ambio* 2016; 45: 331-349.
- Battin TJ, Besemer K, Bengtsson MM, Romani AM, Packmann AI. The ecology and biogeochemistry of stream biofilms. *Nat. Rev. Microbiol.* 2016; 14: 251-263.
- Berggren M, Sponseller RA, Alves Soares AR, Bergstrom A-K. Towards an ecologically meaningful view of resource stoichiometry in DOM-dominated aquatic systems. *J. Plankton. Res.* 2015; Doi: 10.1093/plankt/fbv018
- Berggren M, Laudon H, Jansson M. Landscape regulation of bacterial growth efficiency in boreal freshwaters. *Global Biogeochem. Cy.* 2007; 21: doi: 10.1029/2006GB002844
- Boano F, Harvey JW, Marion A, Packman AI, Revelli R, Ridolfi L, Wörman A. Hyporheic flow and transport processes: mechanisms, models, and biogeochemical implications. *Rev. Geophys.* 2014; 52: 603–679.
- Bott TL, Newbold JD. Ecosystem metabolism and nutrient uptake in Peruvian headwater streams. *International Review of Hydrobiology* 2013; 98: 117-131. DOI: 10.1002/iroh.201201612
- Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens KE, et al. Controlling Eutrophication: Nitrogen and Phosphorus. *Science* 2009; 323: 1014–15.
- Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, et al. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 2007; 10: 172-185.
- Cui Z, Dou Z, Chen X, Ju X, Zhang F. Managing agricultural nutrients for food security in China: past, present and future. *Agron. J.* 2014; 106: 191-8.
- Dodds WK, Marti E, Tank JL, Pontius J, Hamilton SK, Grimm NB, et al. Carbon and nitrogen stoichiometry and nitrogen cycling rates in streams. *Ecosystem Ecology* 2004; 140: 458-67.
- Dodds WK, Bouska WW, Eitzmann JL, Pilger TJ, Pitts KL, Riley AJ, et al. Eutrophication of U.S. freshwaters: analysis of potential economic damages. *Env. Sci. Technol.* 2009; 43: 12-19.

Ensign SH, Doyle MW. Nutrient spiralling in streams and river networks. *J. Geophys. Res.* 2006; 111: G04009, doi: 10.1029/2005JG000114

Fellman JB, D'Amore DV, Hood E, Boone RD. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, *Biogeochemistry* 2008; 88: 169–184, doi:10.1007/s10533-008-9203-x.

Frost PC, Benstead JP, Cross WF, Billebrand H, Larson JH, Xenopoulos MA, Yoshida T. Threshold elemental ratios of carbon and phosphorus in aquatic consumers. *Ecol. Lett.* 2006; 9: 774-9.

Frost PC, Kinsman LE, Johnston CA, Larson JH. Watershed discharge modulates relationships between landscape components and nutrient ratios in stream seston. *Ecology* 2009; 90: 1631-40.

Gardner RC, Barchiesi S, Beltrame C, Finlayson CM, Galewski T, Harrison I, et al. State of the World's Wetlands and their Services to People: A Compilation of Recent Analyses. Ramsar Briefing Note no. 7. Gland, Switzerland: Ramsar Convention Secretariat; 2015.

Godwin CM, Cotner JB. Stoichiometric flexibility in diverse aquatic heterotrophic bacteria is coupled to differences in cellular phosphorus quotas. *Front. Microbiol.* 2015; 6: doi:10.3389/fmicb.2015.00159

Graeber D, Boëchat IG, Encina-Montoya F, Esse C, Gellbrecht J, Goyenola G, Gucker B, Heinz M, Kronvang B, Meerhoff M, Nimptsch J, Pusch MT, Silva RCS, von Schiller D, Zwirnmann E. Global effects of agriculture on fluvial dissolved organic matter. *Nature Sci. Rep.* 2015; 5, doi:10.1038/srep16328

Graeber, D., Poulsen, J.R., Heinz, M., Rasmussen, J.J., Zak, D., Gücker, B., Kronvang, B., Kamjunke, N., 2018. Going with the flow: Planktonic processing of dissolved organic carbon in streams. *Sci. Tot. Environ.* 2018; 625: 519–530, [doi.org/10.1016/j.scitotenv.2017.12.285](https://doi.org/10.1016/j.scitotenv.2017.12.285)

Gücker B, Silva RCS, Graeber D, Monteiro JAF, Brookshire ENJ, Chaves RC, et al. Dissolved nutrient exports from natural and human-impacted Neotropical catchments. *Global Ecology and Biogeography* 2016; 25:378–390. doi: 10.1111/geb.12417.

Hansen AT, Dolph CL, Finlay JC. Do wetlands enhance downstream denitrification in agricultural landscapes? *Ecosphere* 2016; 7: e01516.10.1002/ecs2.1516

Johnson LT, Royer TV, Edgerton JM, Leff LG. Manipulation of the Dissolved Organic Carbon Pool in an Agricultural Stream: Responses in Microbial Community Structure, Denitrification, and Assimilatory Nitrogen Uptake. *Ecosystems* 2012; 15: 1027–1038, [doi.org/10.1007/s10021-012-9563-x](https://doi.org/10.1007/s10021-012-9563-x)

Johnson ZC, Warwick JJ, Schumer R. Nitrogen retention in the main channel and two transient storage zones during nutrient addition experiments. *Limnol. Oceanogr.* 2015; 60: 57–77. [doi.org/10.1002/lno.10006](https://doi.org/10.1002/lno.10006)

Kandasamy S, Nagender Nath B. Perspectives on the terrestrial organic matter transport and burial along the land-deep sea continuum: caveats in our understanding of biogeochemical processes and future needs. *Front. Mar. Sci.* 2016; 3: 259, doi: 10.3389/fmars.2016.00259.

Kupilas B, Hering D, Lorenz AW, Knuth C, Gücker B. Hydromorphological restoration stimulates river ecosystem metabolism. *Biogeosci.* 2017; 14: 1989-2002.

Lambert T, Bouillon S, Darchambeau F, Morana C, Roland FAE, Descy J-P, Borges AV. Effects of human land use on the terrestrial and aquatic sources of fluvial organic matter in a temperate river basin (the Meuse River, Belgium). *Biogeochem.* 2017; 136: 191-211.

Li F, Yuasa A, Muraki Y, Matsui Y. Impacts of a heavy storm of rain upon dissolved and particulate organic C, N and P in the main river of a vegetation-rich basin area in Japan. *Sci. Tot. Environ.* 2005; 345: 99-113.

Li Y, Gal G, Makler-Pick V, Waite AM, Bruce LC, Hipsey MR. Examination of the microbial loop in regulating lake nutrient stoichiometry and phytoplankton dynamics. *Biogeosci.* 2014; 11: 2939-60.

Marx, A., Dusek, J., Jankovec, J., Sanda, M., Vogel, T., van Geldern, R., Hartmann, J., Barth, J. a. C., 2017. A review of CO<sub>2</sub> and associated carbon dynamics in headwater streams: A global perspective. *Rev. Geophys.* 55, 2016RG000547, [doi.org/10.1002/2016RG000547](https://doi.org/10.1002/2016RG000547)

Mineau MM, Wollheim WM, Buffam I, Findlay SEG, Hall RO, Hotchkiss ER, Koenig LE, McDowell WH, Parr TB. Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements: DOC Uptake in Streams. *Journal of Geophysical Research: Biogeosciences* 2016; 121: 2019–2029, [doi.org/10.1002/2015JG003204](https://doi.org/10.1002/2015JG003204)

Moreno-Mateos D, Power ME, Comin FA, Yockteng R. Structural and functional loss in restored wetland ecosystems. *PLOS Biology* 2012; 10: doi:10.1371/journal.pbio.1001247.

Mulholland PJ. The importance of in-stream uptake for regulating stream concentrations and output of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. *Biogeochem.* 2004; 70: 403-26.

Mulholland PJ, Helton AM, Poole GC, Hall RO, Hamilton SK, Peterson BJ, Tank JL, Ashkenas LR, Cooper LW, Dahm CN, Dodds WK, Findlay SEG, Gregory SV, Grimm NB, Johnson SL, McDowell WH, Meyer JL, Valett HM, Webster JR, Arango CP, Beaulieu JJ, Bernot MJ, Burgin AJ, Crenshaw CL,

Johnson LT, Niederlehner BR, O'Brien JM, Potter JD, Sheibley RW, Sobota DJ, Thomas SM. Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature* 2008; 452: 202-U46-202-U46.

Newcomer Johnson TA, Kaushal SS, Mayer PM, Smith RM, Svirichi GM. Nutrient retention in restored streams and rivers: a global review and synthesis. *Water* 2016; 8: doi:10.3390/w8040116.

OECD. Agriculture and Water Quality: Monetary Costs and Benefits across the OECD Countries. Andrew Moxey, Pareto Consulting, Edinburgh, COM/TAD/CA/ENV/EPOC(2010)43/FINAL. Available at: [www.oecd.org/agriculture/water](http://www.oecd.org/agriculture/water); 2012.

Oviedo-Vargas D, Royer TV, Johnson LT. Dissolved organic carbon manipulation reveals coupled cycling of carbon, nitrogen, and phosphorus in a nitrogen-rich stream. *Limnol. Oceanogr.* 2013; 58, 1196–1206, [doi.org/10.4319/lo.2013.58.4.1196](https://doi.org/10.4319/lo.2013.58.4.1196)

Pinto U, Maheshwari BL. River health assessment in peri-urban landscapes: An application of multivariate analysis to identify the key variables. *Wat. Res.* 2011; 45: 3915-24.

Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luysaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Godd ris Y, Goossens N, Hartmann J, Heinze C, Ilyina T, Joos F, LaRowe DE, Leifeld J, Meysman FJR, Munhoven G, Raymond PA, Spahni R, Suntharalingam P, Thullner M. Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience* 2013; 6: 597–607. <https://doi.org/10.1038/ngeo1830>

Robbins CJ, King RS, Yeager AD, Walker CM, Back JA, Doyle RD, Whigham DF. Low-level addition of dissolved organic carbon increases basal ecosystem function in a boreal headwater system. *Ecosphere* 2017; 8: e01739.10.1002/ecs2.1739.

Rockstr m J, Steffen W, Noone K, Persson A, Stuart Chapin III F, Lambin EF, et al. A safe operating space for humanity. *Nature* 2009; 461: 472–5.

Rode M, Halbedel nee Angelstein S, Rehan Anis M, Borchardt D. Continuous in-stream assimilatory nitrate uptake from high-frequency sensor measurements. *Env. Sci. Technol.* 2016; 50: 5685-94.

Sinsabaugh RL, Hill BH, Follstad Shah JJ. Ecoenzymatic stoichiometry of microbial organic nutrient acquisition in soil and sediment. *Nature* 2009; 462: 795-8.

Stanley EH, Powers SM, Lottig NR, Buffam I, Crawford JT. 2012. Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? *Freshwater Biol.* 57 (suppl. 1), 26-42.

Stepanauskas R, Jorgensen NOG, Eigaard OR, Zvikas A, Tranvik LJ, Leonardson L. Summer inputs of riverine nutrients to the Baltic Sea: Bioavailability and eutrophication relevance. *Ecol. Monogr.* 2002; 72: 579-97.

Strokal M, Ma L, Bai Z, Luan S, Kroeze C, Oenema O, et al. Alarming nutrient pollution of Chinese rivers as a result of agricultural transitions. *Environ. Res. Lett.* 2016; 11: doi: 1088/1748-9326/11/2/024014.

Stutter MI, Langan SJ, Demars BOL. River sediments provide a link between catchment pressures and ecological status in a mixed land use Scottish River system. *Wat. Res.* 2007; 41: 2803-15.

Stutter MI, Cains J. Changes in aquatic microbial responses to C-substrates with stream water and sediment quality related to land use pressures. *Chemosphere* 2017; 184: 548-558.

Tanentzap AJ, Szkokan-Emilson EJ, Kielstra BW, Arts MT, Yan ND, Gunn JM. Forests fuel fish growth in freshwater deltas. *Nature Comm.* 2014; 5: doi:10.1038/ncomms5077.

Taylor PG, Townsend AR. Stoichiometric control of organic carbon-nitrate relationships from soils to the sea. *Nature* 2010; 464: 1178-81.

Thomas SA, Royer TV, Snyder EB, Davis JC. Organic carbon spiraling in an Idaho river. *Aquat. Sci.* 2005; 67: 424-433.

von Schiller D, Acuña V, Aristi I, Arroita M, Basaguren A, Bellin A, Boyero L, Butturini A, Ginebreda A, Kalogianni E, Larrañaga A, Majone B, Martínez A, Monroy S, Muñoz I, Paunović M, Pereda O, Petrovic M, Pozo J, Rodríguez-Mozaz S, Rivas D, Sabater S, Sabater F, Skoulikidis N, Solagaistua L, Vardakas L, Elosegi A. River ecosystem processes: A synthesis of approaches, criteria of use and sensitivity to environmental stressors. *Sci. Tot. Environ.* 2017; 596–597: 465–480. <https://doi.org/10.1016/j.scitotenv.2017.04.081>

Wymore AS, Coble AA, Rodriguez-Cardona B, McDowell WH. Nitrate uptake across biomes and the influence of elemental stoichiometry: A new look at LINX II. *Global Biogeochem. Cy.* 2016; 30: 1183-91.

Xu Z, Wang Y, Li H. Stoichiometric Determination of Nitrate Fate in Agricultural Ecosystems during Rainfall Events. *PLOS ONE* 2015; 10: e0122484.

Zeglin LH. Stream microbial diversity in response to environmental changes: review and synthesis of existing research. *Front. Microbiol.* 2015; 6(454): doi:10.3389/fmicb.2015.00454

**Supplementary Material** is linked to the online version of the paper.

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## Supplementary Material

### Balancing macronutrient stoichiometry to alleviate eutrophication

M.I. Stutter<sup>1</sup>, D. Graeber<sup>2</sup>, C.D Evans<sup>3</sup>, A. J. Wade<sup>4</sup>, P. J. A. Withers<sup>5</sup>

<sup>1</sup>The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, UK; <sup>2</sup>Aquatic Ecosystem Analysis, Helmholtz Centre for Environmental Research, Magdeburg, Germany; <sup>3</sup>Centre for Ecology and Hydrology, Environment Centre Wales, Bangor LL57 2UW, UK; <sup>4</sup>Dept. of Archaeology, Geography and Environmental Science, University of Reading, Reading RG6 6AB, UK; <sup>5</sup>School of Environment, Natural Resources and Geography, Bangor University, Bangor LL57 2UW, UK.

## Supplementary Methods

### Catchment nutrient stoichiometry data

Data were taken from a variety of literature and authors' primary data sources indicated in Supplementary Table 1 and described briefly in main Methods section. The UK Centre for Ecology and Hydrology led studies of lowland rivers in England (the Kennet, Lambourn and Pang tributaries to the Thames; <https://catalogue.ceh.ac.uk/documents/8e23a86b-6b54-4564-9789-23f4b4e045ea>) and the River Conwy system in Wales (<https://catalogue.ceh.ac.uk/documents/23ca75d4-9995-4dc3-aa89-51ab218cb352>) where the raw data are available.

In Scotland, the James Hutton Institute sampled on four occasions (2014) major Scottish rivers at the Harmonised Monitoring Scheme sites (locations in Ferrier et al. 2001). To assess data consistency we evaluated analytical methods for the compiled freshwater nutrient speciation datasets. River datasets are differentiated in Supplementary Table 1. Samples for Scottish and Welsh rivers were filtered to 0.45  $\mu\text{m}$  and those for English rivers to 1.2  $\mu\text{m}$ . For Welsh rivers equivalent methods are summarised at <https://catalogue.ceh.ac.uk/documents/c53a1f93-f64c-4d84-82a7-44038a394c59> and for English rivers at <https://catalogue.ceh.ac.uk/documents/8e23a86b-6b54-4564-9789-23f4b4e045ea>.

For rivers in Scotland dissolved organic carbon (DOC) was analysed following chemical (persulphate) oxidation and detection of phenolphthalein colour (Skalar San++, the Netherlands), for Welsh and English rivers as non-purgeable organic carbon following thermal oxidation and conductivity detection using a Shimadzu TOCVSH (Japan) for Welsh rivers and Shimadzu TOCsinII, then latterly Analytical Sciences Thermalox for English rivers.

For phosphorus speciation all followed the differentiation that dissolved unreactive P represented dissolved organically-complexed P (DOP), as calculated from total dissolved P (TDP) minus dissolved reactive P (DRP) by the molybdate colour reaction (approximating to orthophosphate inorganic P). For rivers in Scotland TDP and DRP were determined by automated colorimetry, for TDP incorporating heated chemical (acid persulphate) oxidation (Skalar San++). For English and Welsh rivers TDP and DRP were determined similarly by automated colorimetry (Seal AQ2), the former following heated chemical (persulphate) oxidation.

Nitrate-N and ammonium-N were determined colorimetrically, based on the reduction of  $\text{NO}_3$  to  $\text{NO}_2$  and diazotisation reaction with sulphanilamide and using a modified Berthelot reaction for  $\text{NH}_4$  using the Skalar San++ for Scottish rivers and Seal AQ2 for Welsh and English rivers (although for English rivers a change occurred in 2007 to ion chromatography for  $\text{NO}_3$ -N).

Dissolved organic nitrogen (DON) was determined by difference of the sum of inorganic N species from total dissolved N, the latter analysed following heated chemical oxidation for Scottish rivers (Skalar San++) and thermal oxidation for Welsh rivers (Shimadzu TNM-1) and English rivers (Analytical Sciences Thermalox).

Published method statements for the sources of the Scandinavian river data (Stepanuskas et al. 2002; Berggren et al. 2007; Autio et al. 2016) showed comparable methods with DOC and TDN measured by thermal oxidation on Shimadzu instruments, inorganic N by standard methods, TDP

and DRP by molybdate-reaction colorimetry respectively with and without chemical oxidation. Slight differences in pre-treatment were the use of 0.2µm filters and freeze-storing prior to analyses.

### **Development of a model for scaling bioavailability of nutrient resources**

Literature metadata was used to explore documented evidence of the bioavailability of organically-complexed macronutrient resources. Literature was searched on terms 'dissolved organic matter', 'DOM', 'DOC', 'DON', 'DOP', 'decomposition', 'biodegradability', and 'bioavailable' (and abbreviations: BDOC (bioavailable DOC), BDON, BDOP) then exploring cited and citing references from these. This resulted in forty-seven studies being evaluated from 1987 to 2016 (that half of these were in the last five years suggests this is a recent research field). Inclusion was on the basis that one of any, or combinations of BDOC, BDON and BDOP had to be recorded with method and site metadata (for example land use, catchment size, location). An insufficient number had soil metadata such as organic soil occurrence.

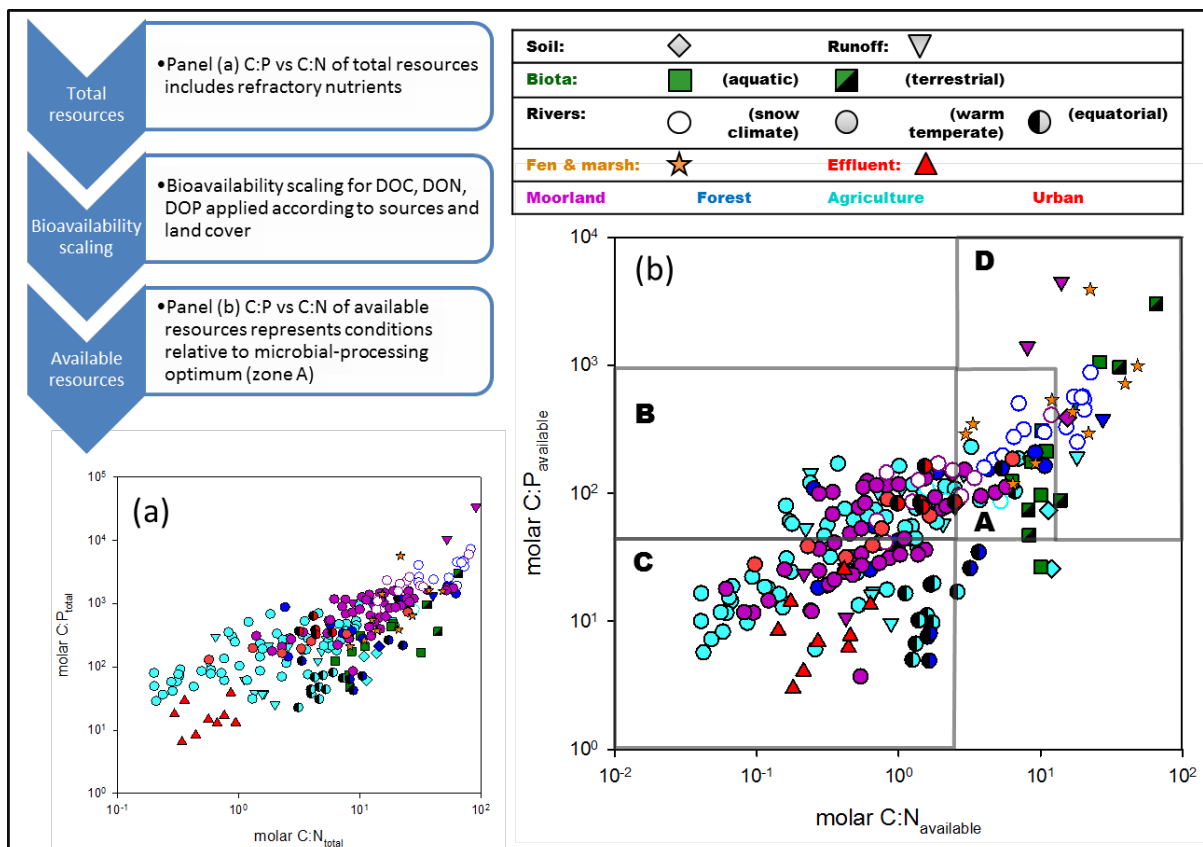
Data covered the latitudes 27-69°N and 3-46°S. Entries were compiled to single rows for either grouped data where key metadata such as land cover was not fully recorded, or individual sites to rows where full metadata was recorded; henceforth rows are termed database entries. Importantly, data were split between studies utilising dark-only assays (corresponding to microbial uptake) and (b) those reporting light and light:dark cycle assays (including algal uptake). The statistical development was limited to dark-only assays but this excluded a body of work on N and P uptake by algae that was more numerous than that reported for microbial uptake of organically-complexed N and P. Bioavailable resources were recorded in one hundred and twenty-one, fifty-four and five database entries of dark-only assays for %BDOC, %BDON and %BDOP, respectively. No studies recorded bioavailability for all three nutrients simultaneously.

The total number of spatial sites (including multiple sites reported within studies and represented by database entries) and the numbers of studies are given for water and land cover combinations in Supplementary Data Table 2. Bioavailable nutrients in seawater were excluded since this was deemed a different biogeochemical system. In terms of methods most studies derived BDOM by concentration difference, with less by bacterial or algal growth calibration and for C by respiration. Most studies used bacterial inoculum from coarsely filtered/unfiltered source waters, or sediment slurries, although few had no added inoculum, just coarse pre-filtration. Incubation temperatures (absolute range 3-25°C) were dominantly 20-25°C. One enzyme-labile DOP study used 37°C and four studies varied incubation temperatures seasonally, or specific to sites. The database entries are summarised in Supplementary Table 2.

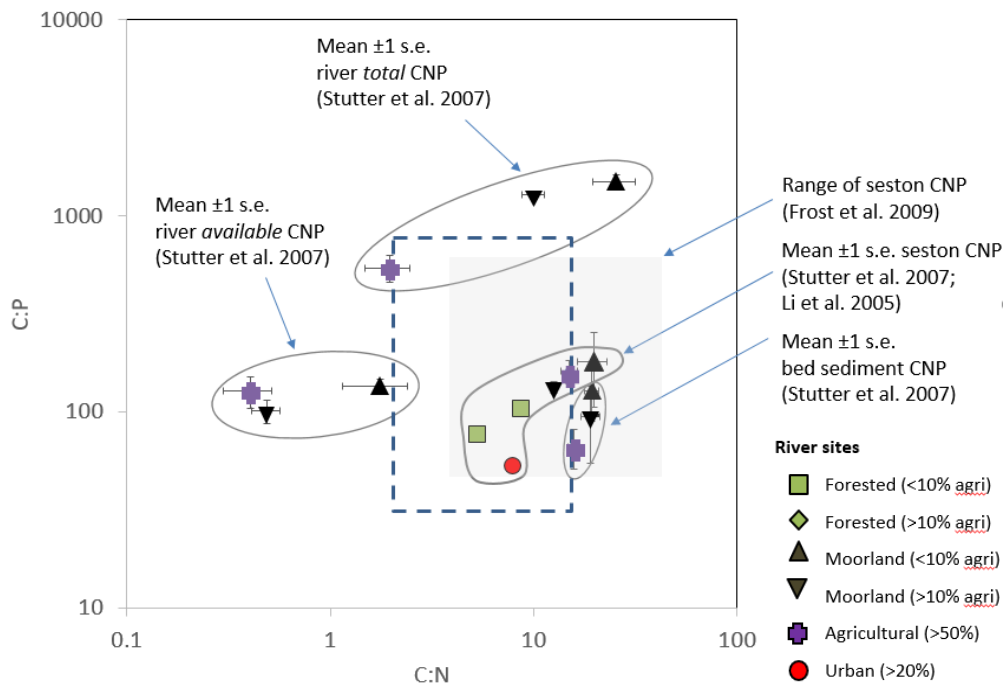
Additional methods references not in main paper:

Ferrier RC, Edwards AC, Hirst D, Littlewood IG, Watts CD, Morris R. Water quality of Scottish rivers: spatial and temporal trends. *Sci. Total Environ.* 2001; 265:327-42.

**Supplementary Figure S1.** Full stoichiometric plots of individual database data points shown firstly for total resources (panel a) then scaled to ‘available’ resources (panel b) according to land-cover categories (colours) and comparing rivers (circles; according to three climatic zones) with other catchment nutrient sources and biota. The four eutrophication zones (A – D) are explained in Table 1. Twenty-eight studies provided sample data over five land-cover/habitat categories (agricultural, n=88; fen and marsh, n=10; forest, n=34; moorland and mire, n=62; urbanized, n=22), biota (algal, bacterial and plant tissue, n=15) and according to three climate zones (boreal, n=33; warm temperate, n=165; equatorial, n=23). Ratios of C:N and C:P refer to organic C forms only.



**Supplementary Figure S3.** Comparison of total resource C:P vs C:N stoichiometry of seston (suspended particulate matter) by catchment land cover categories as used in main paper data figures. Data were not available to make comparative plots of bioavailable resources for seston. These are compared to a single study of seston, bed sediment and, for dissolved resources in the water column, total resource and available resource stoichiometry by land cover type. The data are presented along with data sources in Supplementary Table S3. Ratios of C:N and C:P refer to organic C forms only.



**Table S1. Database of catchment nutrient sources, biological components and river ecosystem C, N and P concentrations, N and P speciation, C:N and C:P values used to construct Figure 2. Ratios of C:N and C:P refer to organic C forms only.**

Component	n, spatial	Description	Country	Koppein climate zones	Land cover	Catchment (km <sup>2</sup> )	Organic C, or DOC (μmol/kg)	Total N, or TDN (μmol/kg)	% org N	Total P, or TDP (μmol/kg)	% org P	C:N total	C:P total	Obs or Mod	C:N avail	C:P avail	Ref
Soil	13	Arable soils	UK	Cfb	Agr		1865385	163071	95	30273.0	26	11.4	62	M	12.0	26	22
Soil	6	Intensive grassland soil	UK	Cfb	Agr		4258333	390083	95	29038.7	49	10.9	147	M	11.4	74	22
Soil	10	Semi-natural soil	UK	Cfb	Peat		13166667	892176	95	21268.8	71	14.8	619	M	15.4	389	22
Soil	72-75	Grassland	Global		Agr							13.8	166	M			4
Soil	47-55	Forest	Global		For							14.5	212	M			4
Soil		Elliott soil humic acid	US	Dfa	Peat		48441667	2957143	100	77419.4	100	16.4	626	M	2.5	83	26
Soil		Elliott soil fulvic acid	US	Dfa	Peat		41766667	2678571	100	38709.7	100	15.6	1079	M	2.4	144	26
Runoff	9	Agricultural drainflow (Avon-Wye)	UK	Cfb	Agr		584	1033	15	5.0	37	0.6	117	M	0.2	53	25
Runoff	17	Arable drainflow	UK	Cfb	Agr		348	540	8	1.2	43	0.6	300	M	0.2	143	23
Runoff	11	Intensive grassland drainflow	UK	Cfb	Agr		456	178	21	2.2	53	2.6	209	M	1.0	109	23
Runoff	1	Riparian forest soil extract	UK	Cfb	For		4030	100	71	3.0	33	40.3	1343	M	27.4	381	23
Runoff	1	Upland pasture soil extract	UK	Cfb	Agr		1100	60	85	2.0	0	18.3	550	M	18.1	193	23
Runoff	4	Farm track runoff (Loddington)	UK	Cfb	Agr		663	137	46	3.7	34	4.8	178	M	2.5	79	25
Runoff	9	Rural paved roads runoff (Avon-Wye)	UK	Cfb	Agr		461	341	42	11.9	32	1.4	39	M	0.7	17	25
Runoff	3	Arable surface runoff (Loddington)	UK	Cfb	Agr		818	154	50	3.0	53	5.3	273	M	2.9	142	25
Runoff	2	Arable field drain (Loddington)	UK	Cfb	Agr		753	425	19	3.4	40	1.8	220	M	0.7	103	25
Runoff	1	Farm yard runoff (Loddington)	UK	Cfb	Agr		1017	225	33	8.2	40	4.5	124	M	2.1	58	25
Runoff	3	Farm yard runoff (Avon-Wye)	UK	Cfb	Agr		1271	637	30	50.1	13	2.0	25	M	0.9	10	25
Runoff	12	Arable soil extract	UK	Cfb	Agr		490	440	11	7.8	26	1.1	63	M	0.4	26	19
Runoff	6	Intensive pasture soil extract	UK	Cfb	Agr		445	284	21	12.0	32	1.6	37	M	0.6	16	19
Runoff	12	Arable buffer soil extracts	UK	Cfb	Agr		790	487	17	20.9	29	1.6	38	M	0.6	16	19
Runoff	1	O hor podzol	UK	Cfb	Peat		3832	315	49	8.9	23	12.2	430	M	0.4	11	21
Runoff	1	AE hor podzol	UK	Cfb	Peat		4379	339	54	4.9	54	12.9	899	M	0.5	33	21
Runoff	63	Peatland springs	UK	Cfb	Peat		340	39	24	0.3	41	8.8	1026	M	0.2	24	21

Biota_terrestrial	57-77	Microbes in grassland soils	Global		Agr							8.3	47	M		8.3	47	4
Biota_terrestrial	57-63	Microbes in forest soils	Global		For							8.2	74	M		8.2	74	4
Biota_terrestrial	1	Decomposed leaf water extract	UK	Cfb	For		38200	860	69	105.0	60	44.4	364	M		13.8	88	23
Biota_terrestrial	~410	Terrestrial plants	Global									36.0	968	M				7
Biota_terrestrial	Plant litter	Global									65.2	3000	M				15	
Fen and marsh	3	Bog	US	Dfc	We		2250	60	95	1.4	58	37.4	1626	Ob, C		48.2	987	8
Fen and marsh	3	Forested wetland	US	Dfc	We		2667	55	91	1.7	60	48.6	1593	Ob, C		39.4	719	8
Fen and marsh	3	Fen	US	Dfc	We		1217	58	74	3.1	53	21.1	387	Ob, C		21.8	294	8
Fen and marsh	1	Pristine wetland	US	Cfa	We		537	49	36	2.0	98	10.9	264	Ob, CN		3.0	290	24
Fen and marsh	1	Pristine wetland	US	Cfa	We		430	52	35	2.0	98	8.3	211	Ob, CN		3.3	348	24
Fen and marsh	3	Chapel Mires	UK	Cfb	We		1473	54	68	2.3	68	27.3	645	M		16.9	429	23
Fen and marsh	1	Wetland 2	G	Cfb	We		2914	134	91	0.5	70	21.8	5690	M		22.4	3908	10
Fen and marsh	1	Wetland 3	G	Cfb	We		1426	93	81	1.0	31	15.3	1408	M		12.0	535	10
Fen and marsh	1	Wetland 21	G	Cfb	We		1305	94	48	3.5	13	13.9	375	M		6.4	118	10
Fen and marsh	1	Wetland 24	G	Cfb	We		965	76	77	1.7	11	12.7	553	M		9.2	171	10
Effluent	32	Rural domestic septic tanks	UK	Cfb	Urb		3984	4213	6	305.1	11	0.9	13	M		0.4	6	16
Effluent	1	Hungerford STW	UK	Cfb	Urb		626	2123	10	35.0	10	0.3	18	M		0.1	8	14
Effluent	1	Marlborough STW	UK	Cfb	Urb		378	1058	12	12.9	15	0.4	29	M		0.2	14	14
Effluent	1	Newbury STW	UK	Cfb	Urb		458	812	10	31.0	9	0.6	15	M		0.3	7	14
Effluent	4	Sewage	Fr	Cfb	Urb		597000	785000	18	35200.0	13	0.8	17	Ob, C		0.6	13	17
Effluent	5	Sewage	Fr	Cfb	Urb		286000	645000	7	34400.0	12	0.4	8	Ob, C		0.2	4	17
Effluent	1	Tarland STW	UK	Cfb	Urb		990	1490	57	77.0	49	0.7	13	M		0.5	8	23
Effluent	1	Laurencekirk STW	UK	Cfb	Urb		310	360	6	8.0	63	0.9	39	M		0.4	25	23
Effluent	1	Rosemaud	UK	Cfb	Urb		550	1617	25	84.8	5	0.3	6	M		0.2	3	25
Biota_aquatic	268	River vascular plants	UK	Cfb			36500000	1921429	0	74193.5	0	19.0	492	M				6
Biota_aquatic	105	River bryophytes	UK	Cfb			34083333	1307143	0	32258.1	0	26.1	1057	M				6
Biota_aquatic	3	Lake macrophytes	Sw	Dfb								8.6	176	M				12
Biota_aquatic	3	Lake benthic algae	Sw	Dfb								11.0	212	M				12
Biota_aquatic	6	Aquatic macrophytes: plant material	Ch	Cfa			32416667	1792857		74193.5	52	18.1	437	M		10.0	96	13
Biota_aquatic	6	Aquatic macrophytes: water extracts 1g:30mL)	Ch	Cfa			7141667	221429		41935.5	15	32.3	170	M		10.0	27	13
Biota_aquatic	24	Lake bacterial ranges_experimentally induced	US	Dsb								2.3-11	47-994	M		2.3-11	47-994	9
Biota_aquatic	~270	Lake seston	Global									10.2	307	M				7
Biota_aquatic	~40	Lake zooplankton	Global									6.3	124	M		6.3	124	7
Biota_aquatic		Suwannee river humic acid	US	Cfa			43858333	835714	100	4193.5	100	52.5	10459	M		8.1	1396	26
Biota_aquatic		Suwannee river fulvic acid	US	Cfa			43616667	478571	100	1290.3	100	91.1	33803	M		14.0	4508	26

River	1	River Dee main stem	UK	Cfb	Peat	1005	402	16	45	0.3	79	25.5	1587	M	1.6	142	20
River	1	River Dee main stem	UK	Cfb	Peat	1348	410	27	34	0.3	81	15.1	1243	M	0.8	115	20
River	1	River Dee main stem	UK	Cfb	Peat	1775	422	35	25	0.3	79	12.0	1394	M	0.6	124	20
River	1	River Dee main stem	UK	Cfb	Peat	2005	434	57	14	0.4	78	7.6	1165	M	0.3	102	20
River	1	River Dee, Tributary	UK	Cfb	Peat	94	465	13	64	0.3	81	36.0	1650	M	2.9	152	20
River	1	River Dee, Tributary	UK	Cfb	Peat	212	404	39	25	0.3	48	10.5	1279	M	0.5	77	20
River	1	River Dee, Tributary	UK	Cfb	For	35	388	161	7	0.4	73	2.4	887	M	0.3	109	20
River	1	River Dee, Tributary	UK	Cfb	Agr	4	144	162	2	0.5	14	0.9	302	M	0.2	60	20
River	1	River Dee, Tributary	UK	Cfb	Agr	71	413	199	7	1.2	44	2.1	338	M	0.4	76	20
River	1	River Dee, Tributary	UK	Cfb	Agr	51	304	252	4	0.6	55	1.2	516	M	0.2	120	20
River	1	River Dee, Tributary	UK	Cfb	Agr	37	229	278	3	0.6	47	0.8	354	M	0.2	80	20
River	1	River Dee, Tributary	UK	Cfb	Agr	31	835	182	18	1.2	52	4.6	707	M	1.0	163	20
River	1	River Dee, Tributary	UK	Cfb	Agr	58	529	290	9	0.8	69	1.8	688	M	0.4	171	20
River	1	A Hiraethlyn Pont Newydd	UK	Cfb	Agr	21	196	257	7	3.2	27	0.8	61	M	0.2	13	5
River	1	Afon Ddu Upper	UK	Cfb	For	7	894	17	62	0.5	24	53.7	1960	M	9.2	208	5
River	1	Carreg Ddefod	UK	Cfb	For	3	928	15	63	0.6	45	62.2	1449	M	10.7	163	5
River	1	Conwy above Serw	UK	Cfb	Peat	<1	785	15	71	0.4	43	52.8	1766	M	4.8	101	5
River	1	Cwm-clorad-isaf	UK	Cfb	Agr	1	135	9	34	0.2	51	14.4	708	M	3.7	89	5
River	1	Cwm-Llanerch	UK	Cfb	Agr	7	500	51	54	0.5	51	9.8	1003	M	3.2	230	5
River	1	Dyffryn Mymbyr outlet	UK	Cfb	Peat	364	131	10	36	0.3	23	13.2	513	M	0.4	24	5
River	1	Eidda above confluence	UK	Cfb	Peat	72	329	43	16	0.5	47	7.7	693	M	0.4	41	5
River	1	Glasgwm 1	UK	Cfb	Peat	74	226	8	37	0.2	52	27.3	1221	M	1.5	36	5
River	1	Glasgwm at Penmachno	UK	Cfb	Peat	41	208	17	13	0.3	31	12.3	655	M	0.5	34	5
River	1	Glasgwm automatic sampler	UK	Cfb	Agr	42	331	13	37	0.3	35	26.0	1204	M	7.0	186	5
River	1	Gwahallwy	UK	Cfb	Peat	1	447	81	24	0.8	18	5.5	542	M	0.3	25	5
River	1	Gyffyllog	UK	Cfb	Peat	1	198	142	10	0.6	44	1.4	310	M	0.1	18	5
River	1	Hiraethlyn automatic sampler	UK	Cfb	Peat	1	567	249	5	2.7	40	2.3	209	M	0.1	12	5
River	1	Lledr at Pont-Lledr EA25009	UK	Cfb	Peat	1	206	17	16	0.5	53	12.0	430	M	0.5	27	5
River	1	Llugwy at Betws	UK	Cfb	Agr	2	166	18	21	0.3	30	9.4	536	M	2.1	114	5
River	1	Machno at Roman Bridge EA25010	UK	Cfb	Agr	1	213	27	0	0.4	43	7.8	482	M	1.5	107	5
River	1	Merddwr at Pont Newydd EA25013	UK	Cfb	Peat	6	461	81	21	0.8	57	5.7	553	M	0.3	37	5
River	1	Nant Cwm Caseg Fraith	UK	Cfb	Peat	<1	198	11	22	0.2	42	17.7	859	M	0.9	31	5
River	1	Nant Ddu	UK	Cfb	For	<1	73	10	36	0.2	45	7.3	340	M	0.6	25	5
River	1	Nant-y-Brwyn Upper	UK	Cfb	Peat	<1	1164	20	74	0.7	53	59.4	1758	M	5.7	112	5
River	1	Nant-y-Coed	UK	Cfb	Peat	<1	601	68	28	0.8	56	8.8	734	M	0.5	49	5
River	1	Nant-y-Rhiw-felen	UK	Cfb	Peat	<1	324	172	9	1.8	56	1.9	178	M	0.1	12	5
River	1	Pennant Lodge	UK	Cfb	Agr	<1	480	320	11	5.5	38	1.5	87	M	0.3	19	5



River	1	Pont ar Gonwy	UK	Cfb	Peat	12	816	16	57	0.5	45	52.0	1628	M	3.8	95	5
River	1	Trebeddau	UK	Cfb	Peat	<1	328	96	16	0.9	63	3.4	355	M	0.2	25	5
River	1	Trib of Glasgwm 2	UK	Cfb	Peat	341	252	12	25	0.3	22	21.9	935	M	1.1	44	5
River	1	Trib of Glasgwm 4	UK	Cfb	Peat	16	190	8	34	0.3	14	25.0	751	M	1.4	33	5
River	1	Trib of Llynnau Mymbyr 1	UK	Cfb	Peat	8	74	11	32	0.3	36	6.6	223	M	0.2	12	5
River	1	Ysgubor Newydd	UK	Cfb	For	<1	587	102	23	1.3	61	5.7	467	M	0.7	55	5
River	1	Lambourn, Boxford	UK	Cfb	Agr	165	117	560	8	4.0	12	0.2	29	M	0.0	6	14
River	1	Lambourn, E Shefford	UK	Cfb	Agr	145	114	565	7	1.4	22	0.2	81	M	0.0	17	14
River	1	Lambourn, Shaw	UK	Cfb	Agr	235	129	545	8	3.5	14	0.2	36	M	0.0	7	14
River	1	Pang, Bucklebury	UK	Cfb	Agr	109	180	631	7	4.3	15	0.3	41	M	0.1	8	14
River	1	Pang, Frilsham	UK	Cfb	Agr	90	126	626	7	2.5	17	0.2	50	M	0.0	10	14
River	1	Pang, Tidmarsh	UK	Cfb	Agr	176	186	564	8	2.0	21	0.3	92	M	0.1	19	14
River	1	Dun, Hungerford	UK	Cfb	Agr	100	136	418	8	1.9	16	0.3	72	M	0.1	14	14
River	1	Kennet, Clatford	UK	Cfb	Agr	112	192	621	5	3.3	13	0.3	59	M	0.1	12	14
River	1	Kennet, Mildenhall	UK	Cfb	Agr	214	161	579	6	2.8	17	0.3	58	M	0.1	12	14
River	1	Kennet Hungerford	UK	Cfb	Agr	319	148	464	6	1.9	16	0.3	77	M	0.1	15	14
River	1	Kennet, Woolhampton	UK	Cfb	Agr	846	187	438	7	3.8	13	0.4	49	M	0.1	10	14
River	1	Kennet, Fobney	UK	Cfb	Agr	1045	240	405	8	2.7	16	0.6	90	M	0.1	18	14
River	1	River Avon	UK	Cfb	Agr	188	541	218	11	4.7	24	2.5	115	M	0.5	24	23
River	1	River Almond	UK	Cfb	Urb	395	555	424	4	2.8	25	1.3	199	M	0.2	39	23
River	1	Water of Leith	UK	Cfb	Urb	117	498	64	28	1.5	31	7.8	332	M	1.7	67	23
River	1	River Esk (Lothian)	UK	Cfb	Agr	323	331	97	15	1.8	44	3.4	183	M	0.7	41	23
River	1	River Tyne	UK	Cfb	Agr	313	296	253	9	4.8	10	1.2	62	M	0.2	12	23
River	1	River Devon	UK	Cfb	Agr	198	250	67	18	3.3	53	3.7	76	M	0.8	18	23
River	1	Allan Water	UK	Cfb	Agr	217	386	60	12	2.1	26	6.5	183	M	1.4	38	23
River	1	River Forth	UK	Cfb	Peat	584	288	18	0	0.2	67	16.1	1489	M	0.6	112	23
River	1	River Carron (Falkirk)	UK	Cfb	Agr	192	395	173	22	5.6	2	2.3	70	M	0.5	13	23
River	1	River Leven (Fife)	UK	Cfb	Agr	422	420	77	20	2.1	45	5.5	198	M	1.2	44	23
River	1	River Forth	UK	Cfb	For	444	513	60	19	1.4	46	8.6	376	M	1.0	43	23
River	1	River North Esk (Tayside)	UK	Cfb	Peat	766	294	108	13	1.1	35	2.7	274	M	0.1	15	23
River	1	River South Esk (Tayside)	UK	Cfb	Agr	564	196	130	11	0.8	61	1.5	236	M	0.3	57	23
River	1	Dighty Water	UK	Cfb	Urb	129	192	337	1	1.5	40	0.6	131	M	0.1	28	23
River	1	River Eden	UK	Cfb	Agr	319	353	489	6	4.4	19	0.7	80	M	0.1	16	23
River	1	River Tay	UK	Cfb	Peat	4991	322	45	21	0.4	67	7.2	908	M	0.3	69	23
River	1	River Earn	UK	Cfb	Agr	868	401	72	19	1.5	30	5.5	261	M	1.2	55	23
River	1	Eye Water	UK	Cfb	Agr	120	369	395	0	1.5	53	0.9	249	M	0.2	58	23
River	1	Whiteadder Water	UK	Cfb	Agr	535	789	117	0	1.6	65	6.8	479	M	1.3	117	23
River	1	River Tweed	UK	Cfb	Agr	4440	409	122	8	1.3	53	3.4	321	M	0.7	74	23
River	1	Urr Water	UK	Cfb	Agr	197	361	103	23	0.7	48	3.5	533	M	0.8	121	23
River	1	River Dee (Solway)	UK	Cfb	For	900	471	39	51	0.4	84	12.1	1146	M	1.8	145	23
River	1	River Cree	UK	Cfb	For	368	597	29	77	0.5	80	20.8	1234	M	4.3	154	23
River	1	Water of Luce	UK	Cfb	Peat		648	33	61	0.7	80	19.8	873	M	1.5	80	23
River	1	River Esk (Solway)	UK	Cfb	For	323	445	42	35	1.6	70	10.6	281	M	1.4	34	23

River	1	River Annan	UK	Cfb	Agr	950	203	77	21	0.7	55	2.6	285	M	0.6	67	23
River	1	River Nith	UK	Cfb	Agr	1115	184	79	11	0.7	48	2.3	272	M	0.5	62	23
River	1	River Clyde	UK	Cfb	Agr	1939	355	273	5	11.4	5	1.3	31	M	0.3	6	23
River	1	River Clyde	UK	Cfb	Urb	98	345	151	12	2.1	22	2.3	165	M	0.4	32	23
River	1	River Clyde	UK	Cfb	Urb	130	568	172	20	2.9	31	3.3	195	M	0.7	39	23
River	1	River Kelvin	UK	Cfb	Urb	356	442	103	17	1.2	58	4.3	376	M	0.8	90	23
River	1	White Cart Water	UK	Cfb	Urb	244	461	116	15	1.8	36	4.0	255	M	0.8	53	23
River	1	Black Cart Water	UK	Cfb	Agr	136	439	47	36	1.0	57	9.4	459	M	2.5	108	23
River	1	River Leven (Loch Lomond)	UK	Cfb	Peat	796	280	52	41	0.8	42	5.4	343	M	0.3	19	23
River	1	River Garnock	UK	Cfb	Agr	235	490	54	45	1.2	58	9.1	407	M	2.7	96	23
River	1	River Garnock	UK	Cfb	Agr	57	589	84	36	2.2	48	7.0	262	M	1.9	60	23
River	1	River Irvine	UK	Cfb	Agr	116	655	85	22	1.8	59	7.7	374	M	1.8	89	23
River	1	River Irvine	UK	Cfb	Agr	76	637	113	24	2.0	57	5.6	324	M	1.3	76	23
River	1	River Irvine	UK	Cfb	Urb	76	1064	43	47	1.5	66	25.0	733	M	6.4	185	23
River	1	River Irvine	UK	Cfb	Agr	98	481	129	16	1.7	50	3.7	284	M	0.8	65	23
River	1	River Ayr	UK	Cfb	Agr	584	387	66	19	1.8	22	5.9	216	M	1.3	44	23
River	1	River Irvine	UK	Cfb	Agr	116	327	65	17	1.5	69	5.1	217	M	1.1	54	23
River	1	River Lochy	UK	Cfb	Peat	1325	227	18	41	0.7	81	12.4	308	M	0.7	28	23
River	1	River Beaully	UK	Cfb	Peat	987	321	22	24	0.2	71	14.7	1461	M	0.7	116	23
River	1	River Carron (Wester Ross)	UK	Cfb	Peat	163	215	21	34	0.3	55	10.0	814	M	0.5	53	23
River	1	River Findhorn	UK	Cfb	Peat	787	717	26	56	0.6	52	28.0	1202	M	2.0	76	23
River	1	River Nairn	UK	Cfb	Peat	336	723	117	13	0.6	75	6.2	1180	M	0.3	99	23
River	1	River Ness	UK	Cfb	Peat	1859	365	32	27	0.3	64	11.3	1150	M	0.6	84	23
River	1	River Conon	UK	Cfb	Peat	1177	372	20	33	0.2	66	19.0	1591	M	1.0	118	23
River	1	River Shin	UK	Cfb	Peat	583	501	20	43	0.3	75	25.4	1554	M	1.5	131	23
River	1	Wick River	UK	Cfb	Peat	263	1094	44	69	0.9	55	24.6	1211	M	2.2	79	23
River	1	River Thurso	UK	Cfb	Peat	487	739	29	54	0.7	76	25.7	1079	M	1.8	93	23
River	1	River Spey	UK	Cfb	Peat	2948	276	34	39	1.0	72	8.2	285	M	0.5	23	23
River	1	River Lossie	UK	Cfb	For	271	443	173	8	3.1	84	2.6	145	M	0.3	18	23
River	1	River Dee (Grampian)	UK	Cfb	Agr	149	545	151	14	2.9	44	3.6	189	M	0.8	42	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	242	317	39	12	1.1	67	8.2	279	M	0.4	21	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	2083	349	40	44	4.1	10	8.8	86	M	0.5	4	23
River	1	River Don	UK	Cfb	Agr	1318	224	221	1	2.1	55	1.0	104	M	0.2	24	23
River	1	River Ythan	UK	Cfb	Agr	539	235	475	2	2.7	77	0.5	86	M	0.1	22	23
River	1	River Ugie	UK	Cfb	Agr	70	426	284	17	2.9	38	1.5	145	M	0.3	32	23
River	1	River Ugie	UK	Cfb	Agr	162	250	425	2	3.2	58	0.6	78	M	0.1	19	23
River	1	River Ugie	UK	Cfb	Agr	100	312	411	14	2.3	48	0.8	136	M	0.2	31	23
River	1	River Deveron	UK	Cfb	Agr	1232	282	179	0	1.5	60	1.6	194	M	0.3	46	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	50	348	24	54	0.9	74	14.7	399	M	1.0	33	23
River	1	River Irvine	UK	Cfb	Agr	44	971	37	54	1.3	70	26.1	762	M	8.5	190	23
River	1	Vargstugbäcken	Sw	Dfb	Peat	3.1	2333	29	93	0.4	58	79.7	6028	M	11.9	408	2
River	1	Stortjücken outlet	Sw	Dfb	For	1.1	1833	26	96	0.4	67	71.3	4736	M	19.9	568	2
River	1	Kalkällsmyren	Sw	Dfb	For	<1	2833	34	94	0.4	67	82.6	7319	M	22.5	878	2
River	1	Stormyrbäcken	Sw	Dfb	For	2.9	1917	26	96	0.4	62	72.5	4571	M	20.2	540	2

River	1	Övre Krycklan	Sw	Dfb	For	20	1167	21	96	0.5	86	54.4	2583	M	15.2	329	2
River	1	Kalkällsbäcken	Sw	Dfb	For	<1	2250	31	96	0.6	56	73.3	3875	M	20.4	450	2
River	1	Langbäcken	Sw	Dfb	For	7.2	1500	24	97	0.8	92	63.6	1938	M	18.2	251	2
River	1	Risbäcken	Sw	Dfb	For	0.7	1917	30	94	0.4	77	63.9	4571	M	17.2	566	2
River	1	Västrabäcken	Sw	Dfb	For	<1	1583	23	96	0.4	82	69.3	4462	M	19.5	561	2
River	1	Perhonjoki	F	Dfb	For	nd	1280	51	73	0.9	77	25.1	1470	Ob, NP	4.7	182	18
River	1	Siikajoki	F	Dfb	For	nd	1320	55	60	1.0	53	24.0	1376	Ob, NP	4.0	159	18
River	1	Oulujoki	F	Dfb	For	nd	680	22	82	0.3	63	30.9	2656	Ob, NP	7.6	315	18
River	1	Iijoki	F	Dfb	For	nd	680	34	94	0.4	69	20.0	1627	Ob, NP	5.4	197	18
River	1	Simojoki	F	Dfb	For	nd	1560	51	84	0.4	75	30.6	4088	Ob, NP	7.0	503	18
River	1	Kalixälven	Sw	Dfb	For	nd	430	14	79	0.2	83	30.7	2172	Ob, NP	6.5	274	18
River	1	Alterälven	Sw	Dfb	For	nd	1020	25	92	0.4	77	40.8	2423	Ob, NP	10.6	300	18
River	1	Vantaanjoki River	F	Dfb	Peat	13.3	752	24	80	0.4	59	31.6	1928	Ob, CN	3.4	131	1
River	1	Vantaanjoki River	F	Dfb	Peat	274	624	25	75	0.3	56	24.6	2311	Ob, CN	2.4	151	1
River	1	Vantaanjoki River	F	Dfb	For	11.9	742	58	28	0.7	31	12.9	1003	Ob, CN	1.6	109	1
River	1	Vantaanjoki River	F	Dfb	Peat	312	1562	61	58	0.6	54	25.8	2647	Ob, CN	1.9	171	1
River	1	Vantaanjoki River	F	Dfb	Peat	369	1178	70	23	0.5	50	16.8	2356	Ob, CN	0.8	145	1
River	1	Vantaanjoki River	F	Dfb	For	46.1	880	58	43	1.1	33	15.3	800	Ob, CN	2.1	87	1
River	1	Vantaanjoki River	F	Dfb	Peat	161	2316	69	65	1.3	31	33.5	1853	Ob, CN	2.8	95	1
River	1	Vantaanjoki River	F	Dfb	Peat	520	1634	76	47	0.8	49	21.5	2068	Ob, CN	1.4	126	1
River	1	Vantaanjoki River	F	Dfb	Peat	94.7	1847	88	42	1.2	38	20.9	1579	Ob, CN	1.2	86	1
River	1	Vantaanjoki River	F	Dfb	For	15.6	5517	194	68	6.7	21	28.5	821	Ob, CN	5.2	87	1
River	1	Vantaanjoki River	F	Dfb	Peat	108	890	65	40	1.1	30	13.8	817	Ob, CN	0.8	41	1
River	1	Vantaanjoki River	F	Dfb	Peat	29.6	971	69	25	0.9	40	14.1	1103	Ob, CN	0.7	61	1
River	1	Concepcion	P	Af	For		662	31	87	0.5	74	21.1	1207	Ob, C	5.3	157	3
River	1	Abejitas	P	Af	Agr		222	11	69	0.5	89	19.4	458	Ob, C	6.6	104	3
River	1	Tambopata	P	Af	For		68	21	27	0.5	61	3.3	125	Ob, C	1.0	36	3
River	1	Capitão Anselmo	B	Aw	Agr	<10	116	23	56	1.6	82	5.0	74	M	1.7	19	11
River	1	Carandai	B	Aw	Agr	<10	148	25	45	1.8	63	6.0	82	M	1.8	20	11
River	1	Mexerica	B	Aw	Agr	<10	118	16	60	1.8	75	7.3	67	M	2.6	17	11
River	1	Nelson	B	Aw	Agr	<10	61	15	71	1.6	68	4.0	38	M	1.7	9	11
River	1	São Caetano	B	Aw	Agr	<10	166	39	35	2.4	63	4.2	68	M	1.1	17	11
River	1	Aguas Santas	B	Aw	For	<10	72	9	72	1.1	63	8.3	64	M	1.6	8	11
River	1	Arenoso	B	Aw	For	<10	361	21	79	1.4	93	17.3	267	M	3.7	35	11
River	1	Complexo Cafezinho	B	Aw	For	<10	104	10	55	1.5	42	10.5	72	M	1.7	8	11
River	1	Correias	B	Aw	For	<1	111	13	69	2.6	54	8.8	43	M	1.6	5	11
River	1	Mangue	B	Aw	For	<10	247	11	43	1.1	63	22.8	219	M	3.2	26	11
River	1	Alves Melo	B	Aw	Agr	<10	59	13	58	1.2	53	4.6	48	M	1.6	11	11
River	1	Capoeirinha	B	Aw	Agr	<10	50	16	68	2.2	40	3.1	23	M	1.2	5	11
River	1	Darcy	B	Aw	Agr	<10	77	20	58	1.7	50	4.0	44	M	1.4	10	11
River	1	Oficina de Agosto	B	Aw	Agr	<10	70	13	54	1.6	41	5.3	44	M	1.7	10	11
River	1	Sossego	B	Aw	Agr	<10	59	13	43	1.9	36	4.6	31	M	1.3	7	11
River	1	C. Palmital	B	Aw	Urb	<10	828	139	83	2.4	60	5.9	351	M	2.5	86	11
River	1	C. Santo Antonio	B	Aw	Urb	11.9	945	220	68	2.4	43	4.3	391	M	1.4	84	11
River	1	Cel. Xavier Chaves	B	Aw	Urb	<10	1219	295	76	1.9	66	4.1	641	M	1.5	163	11
River	1	Prados	B	Aw	Urb	<10	1058	336	64	2.9	49	3.1	369	M	1.0	83	11

River	1	Ritápolis	B	Aw	Urb	<10	927	213	70	2.8	58	4.3	326	M	1.5	78	11
<p>Countries: B, Brazil; F, Finland; Sw, Sweden; UK, United Kingdom; US, United States; Ch, China; Fr, France; P, Peru; G, Germany.  World Climate Zones: Derived from the lat, long position data available at: <a href="http://koeppen-geiger.vu-wien.ac.at/present.htm">http://koeppen-geiger.vu-wien.ac.at/present.htm</a>  Land Use: For, Forestry; Agr, Agriculture; Wet, Wetland/peatland; Ur, Urban; Peat, Peatland; nd, Not determined.  n denotes number of samples in the format n, spatial samples  Mod vs Obs: denotes whether modelled (mod), or observed (obs) data were used in the scaling of bioavailability of organic C, N and P resources to transfer from total to available resource stoichiometry. Observed data refers to reported evidence of bioavailability for that sample (indicated for components C, N or P). Modelled data refers to that derived from the database in Supporting Table 2 and Extended Data Figure 1.</p>																	

- 1 Autio et al. *Ambio* 45, 331-349, 2016
- 2 Berggren et al. *Global Biogeochem. Cycles* 21, doi: 10.1029/2006GB002844, 2007
- 3 Bott and Newbold. *Internat. Rev. Hydrobiology*. 98, 117-131, 2013.
- 4 Cleveland & Liptzin. *Biogeochem.* 85, 235-252, 2007.  
Cooper, D.; Evans, C.; Norris, D.; Burden, A.; Lawler, A. (2013). Conwy catchment - spatial water chemistry dataset. NERC Environmental Information Data Centre.  
https://doi.org/10.5285/c53a1f93-f64c-4d84-82a7-44038a394c59
- 5 Demars & Edwards. *Freshwater Biology* 52, 2073-2086, 2007.
- 7 Elser et al. *Nature* 408, 578-579, 2000.
- 8 Fellman et al. *Biogeochemistry*, doi:10.1007/s10533-008-9203-x, 2008.
- 9 Godwin & Cotner. *Frontiers in Microbiol.* Doi: 10.3389/fmicb.2015.00159
- 10 Graeber et al. *Science Of The Total Environment* 438 (2012): 435–46. doi:10.1016/j.scitotenv.2012.08.087.
- 11 Gücker et al. *Sci. Tot. Environ.* 550, 785-792, 2016.
- 12 Kahlert, M. C:N:P ratios of freshwater benthic algae. *Arch. Hydrobiol.* 51, 105-114, 1998.
- 13 Liu et al. *Sci. Tot. Environ.* 543, 746-756, 2016
- 14 Neal et al. *Hydrol. Process.* 26, 949-960, 2012.
- 15 Reich & Oleskyn. *PNAS* 101, 11001-11006, 2004.
- 16 Richards et al. (2016) *Science of the Total Environment*, 542, 854-863.
- 17 Servais et al. *Wat. Res.* 33, 3521-3531, 1999
- 18 Stepanauskas et al. *Ecol. Monographs* 72, 579-597, 2002.
- 19 Stutter & Richards. *JEQ* 41, 400-409, 2012.
- 20 Stutter et al. 2007. *Water Research*, 41: 2803-2815.
- 21 Stutter et al. *Biogeosciences* 9, 2159-2175, 2012.

- 22 Stutter et al. *Geoderma*, 257-258, 29-39, 2015.
- 23 Stutter et al. Unpubl. data
- 24 Wiegner & Seitzinger. *Limnol. Oceanogr.* 49, 1703-1712, 2004.
- 25 Withers et al. *Journal of Environmental Quality* 38, 1998-2011, 2009.
- 26 [www.humicsubstances.org](http://www.humicsubstances.org)

**Table S2. Metadatabase of literature evidence on the bioavailability of dissolved organic carbon (BDOC), nitrogen (BDON) and phosphorus (BDOP) in freshwater aquatic samples.**

Category	Country	Land use	Size	n	BDOC	BDON	BDOP	Incubation time	Temperature	Methods	Koepfen climate zones	Ref	
(a) Dark only incubations													
(i) Groundwaters													
Gw	US	nd	nd	14; 1	5				nd	20	b, f, h, p	Cfa	26
Gw	US	nd	nd	8; 1	15				nd	20	b, f, h, p	Cfa	26
Gw	US	nd	nd		8				nd	nd	nd	Cfa	34
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					9.9 $\pm 1.5$ ; n=23 (2)	nd	nd						
(ii) Lakes													
L	Au	Agr	nd	2; nd	18	(15-21)			28	20	a, f, h, p	Cfa	6
L	Au	Agr	nd	3; nd	16	(5-27)			28	20	a, f, h, p	Cfa	6
L	US	For,Wet	3.6	1; 12	9		15		30	20	a, f, h, p	Dfb	16
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					15.7 $\pm 2.2$ ; n=6 (2)	15.0 $\pm 18$ ; n=1 (1)	nd						
(iii) leaf litter													
Le	US	Forest throughfall		1; 4	19				42	35	a, f, i, p	Cfb	25
Le	G	Spruce litter		1; 1	56				42	35	a, f, i, p	Cfb	25
Le	UK	For	nd	1; 1	10	(3-18)			1	20	c, f, n, r	Cfb	39
Le	Cz	For	nd	1; 3	17	(13-23)			42	20	a, f, i/l, p	Cfb	41
Le	US	For	nd	4; nd	3				nd	20	a, f, j, r	Cfa	47
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					14.3 $\pm 6.5$ ; n=8 (4)	nd	nd						
(iv) Rivers; agricultural													

R	F	For(39),Agr(50)	12	1; 1	4					30	3	a, f, i, p	Dfb	4
R	F	For(39),Agr(50)	12	1; 1	13		68			30	15	a, f, k, p	Dfb	4
R	F	For(42),Agr(43)	46	1; 2	5		48			30	15	a, f, k, p	Dfb	4
R	F	For(39),Agr(49)	16	1; 6	0		20			30	15	a, f, k, p	Dfb	4
R	Au	Agr(90), Ur(10)	nd	1; nd	39					28	20	a, f, h, p	Cfa	6
R	Au	Agr, Urb	nd	5; nd	24	(9-38)				28	20	a, f, h, p	Cfa	6
R	US	For(23),Agr (74)	0.7	1; 1	26					0.05	20	b, f, j, p	Cfa	8
R	US	For(23),Agr (74)	1.7	1; 1	31					0.05	20	b, f, j, p	Cfa	8
R	Br	Agr, For	nd	1; 2	31					10	20	a, f, h, p	Cfa	18
R	US	For(23),Agr (74)	7.2	1; 12	13	(2-37)				1.2	20	b, f, h, p	Cfa	26
R	Au	For(27),Agr(85),Urb(6)	119035	1; 1	3		20			14	25	a, f, j, p	Csa	29
R	Au	For(22),Agr(67),Urb(25)	149	1; 1	13		44			14	25	a, f, j, p	Csa	29
R	US	nd	nd	14; 2				66	(0-100)	0.25	37	a, f, j, o, p	Cfa	43
R	US	For(36),Agr(45),Wet(17),Ur(1)	479	1; 1	3		1			6	25	a, f, j, p	Cfa	46
R	US	For(26),Agr(55),Wet(14),Ur(2)	917	1; 1	2		22			6	25	a, f, j, p	Cfa	46
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					18.5 $\pm 4.2$ ; n=18 (7)	21.5 $\pm 0.4$ ; n=4 (2)	66.0 $\pm 11.0$ ; n=14 (1)							
(v) Rivers; forested														
R	Br	For(100)	50000 0	1; 1	12					4	25	a, f, j, p	Af	1
R	Br	For(100)	71500 0	1; 1	12					3	25	a, f, j, p	Af	1
R	F	For(46),Agr(19),Wet(3),Ur(10)	2046	1; 4	11		10			18	4-18a	a, f, h, p	Dfb	3
R	F	For(36),Agr(25),Wet(19),Ur(5)	4923	1; 4	9		22			18	4-18a	a, f, h, p	Dfc	3
R	F	For(89),Agr(0)	13	1; 1	4					30	3	a, f, i, p	Dfb	4
R	F	For(71),Agr(4)	274	1; 1	11					30	3	a, f, i, p	Dfb	4
R	F	For(67),Agr(13)	312	1; 1	4					30	3	a, f, i, p	Dfb	4
R	F	For(55),Agr(23)	369	1; 1	9					30	3	a, f, i, p	Dfb	4
R	F	For(47),Agr(23)	514	1; 1	5					30	3	a, f, i, p	Dfb	4
R	F	For(62),Agr(17)	816	1; 1	3					30	3	a, f, i, p	Dfb	4
R	F	For(89),Agr(0)	13	1; 1	12		17			30	15	a, f, k, p	Dfb	4
R	F	For(71),Agr(4)	274	1; 1	3		23			30	15	a, f, k, p	Dfb	4

R	F	For(67),Agr(13)	312	1; 1	6		23			30	15	a, f, k, p	Dfb	4	
R	F	For(55),Agr(23)	369	1; 1	8		89			30	15	a, f, k, p	Dfb	4	
R	F	For(74),Agr(8)	161	1; 3	7		18			30	15	a, f, k, p	Dfb	4	
R	F	For(60),Agr(19)	520	1; 4	2		29			30	15	a, f, k, p	Dfb	4	
R	F	For(51),Agr(18)	95	1; 5	2		46			30	15	a, f, k, p	Dfb	4	
R	F	For(39),Agr(31)	108	1; 7	8		61			30	15	a, f, k, p	Dfb	4	
R	F	For(46),Agr(35)	30	1; 8	8		92			30	15	a, f, k, p	Dfb	4	
R	US	For(100)	5	1;9	15					40	25	a, f, h, p	Dfc	5	
R	US	For(100)	6	1;9	5					40	25	a, f, h, p	Dfc	5	
R	US	For(100)	10	1;9	35					40	25	a, f, h, p	Dfc	5	
R	US	For(100)	42	1;9	15					40	25	a, f, h, p	Dfc	5	
R	Sw	For(39-100),Wet	0.1-20	9; nd	4.4	(4-8)				11	20	a, f, h, q, r	Dfc	7	
R	A	For, Peat	1st	20; 1	4.6	(2-9)				20	18	a, f, j, p, r	Bwh	11	
R	US	Forested winter			4.5					28	20	a, f, i, p	Cfa	15	
R	US	Forested summer			5					28	20	a, f, i, p	Cfa	15	
R	US	For,Wet	1.5	1; 12	7		12			30	20	a, f, h, p	Dfb	16	
R	US	For(96), Wet(4)	0.5	1; 12	18		43			30	20	a, f, h, p	Dfb	16	
R	US	For(96), Wet(4)	1.5	1; 12	17		42			30	20	a, f, h, p	Dfb	16	
R	US	For(100)	16	1;9	15	(0-32)	37	(20-70)		14	10	a, f, i, p	Dfc	17	
R	US	For(100)	13	1;9	14	(0-38)	37	(5-60)		14	10	a, f, i, p	Dfc	17	
R	Ja	For, Agr, Urb	500	2; 2-8	31	(29-33)				45	20	a, f, h, p	Cfa	19	
R	US	For	1, 2	113; 3		(0-10)				13	12	a, f, j, p	Dfb	27	
R	Au	For(84),Agr(10), Urb(6)	147	1; 1	1		4			14	25	a, f, j, p	Csa	29	
R	Ch	For, Wet	>1000	8; nd	21	(15-30)	45	(29-57)		55	20	a, f, i, p	Dwb-Dfb	35	
R	Sw, F	nd	nd	13; 1			32	(8-72)		14	18-25a	a, f, j, p	Dfb-Dfc	36	
R	Sw, F	nd	nd	11; 1					75	(4-131)	14	18-25a	a, f, j, p	Cfb-Dfb	36
R	Sw	For(70),Agr(0),Upl(5),Wet(25), Ur(0)	11	1; 6			36	(19-55)		14	20	a, f, k, p	Dfc	37	
R	US	For, Upl	3315	1; 6	20	(6-51)				28	15	a, f, j, r	ET	44	
R	US	For, Wet	6164	1; 6	15	(3-35)				28	15	a, f, j, r	ET	44	



R	US	For, Wet	108520	1; 5	17	(5-43)					28	15	a, f, j, r	ET	44
R	US	For(62), Wet(-20)	831386	1; 16	22	(7-53)					28	15	a, f, j, r	Dfc	44
R	US	For(100)	0.5	1; 1	5		40				6	25	a, f, j, p	Cfa	46
R	US	For(83),Agr(0),Wet(0),Ur(2)	21	1; 1	1		1				6	25	a, f, j, p	Cfa	46
R	US	For(75),Agr(17),Wet(3),Ur(3)	17581	1; 1	16		19				6	25	a, f, j, p	Cfa	46
R	US	For(64),Agr(20),Wet(0),Ur(6)	4403	1; 1	7		33				6	25	a, f, j, p	Cfa	46
R	US	For(64),Agr(26),Wet(5),Ur(3)	36260	1; 1	1		12				6	25	a, f, j, p	Cfa	46
R	US	For(52),Agr(25),Wet(0),Ur(5)	25512	1; 1	1		22				6	25	a, f, j, p	Cfa	46
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					9.5 $\pm 1.4$ ; n=80 (14)		33.1 $\pm 1.0$ ; n=46 (7)		75.0 $\pm 12.4$ ; n=14 (1)						
(vi) Rivers; peatland															
R	F	For(40),Agr(2),Peat(40),Ur(2)	3814	1; 4	8		5				18	4-18a	a, f, h, p	Dfc	3
R	Si	Peat, For	100	15; 1	3	(1-6)					5	15	a, f, h, r	Dfc	13
R	Si	Peat, For	100000	14; 1	5	(1-14)					5	15	a, f, h, r	Dfc	13
R	Si	Peat, For	400000	9; 1	3	(0-15)					5	15	a, f, h, r	Dfc	13
R	Sw	For(30),Agr(0),Upl(30),Wet(40),Ur(0)	9	1; 6			37	(28-45)			14	20	a, f, k, p	Dfc	37
R	UK	Upl(100)	1	1; 12	11						41	15	a, f, i, p	Cfb	40
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					4.0 $\pm 0.4$ ; n=38 (3)		20.8 $\pm 4.5$ ; n=2 (2)		nd						
(vii) Urban runoff															
Ur	US	Urbanized			3.5						28	20	a, f, i, p	Cfa	15
Ur	US	Urbanized			13						28	20	a, f, i, p	Cfa	15
R	Br	Urb, Agr, For	nd	2; 2	38						10	20	a, f, h, p	Cfa	18
R	Ja	Urb, For, Agr	5000	7; 2-8	23	(3-31)					45	20	a, f, h, p	Cfa	19
R	Au	For(18),Agr(10),Urb(64)	386	1; 1	9		21				14	25	a, f, j, p	Csa	29
R	Au	For(32),Agr(18),Urb(36)	53	1; 1	17		23				14	25	a, f, j, p	Csa	29
R	Au	For(26),Agr(53),Urb(42)	99	1; 1	8		25				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(100)	12	1; 1	17		35				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(86),Agr(13)	23	1; 1	16		37				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(100)	10	1; 1	16		27				14	25	a, f, j, p	Csa	29

Ur	Au	Urb(98), Agr(3)	27	1; 1	7		46				14	25	a, f, j, p	Csa	29
R	US	For(19),Agr(10),Wet(0),Ur33)	194	1; 1	2		12				6	25	a, f, j, p	Cfa	46
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					17.1 $\pm 2.3$ ; n=18 (5)	28.8 $\pm 1.9$ ; n=6 (2)	nd								
(viii) Soil water; agricultural															
S,r	NZ	Agr (P)	nd	12; 1	38		100				49	20	a, f, n, p, r	Cfb	14
S,r	NZ	Agr (P)	nd	12; 1	45		100				49	20	a, f, n, p, r	Cfb	14
S,r	NZ	Agr (P)	nd	12; 1	58		100				49	20	a, f, n, p, r	Cfb	14
S,we	NZ	Agr (P)	nd	12; 1	43		100				36	20	a, f, n, p, r	Cfb	14
S,we	NZ	Agr (P)	nd	12; 1	39		100				36	20	a, f, n, p, r	Cfb	14
S,r	NZ	Agr (P)	nd	1; 5					15	(8-20)	nd	37	a, f, o, p	Cfb	24
S,we	NZ	Agr (P)	nd	9; 1					57	(15-85)	nd	37	a, f, o, p	Cfb	24
S,we	NZ	Agr (C)	nd	9; 1					42	(16-60)	nd	37	a, f, o, p	Cfb	24
S,we	G	Agr		1; 1	44						42	35	a, f, i, p	Cfb	25
S,we	G	Agr		1; 1	42						42	35	a, f, i, p	Cfb	25
S,r	US	Agr (P)	nd	23; 1	10						nd	20	b, f, h, p	Cfa	26
S,we	UK	Agr (P)	nd	1; 1	11	(0-15)					1	21	c, f, n, r	Cfb	39
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					34.9 $\pm 0.9$ ; n=86 (4)	nd	nd								
(ix) Soil water; forested															
S,r	Sw	For	nd	2; 16	30						21	20	a, f, i, p	Cfb	2
S,r	Sw	For	nd	2; 16	10						21	20	a, f, i, p	Cfb	2
S,we	Sw	For	nd	10; 1	39						21	20	a, f, i, p	Cfb	2
S,r	Sw	For	nd	2; nd	9						11	20	a, f, h, q, r	Dfc	7
S,we	US	For	nd	3; 8	29						30	26	a, g, i, p	Dfc	12
S,we	G	For		1; 1	5						42	35	a, f, i, p	Cfb	25
S,we	US	For		1; 7	12						42	35	a, f, i, p	Cfb	25
S,we	UK	For	nd	1; 1	3	(0-7)					1	20	c, f, n, r	Cfb	39
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					22.4 $\pm 3.4$ ; n=22 (5)	nd	nd								
(x) Soil water; peatland															
S,r	Sw	Upland	nd	2; nd	4						11	20	a, f, h, q, r	Dfc	7

S,we	Si	Peat	nd	9; 1	2	(0-9)					5	15	a, f, h, r	Dfc	13
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					2.4 $\pm 1.3$ ; n=11 (2)		nd		nd						
(xi) Sewage effluent															
Se,t	Po	Ur	nd	1; 5	35	(28-39)					21	20	a, f, p, s	Cfb	9
Se,t	Po	Ur	nd	1; 5	24	(9-30)					21	20	a, f, p, s	Cfb	9
Se,r	Ja	Ur	nd	5; 2-8	12	(3-16)					45	20	a, f, h, p	Cfa	19
Se,t	Fr	Ur	nd	1; nd	74	(70-77)					45	20	a, f, h, p	Cfb	33
Se,t	Fr	Ur	nd	1; nd	46	(33-56)					45	20	a, f, h, p	Cfb	33
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					44.8 $\pm 9.8$ ; n=27 (5)		nd		nd						
(xii) Lowland wetlands															
We	Au	For,Wet	nd	7; nd	30	(23-40)					28	20	a, f, h, p	Cfa	6
We	US	Wet(100)	nd	3; 8	32						30	26	a, g, i, p	Dfc	12
We	US	For(50),Wet(50)	nd	3; 8	23						30	26	a, g, i, p	Dfc	12
We	US	Wet(100)	nd	3; 8	42						30	26	a, g, i, p	Dfc	12
We	US	Wet(100)	nd	5; 1	45	(24-69)					4	26	a, g, i, p	Cfa	23
We	Ja	Wet(100)	nd	2; 1	18	(16-20)					nd	nd	a, g, i, p	Dfb	31
We	Sw	Wet,For	42	1; 9			4	(2-6)			28	25	a, f, i, p	Cfb	38
We	US	Wet(19),Agr(1),For(80),Urb(0.1)	13	1; 3	18	(11-26)	34	(30-62)			4	25	a, f, i, p	Cfa	45
We	US	Wet(33),Agr(9),For(55),Urb(1)	11	1; 3	27	(17-32)	32	(0-64)			4	25	a, f, i, p	Cfa	45
We	US	Wet(7),Agr(25),For(43),Urb(22)	44	1; 3	11	(7-16)	22	(2-47)			4	25	a, f, i, p	Cfa	45
We	US	Wet(9),Agr(41),For(25),Urb(22)	25	1; 3	12	(9-17)	32	(0-65)			4	25	a, f, i, p	Cfa	45
Weighted means $\pm 1$ s.e. (n, spatial samples (n, studies))					30.7 $\pm 4.0$ ; n=27 (5)		24.9 $\pm 0.4$ ; n=5 (2)		nd						
(b) Light, or light:dark incubations (not included in statistical evaluation)															
R	US	For(3),Agr(28),Wet(12),Urb(28)	<100	1; 1			7				5	nd	a, g, j, p	Cfa	22
R	Be	nd	nd	14; 1							13	21	a, g, m, q	Cfb	42
R	US	For	nd	1; 3			34	(28-44)			12	10-27a	a, g, k, p	Cfa	32

R	US	For	nd	1; 3			23	(8-44)		12	10-27a	a, g, k, p	Cfa	32
R	US	For	nd	1; 3			16	(0-34)		12	10-27a	a, g, k, p	Cfa	32
R	F	Agr(22-43)	6-1088	12; 1				1		21	20	d, e, m, p	Dfb	10
R	F	nd	56000-281000	12; 1				36	(7-55)	21	20	d, e, m, p	Dfb	10
Ur	US	For(2),Agr(3),Ur(83)	<100	1; 1			5			5	nd	a, g, j, p	Cfa	22
Ur	US	Ur	0.11	1; nd			10			5	nd	a, g, j, p	Cfa	21
Ur	US	Ur	0.11	1; nd			39			5	nd	a, g, j, p	Cfa	21
Ur	US	Ur(100)	0.01	1; 3			59	(42-73)		12	10-27a	a, g, k, p	Cfa	32
Ur	US	Ur(100)	0.01	1; 3						12	10-27a	a, g, k, p	Cfa	32
Ur	US	Ur(100)	0.01	1; 3						12	10-27a	a, g, k, p	Cfa	32
S,r	F	Agr (P)	<5	11; 1				1		21	20	d, e, m, p	Dfb	10
S,r	F	For	0.05-0.40	19; 1				9	(0-44)	21	20	d, e, m, p	Dfb	10
S,r	US	Agr (P)		1; 3			58	(51-73)		12	10-27a	d, g, k, p	Cfa	32
S,r	US	Agr (P)		1; 3			67	(52-72)		12	10-27a	d, g, k, p	Cfa	32
S,r	US	Agr (P)		1; 3			52	(42-59)		12	10-27a	d, g, k, p	Cfa	32
S,we	US	Humic substances	nd	5; nd				1	(0-0)	nd	24	a, e, m, q	Aw, Cfa, Dwc	20
Se,t	US	Ur		1; nd			61		75	14	25	a, e, m, p	Cfa	30
Se,t	US	Ur		1; nd			28		74	14	25	a, e, m, p	Cfa	30
Se,t	US	Ur		1; 4			38			14	21	a, g, j, m, p	Csa	28
Se,t	US	Ur		1; 4			33			17	21	a, g, j, m, p	Csa	28
Se,t	Sc	Ur		10; 1				45	(37-54)	17	20	d, e, m, p	Dfb	10
Se,t	Sc	Ur		2; 5				26	(0-75)	21	20	d, e, m, p	Dfb	10
Se,t	Sc	Ur		5; 4				22	(0-74)	21	20	d, e, m, p	Dfb	10
Ww,a	Sc	Agr		5; 1				46	(16-67)	21	20	d, e, m, p	Dfb	10
Ww,b	Sc	For		6; 3				21	(0-54)	21	20	d, e, m, p	Dfb	10
Ww,c	Sc	Agr		10; 1				13	(0-28)	21	20	d, e, m, p	Dfb	10
Sample category: Est, Estuarine; GW, Groundwater; L, Lake; R, River; Ur, Urban runoff; We, Wetland; S, Soil water (r=runoff; we=water extract); Le, Leaf leachate; Se, Sewage effluent (r=raw water, t=treated water); Ww, wastewater (a=dairy; b=forestry; c=fish farm). Countries: B, Brazil; F, Finland; Sw, Sweden; Si, Siberia; UK, United Kingdom; US, United States; Au, Australia; Ja, Japan; Ch, China; NZ, New Zealand; Be, Belgium; Fr, France; Po, Poland; G,														

Germany; Cz, Czech Republic.

World Climate Zones: Derived from the lat, long position data available at: <http://koeppen-geiger.vu-wien.ac.at/present.htm>

Land Use: For, Forestry; Agr, Agriculture (where (P) and (C) denote pasture and cropland for soil water samples); Wet, Wetland/peatland; Upl, Uplands; Ur, Urban; Peat, Peatland; nd, Not determined. Where the percentage of land use within catchments was quantified this is given in brackets.

Catchment size: In km<sup>2</sup> unless specified as 1st, first order streams; 2nd, second order streams.

n denotes number of samples in the format n, spatial samples: n, temporal samples.

Incubation temperatures: A single incubation temperature across all samples unless indicated as a, to denote temperatures varying seasonally according to sample site conditions.

BDOC, BDON and BDOP denote the % of dissolved organic C, N or P that was found to be bioavailable under test conditions, as mean (range).

Method details: a, Bottle tests; b, Plug flow bioreactor; c, Plate-based respiration testing; d, Dual culture assay; e, light incubation; f, dark incubation; g, light:dark cycle; h, No added inoculum; i, River bacterial inoculum from filtered sediment slurry or for the case of soil extracts from soil slurry; j, Unfiltered/coarse-filtered river water; k, Estuarine/coastal water inoculum; l, Direct presence of river sediment or biofilm; m, P or N starved algal culture; n, soil water inoculum; o, Phosphatase enzyme (native, or added); p, Concentration difference; q, Bacterial/algal growth; r, C removal calculated via respired CO<sub>2</sub>; s, activated sludge inoculum.

#### Refs:

- 1 Amon and Benner. *Limnol. Oceanogr.* 41, 41-51, 1996.
- 2 Andreasson et al. *Soil Biol. & Biochem.* 1652-1658, 2009.
- 3 Asmala et al. *Biogeosci.* 10, 6969-6986, 2013.
- 4 Autio et al. *Ambio* 45, 331-349, 2016
- 5 Balcarczyk et al. *Biogeochemistry* 94, 255-270, 2009.
- 6 Baldwin & Valo. *Environ. Sci. Processes Impacts* 17, 619-630, 2015.
- 7 Berggren et al. *Global Biogeochem. Cycles* 21, doi: 10.1029/2006GB002844, 2007
- 8 Cory & Kaplan. *Limnol. Oceanogr.* 57, 1347-1360, 2012
- 9 Czerwionka. *Oceanologia* 58, 39-45, 2016.
- 10 Ekholm & Krogerus. *Hydrobiologia* 492, 29-42, 2003.
- 11 Fasching et al. *Nature Scientific Reports.* 4, 4981, 2014.
- 12 Fellman et al. *Biogeochemistry*, doi:10.1007/s10533-008-9203-x, 2008.
- 13 Frey et al. *Biogeosciences*, 13, 2279-2290, 2016.
- 14 Ghani et al. *Biol. Fertil. Soils* 49, 747-755, 2013
- 15 Hosen et al. *Environ. Sci. Technol.* 48, 7817-7824, 2014.
- 16 Kang & Mitchell. *Biogeochem.* 115, 213-234, 2013.
- 17 Kaushal and Lewis. *Biogeochemistry* 74, 303-321, 2005.

- 18 Knapik et al. *Environ. Monit. Assess* 187, 104, 2015.
- 19 Kubo et al. *Biogeosciences*, 12, 269-279, 2015
- 20 Li & Brett. *Environ. Pollut.* 182, 37-44, 2013.
- 21 Lusk & Toor. *Environ. Sci. Technol.* 50, 3391-3398.
- 22 Lusk & Toor. *Wat. Res.* 96, 225-235.
- 23 Mann and Wetzel. *Biogeochemistry*, 31, 99-120, 1995.
- 24 McDowell & Koopmans. *Soil Biol & Biochem.* 38, 61-70, 2006.
- 25 McDowell et al. *Soil Biology and Biochem* 38, 13933-1942, 2006.
- 26 McLaughlin & Kaplan. *Freshwater Sci.* 32, 1219-1230, 2013.
- 27 Parr et al. *Limnol. Oceanogr.* 60, 885-900, 2015
- 28 Pehlivanoglu & Sedlak. *Wat. Res.* 38, 3189, 3196, 2004.
- 29 Petrone et al. *Biogeochemistry* 92, 27-40, 2009.
- 30 Qin et al. *Sci. Total Environ.* 511, 47-53, 2015
- 31 Satoh and Abe. *Arch Hydrobiol* 111, 25-35, 1987.
- 32 Seitzinger et al. *Limnol. Oceanogr.* 47, 353-366, 2002.
- 33 Servais et al. *Wat. Res.* 33, 3521-3531, 1999
- 34 Shen et al. *Biogeochem.* 122, 61-78, 2015
- 35 Shi et al. *Environ. Monitor. Assess.* 188, doi:10.1007/s10661-016-5120-y
- 36 Stepanauskas et al. *Ecol. Monographs* 72, 579-597, 2002.
- 37 Stepanauskas et al. *Limnol. Oceanogr.* 46, 1298-1307, 2000.
- 38 Stepanauskas et al. *Limnol. Oceanogr.* 44, 1477-1485, 1999.
- 39 Stutter et al. Unpublished data
- 40 Stutter et al. *Wat. Res.* 41, 1169-1180, 2013
- 41 Trulleyova and Rulik. *Science of the Total Environ.* 332, 253-260, 2004.
- 42 van Moorlegghem et al. *Hydrobiologia* 709, 41-53, 2013.
- 43 Wang and Pant. *Journal of Environmental Protection*, 3, 316-323, 2012.
- 44 Wickland et al. *Global Biogeochem. Cycles* 26, doi:10.1029/2012GB004342, 2012
- 45 Wiegner & Seitzinger. *Limnol. Oceanogr.* 49, 1703-1712, 2004.
- 46 Wiegner et al. *Aquatic Microbial Ecol.* 43, 277-287, 2006.
- 47 Wymore et al. *Freshwater Sci.* 34, 857-866, 2015.

**Table S3. Example data for compositions of seston and bed sediment where C, N and P data were available to enable plotting into Supplementary Figure S3. Ratios of C:N and C:P refer to organic C forms only.**

Country	n, spatial, temporal	Koeppen climate zone	Size (km <sup>2</sup> )	% of catchment areas under different land cover categories				C:N <sub>total</sub> of seston (±1 s.e.)		C:P <sub>total</sub> of seston (±1 s.e.)		C:N <sub>total</sub> of bed sediment (±1 s.e.)		C:P <sub>total</sub> of bed sediment (±1 s.e.)		References
				Agric	Urban	Forest	Wetland									
Scotland	3, 3	Cfb	300-1500	2-9				19.7	±3.3	179.9	±73.6	19.3	±1.5	128.7	±39.0	1
Scotland	3, 3	Cfb	200-1800	10-19				15.0	±1.4	161.0	±22.3	19.1	±2.0	95.3	±40.5	1
Scotland	7, 3	Cfb	5-150	50-69				12.5	±0.4	134.1	±9.9	15.8	±0.9	66.3	±15.1	1
Japan	1, 5	Cfa	100	1	2	94		8.6		105.1						2
Japan	1, 6	Cfa	1000	8	4	85		5.3		77.1						2
Japan	1, 6	Cfa	1985	30	32	30		7.9		53.6						2
U.S.	35, 333	Dfb	<10 - 3600	<1-63	0.3-4	36-93	<1-48	13.6	±0.2	191.0	±5.2					3
References:																
1. Stutter et al. 2007. River sediments provide a link between catchment pressures and ecological status in a mixed land use Scottish River system. <i>Wat. Res.</i> 41, 2803-2815;																
2. Li et al. 2005. Impacts of a heavy storm of rain upon dissolved and particulate organic C, N and P in the main river of a vegetation-rich basin area in Japan. <i>Sci. Tot. Environ.</i> 345: 99-113;																
3. Frost et al. 2009. Watershed discharge modulates relationships between landscape components and nutrient ratios in stream seston. <i>Ecology</i> 90: 1631-1640.																