University of Reading

# *Balancing macronutrient stoichiometry to alleviate eutrophication*

Article

Accepted Version



Stutter, M. I., Graeber, D., Evans, C. D., Wade, A. J. and Withers, P. J. A. (2018) Balancing macronutrient stoichiometry to alleviate eutrophication. Science of the Total Environment, 634. pp. 439-447. ISSN 0048-9697 doi: https://doi.org/10.1016/j.scitotenv.2018.03.298 Available at http://centaur.reading.ac.uk/76706/

# Balancing macronutrient stoichiometry to alleviate eutrophication

*M.I. Stutter[1], D. Graeber[2], C.D Evans[3], A. J. Wade[4], P. J. A. Withers[5]

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

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

**Abstract**

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

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

## 1.1. Introduction

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

The microbial nitrogen (N) removal and release as $N_2$ gas into the atmosphere (denitrification) and assimilation and incorporation of N and phosphorus (P) into organic matter are key river ecosystem services, which can regulate nutrients through biological 'self-cleansing' (von Schiller et al., 2017). The potential for microbial processes is becoming realised; in rivers, huge substrate surface areas, hyporheic exchanges (Boano et al., 2014) and biofilm structures (Battin et al., 2016), impart large potential for microbes to modify river solutes. In fact, significant inorganic N and P recycling and cumulative uptake through headwater streams to downstream river reaches has been shown for many streams (Mulholland, 2004; Ensign and Doyle, 2006; Rode et al. 2016). Significant biological uptake has also been shown for organic C in running waters, especially in the form of dissolved organic carbon (DOC) (Mineau et al., 2016). The burial and outgassing of C makes running waters essential components to consider in the global C cycle (e.g. Cole et al., 2007, Regnier et al., 2013, Marx et al., 2017).

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

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

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

## 2. Materials and Methods

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

### *2.1. Catchment nutrient data sources*

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

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

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

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

### *2.2. Nutrient bioavailability studies*

Metadata from 47 literature studies were used to explore evidence of the bioavailability of organically-complexed macronutrients. Studies with information on bioavailable DOC, DON and/or DOP (termed BDOC, BDON, BDOP) were recorded together with method and site metadata (for example land use, catchment size, location). Data covered aquatic ecosystems and catchment nutrient sources (soil and wetland waters, leaf litter, urban runoff and effluents), which allowed exploration of land cover as a grouping factor. We thoroughly reviewed the bioavailability data and metadata described in the supplementary methods and presented in Supplementary Table 2. The data comprise 131 rows of our database, each row summarising 1-113 sites depending on whether these were separated within studies and to maximise the division of results across land cover categories.

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

**3. Calculations**

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

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

Within our microbial ‘self-cleansing’ concept (Fig. 1), we incorporate evidence of stoichiometric flexibility, whereby microbial populations regulate their elemental compositions relative to greater ranges in external freshwater resource environments. To assess the potential bacterial stoichiometric flexibility, we defined zones of stoichiometric balance or imbalance between bacteria and their food and energy sources. Recent work has shown a zone of flexibility for C:P for different strains of freshwater bacteria (Godwin and Cotner, 2015). For this Godwin & Cotner (2015) grew bacteria on substrates at C:P of $10^2$ to $10^5$ and C:N fixed at 3.0. They then reported the resulting celullar C:P and C:N for multiple species that we use to define our ideal stoichiometric zone (zone A, Table 1). Although the C:N range they report results from manipulation of C:P at fixed C:N in the growth media the C:N response of these manipulated bacteria matched other reported ranges (Xu et al., 2015). We interpret this zone of flexibility to represent a microbial 'comfort zone' (Zone A; Table 1), whereby ecosystem available resource ratios are optimal for microbial assimilation. We further defined an N-enriched zone (Zone B) and a zone where N and P are enriched relative to OC (Zone C). We consider these zones as representing river waters and catchment sources that have a strong stoichiometric imbalance presently. Finally, we defined a zone which represents OC-rich resources with N and P-deficiency (Zone D) that we see could provide opportunities for rebalancing stoichiometry by restoration of habitats of these contributing sources. Zone D represents OC-rich resources with N and P-deficiency could provide opportunities for rebalancing stoichiometry by restoration of habitats of these contributing sources.

## 4. Results

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

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

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

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

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

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

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

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

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

## 5. Discussion

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

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

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

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

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

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

Studies of DOC uptake often use simple DOC substances (sugars, acetate, glutamic acid) due to difficulties in adding sufficiently large masses of recovered natural DOC to streams. There remains a lack of inclusion of OC composition and cycling research integrated with nutrient cycling studies (Newcomer Johnson et al., 2016). Where it has been considered, OC is shown as a strong influence on N cycling (Xu et al., 2015; Taylor and Townsend, 2010; Wymore et al., 2016). Study of river C:P coupling is considerably less developed, but crucial to represent C:N:P. The hotspots - for example the stream bed, water column or hyporheic zone - of DOC uptake remain largely unknown, as in-stream compartmental uptake studies are scarce (Graeber et al. 2018). Furthermore, the importance of the different stream compartments is debated for N uptake (e.g. Johnson et al. 2015) and largely unknown for P uptake. Further works should link physico-chemical and biological aspects of linked OC, N, P cycling in rivers and question the extent of in-river processing, the dominant controls, which biotic communities are the main players and where (the river bed vs water column) and interactions with autotrophs that may decouple a reliance on catchment OC sources. Potentially, new high resolution in-situ monitoring can open up new evidence for in-river processes.

## 6. Conclusions

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

Our stoichiometric approach for improving aquatic ecosystem health by rebalancing OC, N, P from catchment inputs highlights the need to improve data, knowledge and practical management in areas of coupled macronutrient processing. We were able to collate dissolved nutrient data that showed globally that agricultural, urbanized and even forests and moorland with a minimal agricultural influence (<10% area) had lower C:N and C:P ratios than reference sites. When stoichiometric ratios of OC, N and P were considered in terms of bioavailable resources these differed from the proposed microbial optimum and other components of biota in catchments across different global climate zones for all but pristine forests. The strongest stoichiometric imbalances were associated with urban factors (e.g. effluents) and agricultural runoff, but also highlighted the importance of bioavailability of DOC. Hence, humic waters were less able to contribute to stoichiometric rebalancing than key source waters such as riparian wetlands and forests that had a beneficial combination of DOC availability and low associated N, P load. Although supported here by literature evidence rather than direct new experimental data there is a growing, but fragmented body of literature that agrees with our concept of variable river resilience to N and P inputs and a mechanistic microbial coupling to inputs of catchment-derived bioavailable OC. We hope that the concepts we have united here will promote experimental evidence of the magnitude and controls on in-river processing and how we may manage it for benefits. However, many important aspects related to manipulations of river OC, N, P stoichiometry are still understudied and especially the lack of information on particulate forms exemplifies this. Still, we feel that our approach generates a strong incentive for the collection of data on all key macronutrients OC, N and P, including particulate and dissolved forms, their bioavailability and key river compartments for their processing.

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

FIGURES

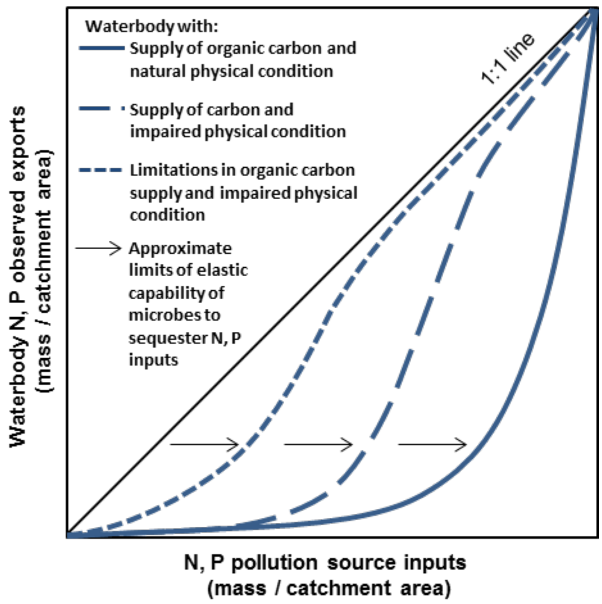



**Figure 1.** Conceptual model of resilience to nitrogen and phosphorus source inputs provided by river microbial nutrient processing mediated by organic carbon. In rivers, resilience to rising nutrient inputs is provided by physical and biochemical factors, crucially by microbial assimilation and longer-term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

Fig. 2

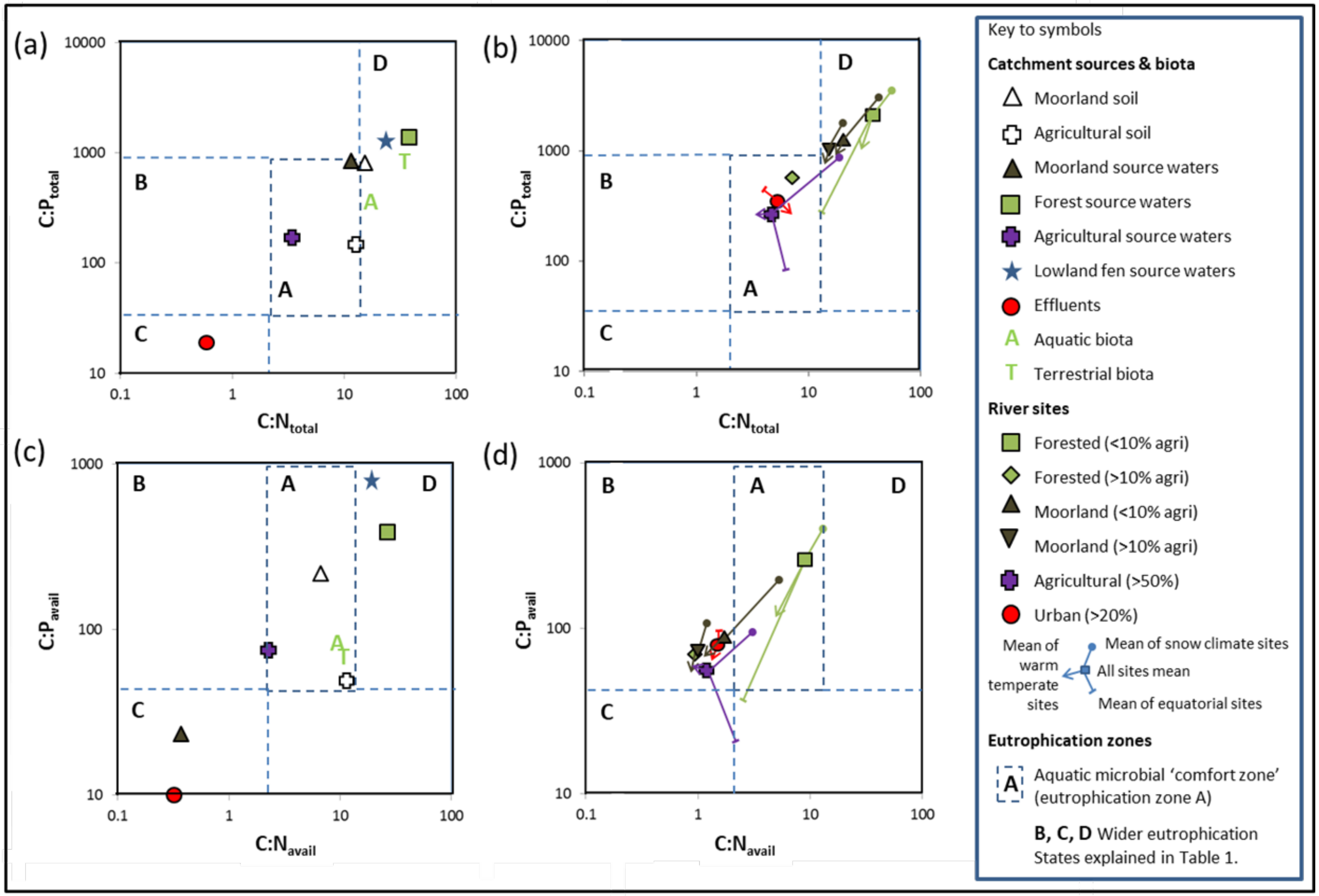

(a)
(b)
(c)
(d)
B
C
D
A
C:$P_{total}$
C:$N_{total}$
C:$P_{avail}$
C:$N_{avail}$
10000
1000
100
10
0.1
1
10
100
Key to symbols
Catchment sources & biota
Moorland soil
Agricultural soil
Moorland source waters
Forest source waters
Agricultural source waters
Lowland fen source waters
Effluents
Aquatic biota
Terrestrial biota
River sites
Forested (<10% agri)
Forested (>10% agri)
Moorland (<10% agri)
Moorland (>10% agri)
Agricultural (>50%)
Urban (>20%)
Mean of warm temperate sites
Mean of snow climate sites
All sites mean
Mean of equatorial sites
Eutrophication zones
Aquatic microbial 'comfort zone' (eutrophication zone A)
B, C, D Wider eutrophication States explained in Table 1.

**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.

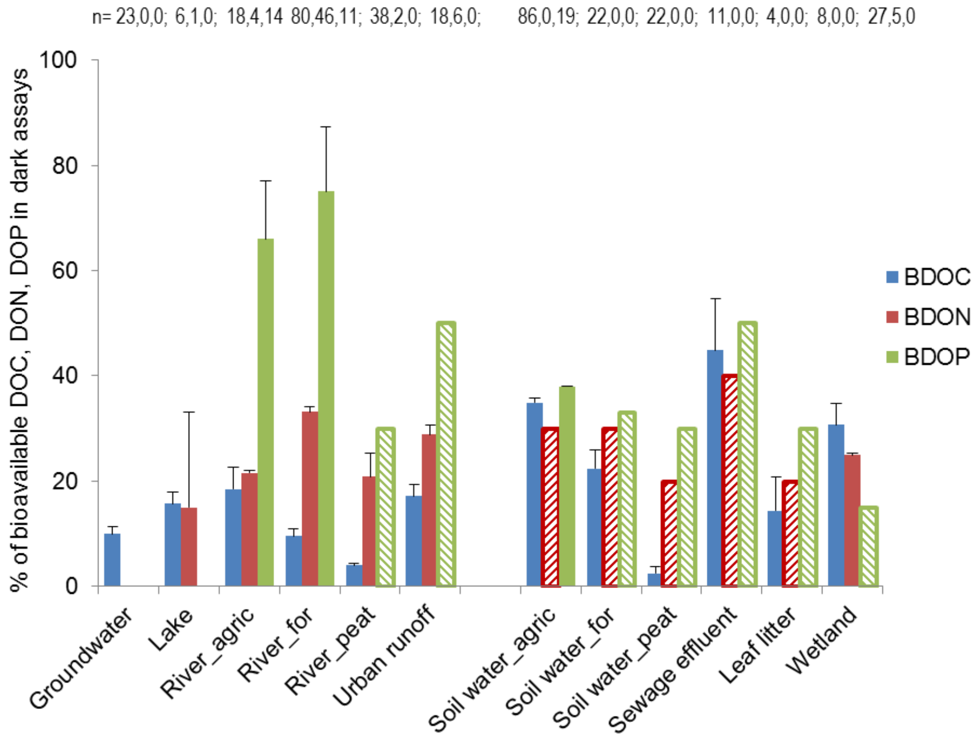



**Figure 3.** Summary of weighted means and variance for bioavailable proportions of dissolved organic C, N and P taken from literature metadata evidence and used for scaling available resources. Mean values are weighted by sample number (±1 weighted standard error, with stated n numbers indicating total 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).

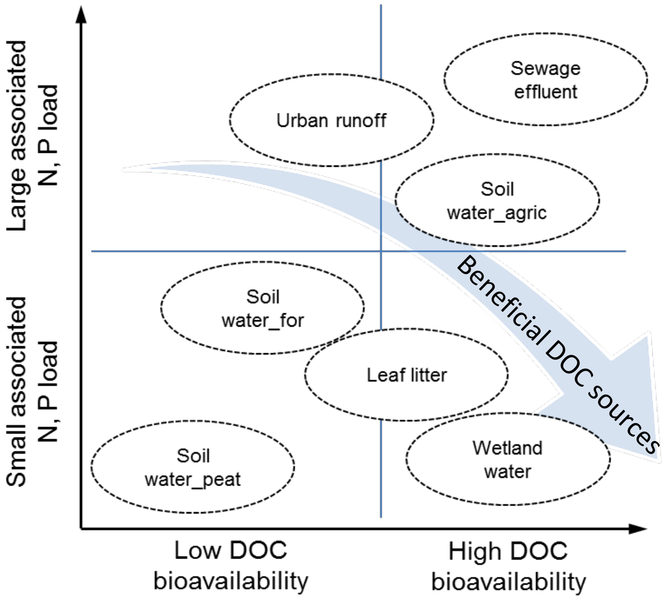



**Figure 4.** A conceptual matrix of catchment OC, N, P sources based on quadrants of low *vs* high available N, P load and low *vs* high DOC bioavailability (<20% and >20%, respectively) to demonstrate more and less appropriate forms of carbon for rebalancing. Wetland water and leaf litter provide optimum 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.

| Zone | Available resource ratios | River nutrient conditions | Microbial nutrient processing |
|---|---|---|---|
| **A** | C:N 2-11<br>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** | C:N 0.01-11<br>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 |
| **C** | C:N 0.01-11<br>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. |
| **D** | C:N 2-100<br>C:P 994-10000, and<br>C:N 11-100<br>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

Autio I, Soinne 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

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

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

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, Darchembeau 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. Biogeocsci. 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 CO2 and associated carbon dynamics in headwater streams: A global perspective. Rev. Geophys. 55, 2016RG000547,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

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, Sivirichi 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; 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

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, Luyssaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Goddéris 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.

Rockström 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.

**Acknowledgements:** The authors acknowledge funding from the UK Natural Environment Research Council (grant numbers: NE/J011908/1; NE/J011991/1; NE/J011967/1 under the Macronutrient Cycles Program) and from Scottish Government's Rural Environment Science and Analytical Services. We acknowledge assistance from S. Halliday in deriving spatial data for UK catchments, B. Demars for discussions on stream-cycling concepts and M. Bowes for early discussions on concepts contributing to Figure 1. We also remember fondly and acknowledge discussions with the late J. Dawson that led to us developing these concepts.

# Supplementary Material

# Balancing macronutrient stoichiometry to alleviate eutrophication

M.I. Stutter[1], D. Graeber[2], C.D Evans[3], A. J. Wade[4], P. J. A. Withers[5]

[1]The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, UK; [2]Aquatic Ecosystem Analysis, Helmholtz Centre for Environmental Research, Magdeburg, Germany; [3]Centre for Ecology and Hydrology, Environment Centre Wales, Bangor LL57 2UW, UK; [4]Dept. of Archaeology, Geography and Environmental Science, University of Reading, Reading RG6 6AB, UK; [5]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 µm and those for English rivers to 1.2 µm. 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 $NO_3$ to $NO_2$ and diazotisation reaction with sulphanilamide and using a modified Berthelot reaction for $NH_4$ 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 $NO_3$-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 (Stepanauskas 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.

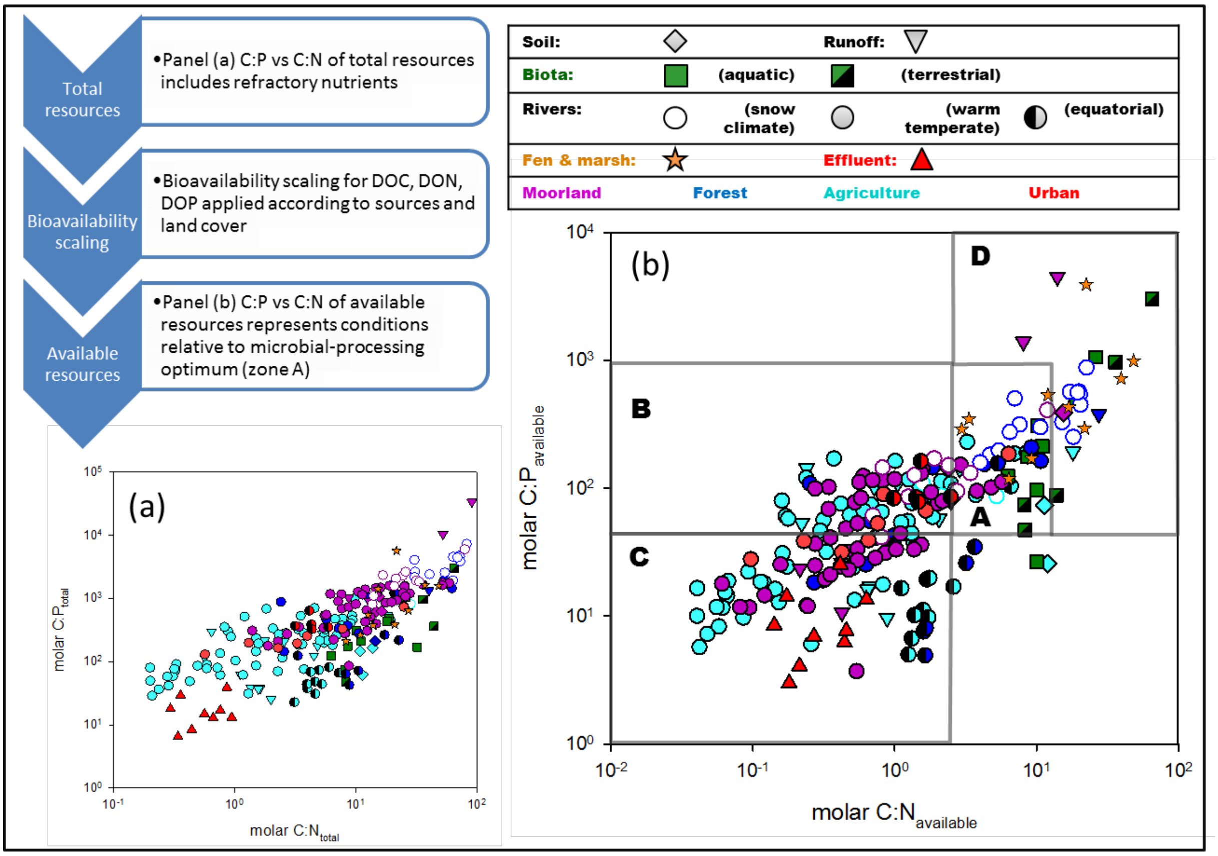
Data covered the latitudes 27-69°N and 3-46°S. Entries were compiled to single rows for either grouped data where key metadata such as land cover was not fully recorded, or individual sites to rows where full metadata was recorded; henceforth rows are termed database entries. Importantly, data were split 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 catgeories 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 dissoved 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.

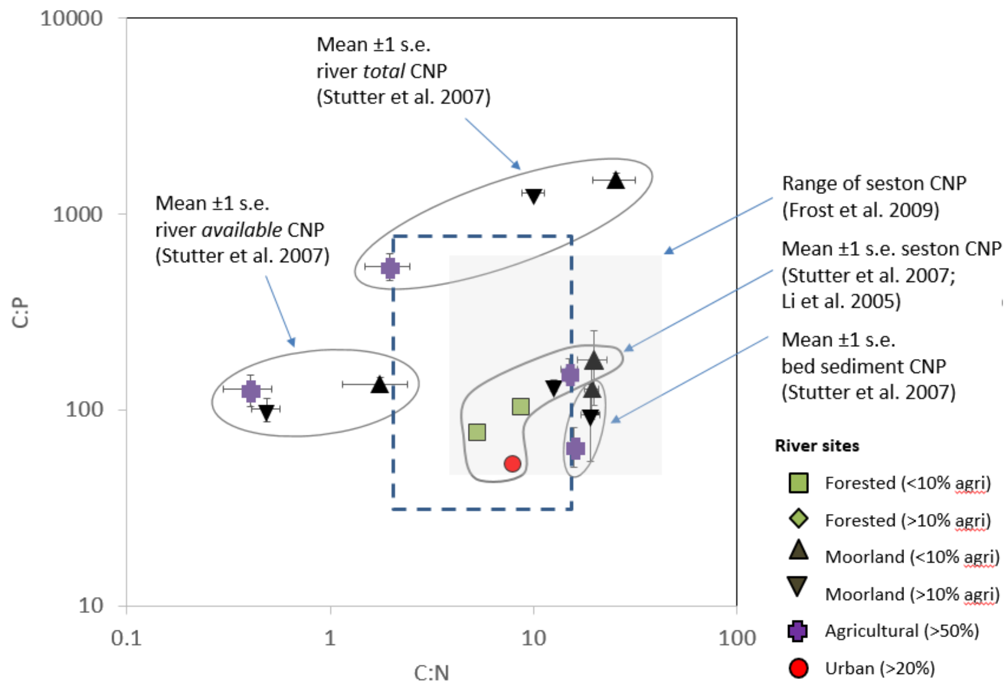


**Table S1. Database of catchment nutrient sources, biological components and river ecosystem C, N and P concentrations, N and P speciation, C:N and C:P values used to construct Figure 2.** Ratios of C:N and C:P refer to organic C forms only.

| Component | n, spatial | Description | Country | Koppein climate zones | Land cover | Catchment ($km^2$) | 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 | Gyffylog | 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 Beauly | 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 | Stortjäcken outlet | Sw | Dfb | For | 1.1 | 1833 | 26 | 96 | 0.4 | 67 | 71.3 | 4736 | M | 19.9 | 568 | 2 |
| River | 1 | Kallkällsmyren | 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 | Kallkällsbäcken | 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 | Carandaí | 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 |

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: http://koeppen-geiger.vu-wien.ac.at/present.htm
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.


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.

5 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

6 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. Hydriobiol. 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

**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 | Koeppen 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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 9.9 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 15.7 ±2.2; n=6 (2) | | 15.0 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 14.3 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 18.5 ±4.2; n=18 (7) | | 21.5 ±0.4; n=4 (2) | | 66.0 ±11.0; n=14 (1) | | | | | | |
| (v) Rivers; forested | | | | | | | | | | | | | | | |
| R | Br | For(100) | 500000 | 1; 1 | 12 | | | | | | 4 | 25 | a, f, j, p | Af | 1 |
| R | Br | For(100) | 715000 | 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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 9.5 ±1.4; n=80 (14) | | 33.1 ±1.0; n=46 (7) | | 75.0 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 4.0 ±0.4; n=38 (3) | | 20.8 ±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 ±1 s.e.<br>(n, spatial samples (n, studies)) | | | | | 17.1 ±2.3; n=18 (5) | | 28.8 ±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 ±1 s.e.<br>(n, spatial samples (n, studies)) | | | | | 34.9 ±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 ±1 s.e.<br>(n, spatial samples (n, studies)) | | | | | 22.4 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 2.4 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 44.8 ±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 ±1 s.e. (n, spatial samples (n, studies)) | | | | | 30.7 ±4.0; n=27 (5) | | 24.9 ±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),Ur(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 $km^2$ 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 $CO_2$; 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. Freswater 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 alLimnol. 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 Moorleghem 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 ($km^2$) | % of catchment areas under different land cover categories | | | | $C:N_{total}$ of seston (±1 s.e.) | | $C:P_{total}$ of seston (±1 s.e.) | | $C:N_{total}$ of bed sediment (±1 s.e.) | | $C:P_{total}$ 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. Wat. Res. 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. Sci. Tot. Environ. 345: 99-113;
3. Frost et al. 2009. Watershed discharge modulates relationships between landscape components and nutrient ratios in stream seston. Ecology 90: 1631-1640.